Critical Phenomena and Crossover Theory

(ST550)

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Preface

This literature study reports on critical phenomena in general. It was meant to improve my knowledgde of the critical point in order to have a firm basis for my graduation project.

I would like to thank Prof. Dr. M. L. Japas and Dr. Ir. C. J. Peters for their comments on this report and for the supply of literature.

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1.1 The critical point

Typical examples of critical points are given by second order phase transitions, in which the quantities describing the macroscopic state of the system vary continuously but present an angular point corresponding to the divergence of the derivatives. The second order phase transition is illustrated in Figure 1.1.

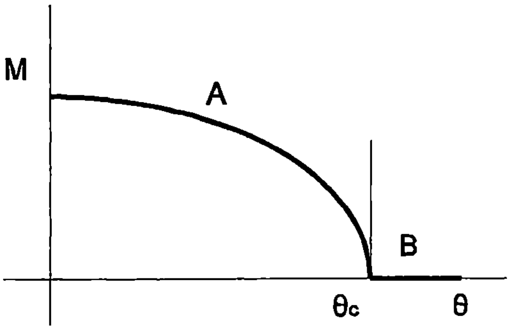


Figure 1.1: Second order (critical) phase transition

The variable θ, adjustable on the macroscopic scale, controls the phase transition by influencing the statistical distribution of the elementary constiuents. For the gas-liquid critical point its critical value θ_c corresponds to the critical temperature. M is the order parameter which vanishes in the fluid phase $T>T_c$, and is non-zero in the zone $T<T_c$. The order parameter is continuous at $T=T_c$, however, its derivative diverges as can be seen by the vertical tangent in Figure 1.1 [1].

According to the phase rule of Gibbs, a one-component fluid has in general two degrees of freedom. When two phases coexist, only one degree of freedom is left. Therefore, the condition of coexistence defines a curve in the space of the two independent field variables. In the two coexisting phases all intensive properties or field variables are equal. Extensive properties or densities are generally not the same in the coexisting phases. The gas-liquid critical point is an endpoint on the coexisting curve at which not only all fields but also all densities are the same. The result is that at the critical point, the two coexisting phases can not be distinguished anymore [2]. See Figure 1.2.

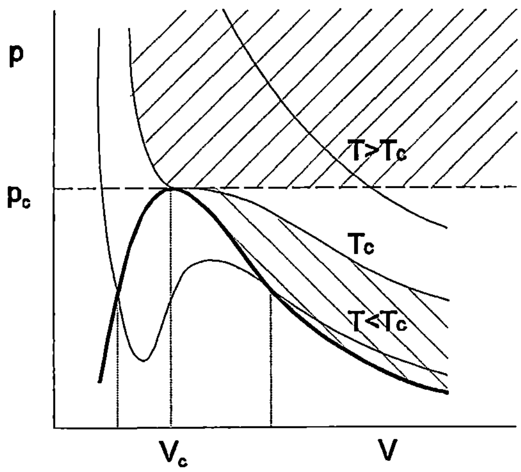


Figure 1.2: Classical behaviour

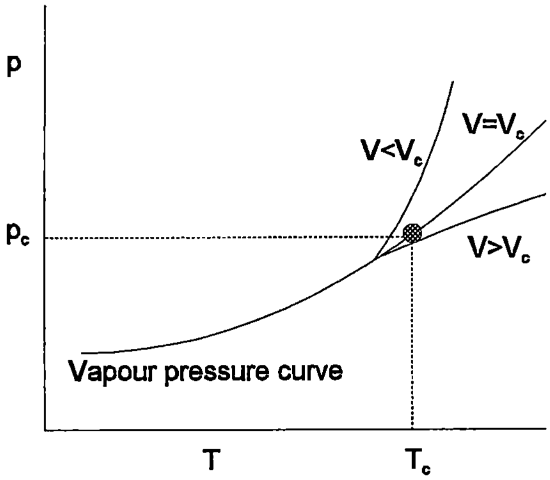


Figure 1.3: p-T-diagram

Critical points are focal points of exceptional thermodynamic behaviour either when they are approached from within the two-phase region or when they are approached from within the one-phase region. Critical points are points of incipient *instability*. At the critical point the isothermal compressibility, isobaric expansivity and isobaric heat capacity diverge strongly. Closely associated with the marginal stability and the divergence of the compressibility is the presence of large *fluctuations* in the vicinity of the critical point [2]. The average size of the critical fluctuations is indicated by the *correlation length* ξ. Near a critical point, this correlation length becomes much longer than the range of molecular interaction. The fluid behaves as a collection of droplets or aggregates of macroscopically fluctuating density, in which the individual molecular interactions are of less importance. Consequently, critical behaviour shows considerable similarity in a large variety of fluids which is expressed in the term *universality*. The presence of a new length scale, ξ, gives thermodynamic properties in the critical region a character of homogeneity which makes it possible to reduce the number of independent variables by a proper choice of scale [2,3].

1.2 Divergences and power laws

We consider the following thermodynamic functions:

$$K_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad \alpha_p=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p=K_T\left(\frac{\partial p}{\partial T}\right)_V$$
$$C_p=C_V+T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p=C_V+TVK_T\left(\frac{\partial p}{\partial T}\right)_V^2 \qquad (1.1)$$

K_T, α_p, and C_p are respectively the isothermal compressibility, isobaric expansivity, and isobaric heat capacity. It follows from Figure 1.2 and Figure 1.3 that the derivative $(\partial p/\partial V)_T$ is zero and the derivative $(\partial p/\partial T)_V$ remains finite in the critical point. It follows from equation (1.1) that the properties K_T, α_p, and C_p diverge in the critical point. In experiments, these properties show a strong divergence in a broad temperature and density region around the critical point. Experiments also show that C_V diverges in the critical point, however the divergence is much less pronounced than that of C_p.

We assume that the thermodynamic properties near and in the critical point can be described by power laws. To define a power law five parameters or variables are needed:

- The property in question *Q*, measured with respect to its critical value Q_c, if it does not diverge;
- An independent variable r_1, measured with respect to its critical value r_{1c};.
- The path of approach, in the form of other independent variables r_2 held constant;
- A non-negative critical exponent ϵ;
- A critical amplitude *E*.

In the case of a diverging property the property is made dimensionless by an appropriate combination of critical parameters. If the property is expressed in reduced units the critical amplitude becomes a dimensionless number.

The power laws for non-diverging and diverging properties are of the following form [3]:

$$\left|\frac{Q - Q_c}{Q_c}\right| = E\left|\frac{r_1 - r_{1c}}{r_{1c}}\right|^{+\varepsilon} \qquad |Q^*| = E\left|\frac{r_1 - r_{1c}}{r_{1c}}\right|^{-\varepsilon} \tag{1.2}$$

It is clear that only dimensionless groups can be scaled in a physically realistic way. The variables are often reduced in the following way [2]:

$$\begin{gathered} \rho^* = \frac{\rho}{\rho_c} \quad T^* = \frac{T}{T_c} \quad p^* = \frac{p}{p_c} \quad \mu^* = \frac{\mu\rho_c}{p_c} \quad K_T{}^* = K_T p_c \quad S^* = \frac{S}{V}\frac{T_c}{p_c} \quad A^* = \frac{A}{Vp_c} \\ C_V{}^* = \frac{C_V T_c}{Vp_c} \quad \Delta T^* = \frac{T - T_c}{T_c} \quad \Delta\rho^* = \frac{\rho - \rho_c}{\rho_c} \quad \Delta\mu^* = \mu^*(\rho, T) - \mu^*(\rho_c, T) \end{gathered} \tag{1.3}$$

The difference in chemical potential $\Delta\mu^*$ is considered with regard to the critical isochore at the same temperature. The thermodynamic properties S^*, A^*, and $C_V{}^*$ are taken per unit volume and can be regarded as densities. Another way of scaling is [4]:

$$\begin{gathered} \tilde{\rho} = \frac{\rho}{\rho_c} \quad \tilde{T} = -\frac{T_c}{T} \quad \tilde{\mu} = \frac{\rho_c T_c}{p_c}\frac{\mu}{T} \quad \tilde{A} = \frac{AT_c}{p_c VT} \quad \tilde{p} = \frac{p}{T}\frac{T_c}{p_c} \\ \tilde{C}_V = -\left(\frac{\partial^2 \tilde{A}}{\partial \tilde{T}^2}\right)_\rho \quad \Delta\tilde{T} = \tilde{T} + 1 \quad \Delta\tilde{\rho} = \tilde{\rho} - 1 \quad \tilde{\mu} = \frac{\mu}{T}\frac{\rho_c T_c}{p_c} \quad \Delta\tilde{\mu} = \tilde{\mu}(\tilde{\rho}, \tilde{T}) - \tilde{\mu}(\tilde{T}) \end{gathered} \tag{1.4}$$

The exponent of the power law depends on the property chosen, the path along which the critical point is approached, and the way the distance from the critical point is measured [2]. A number of power laws with critical amplitudes, critical exponents, and paths of approach are given in Table 1.1.

Table 1.1: Power laws

Property	Power law	Path of approach	Exp.
Chemical potential	$\Delta\mu^*=D(\Delta\rho^*)\lvert\Delta\rho^*\rvert^{\delta-1}$	Critical isotherm ($T=T_c$)	$\delta-1$
Symm. isothermal compressibility	$\chi_T^*=\rho^{*2}K_T^*=\Gamma\lvert\delta T^*\rvert^{-\gamma}$	Critical isochore ($T\geq T_c$, $\rho=\rho_c$)	γ
Symm. isothermal compressibility	$\chi_T^*=\rho^{*2}K_T^*=\Gamma'\lvert\delta T^*\rvert^{-\gamma'}$	Coexistence curve ($T\leq T_c$, $\rho=\rho_{Coex}$), one-phase	γ'
Isochoric heat capacity	$C_V^*/T^*=(A^+/\alpha)\{\lvert\Delta T^*\rvert^{-\alpha}-1\}$	Critical isochore ($T\geq T_c$, $\rho=\rho_c$)	α
Isochoric heat capacity	$C_V^*/T^*=(A^-_I/\alpha')\{\lvert\Delta T^*\rvert^{-\alpha'}-1\}$	Coexistence curve ($T\leq T_c$, $\rho=\rho_{Coex}$)	α'
Isochoric heat capacity	$C_V^*/T^*=(A^-_{II}/\alpha'')\ \{\lvert\Delta T^*\rvert^{-\alpha''}-1\}$	Critical isochore ($T\leq T_c$, $\rho=\rho_c$)	α''
Coexisting densities	$\Delta\rho_{coex}{}^*=\pm B\ \lvert\Delta T^*\rvert^{\beta}$	Two-phase region ($T\leq T_c$, $\rho=\rho_{Coex}$)	β
	$d^2p_{coex}{}^*/dT^{*2}\propto\lvert\Delta T^*\rvert^{-\theta p}$	Two-phase region ($T\leq T_c$)	θ_p
	$d^2\mu_{coex}{}^*/dT^{*2}\propto\lvert\Delta T^*\rvert^{-\theta\mu}$	Two-phase region ($T\leq T_c$)	θ_μ
Pressure	$\Delta p^*=D(\Delta\rho^*)\lvert\Delta\rho^*\rvert^{\delta-1}$	Critical isotherm ($T=T_c$)	δ

1.3 Exponent equalities and exponent inequalities

The critical exponents introduced in Table 1.1 are not all independent of each other. The laws of thermodynamics impose several inequalities between combinations of the thermodynamic exponents [5,6,7].

According to Rushbrooke, we consider a cycle process *CDBAC*, as indicated in the *p-V*-diagram in Figure 1.4. For the cycle process $\oint dU=0$, which results in:

$$\oint TdS=\oint pdV \tag{1.5}$$

After using the equation of Clapeyron and also considering the cycle process CDB'A'C, equation (1.5) results in the following relation [8]:

$$\begin{gathered}\int_{T_1}^{T_c}\frac{T_c-T}{T}C_{V_c}dT\geq x_G(V_c)\int_{V_c}^{V_G}(p_c-p)dV-x_L(V_c)\int_{V_L}^{V_c}(p-p_c)dV\\ x_G(V_C)=\frac{V_C-V_L}{V_G-V_L}\qquad x_L(V_C)=\frac{V_G-V_C}{V_G-V_L}\end{gathered}\tag{1.6}$$

The property C_{vc} equals the heat capacity at the critical isochore. According to the scaling laws in Table 1.1 it follows:

$$\begin{gathered}\int_{T_1}^{T_c}\frac{T_c-T}{T}C_{V_c}dT\sim(T_c-T)^{2-\alpha''}\\ \int_{V_c}^{V_G}(p_c-p)dV\cong\int_{V_L}^{V_c}(p_c-p)dV\sim\lvert V-V_c\rvert^{\delta+1}\sim(T_c-T)^{\beta(\delta+1)}\end{gathered}\tag{1.7}$$

In the vicinity of the critical point, $(T_c-T)/T<1$. Whether $2-\alpha''$ is larger or smaller than $\beta(\delta+1)$ depends on whether $(T_c-T)/T$ is smaller or larger than 1. With the constraint $(T_c-T)/T<1$, equation (1.6) and (1.7) convert into the exponent inequality of Griffiths [5, 9]:

$$\alpha''+\beta(\delta+1)\geq 2 \tag{1.8}$$

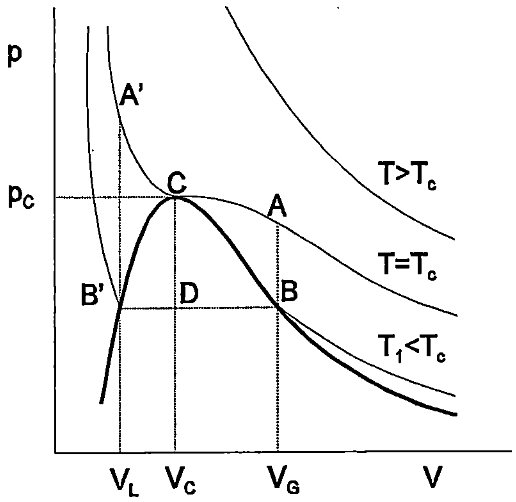


Figure 1.4: Cycle process according to Rushbrooke

A second exponent inequality can be obtained by noticing that the slope of the isochores in Figure 1.3 increases with decreasing V:

$$\frac{\partial^2 p}{\partial T\partial V}\leq 0 \tag{1.9}$$

In the vicinity of the critical point, the following relation holds:

$$\frac{\partial p(V,T_c)}{\partial V}=\frac{\partial p(V,T_1)}{\partial V}+\frac{\partial^2 p}{\partial V\partial T}(T_c-T_1)\ \rightarrow\ \frac{\partial p(V,T_c)}{\partial V}\leq\frac{\partial p(V,T_1)}{\partial V} \tag{1.10}$$

With the scaling laws, the left and right part of equation (1.10) are converted into:

$$\frac{\partial p(V,T_c)}{\partial V}\sim -|V-V_c|^{\delta-1}\sim -(T_c-T_1)^{\beta(\delta-1)} \qquad \frac{\partial p(V,T_1)}{\partial V}\sim -(T_c-T_1)^{\gamma'} \tag{1.11}$$

Equation (1.10) and (1.11) result in the exponent inequality of Liberman [10]:

$$\beta(\delta-1)\leq\gamma' \tag{1.12}$$

The exponent inequality of Rushbrooke is a result of the exponent inequalities of Griffiths and Liberman [8,11,12]:

$$\alpha''+2\beta+\gamma'\geq 2 \tag{1.13}$$

A third exponent inequality can be derived by the following consideration. The mole fractions of coexisting gas and liquid are given by:

$$x_G=\frac{\rho_G}{\rho}\frac{\rho_L-\rho}{\rho_L-\rho_G} \qquad x_L=\frac{\rho_L}{\rho}\frac{\rho-\rho_G}{\rho_L-\rho_G} \tag{1.14}$$

The isochoric heat capacity in the two-phase region satisfies the relation [8]:

$$\overline{C}_V = x_G\overline{C}_{VG} + x_L\overline{C}_{VL} + \frac{x_G T}{\rho_G{}^3 K_T(\rho_G)}\left(\frac{d\rho_G}{dT}\right)^2 + \frac{x_L T}{\rho_L{}^3 K_T(\rho_L)}\left(\frac{d\rho_L}{dT}\right)^2 \qquad (1.15)$$

where $\overline{C}_{VG} = \overline{C}_V(\rho_G)$ and $\overline{C}_{VL} = \overline{C}_V(\rho_L)$

The overlined properties are molar properties. According to equation (1.14), in the limit of disappearing liquid or vapour in the two-phase region, the following relations hold:

$$\begin{aligned} \overline{C}_{VG}{}^{(2)} &\equiv \lim_{x_G\to 1}\overline{C}_V = \overline{C}_{VG} + \frac{T}{\rho_G{}^3 K_T(\rho_G)}\left(\frac{d\rho_G}{dT}\right)^2 \\ \overline{C}_{VL}{}^{(2)} &\equiv \lim_{x_L\to 1}\overline{C}_V = \overline{C}_{VL} + \frac{T}{\rho_L{}^3 K_T(\rho_L)}\left(\frac{d\rho_L}{dT}\right)^2 \end{aligned} \qquad (1.16)$$

All terms in equation (1.15) are positive and we notice from equation (1.16) that the isochoric heat capacity is discontinuous in going from the gas phase to the liquid phase and vice versa. Another observation from equation (1.15) is:

$$\overline{C}_V(\rho_c,T) \geq \frac{x_G(\rho_c)T}{\rho_c{}^3 K_T(\rho_G)}\left(\frac{d\rho_G}{dT}\right)^2 \qquad (1.17)$$

The left part of relation (1.17) diverges in the vicinity of the critical point as $|\Delta T^*|^{-\alpha''}$ and the right part as $|\Delta T^*|^{-2+2\beta+\gamma'}$. Relation (1.17) results in Fisher's proof of Rushbrooke's exponent inequality [11, 12]:

$$\alpha''+2\beta+\gamma' \geq 2 \qquad (1.13)$$

A third result of equation (1.15) is:

$$\overline{C}_V(\rho_c,T) \geq x_G(\rho_c)\overline{C}_{VG} \qquad (1.18)$$

This relation results in the exponent inequality:

$$\alpha' \leq \alpha'' \qquad (1.19)$$

Using equation (1.15) and (1.16) it follows that the isochoric heat capacity in the two-phase region can be described by:

$$\overline{C}_V = x_G\overline{C}_{VG}{}^{(2)} + x_L\overline{C}_{VL}{}^{(2)} \qquad (1.20)$$

Because the liquid and the gas mole fraction at the critical isochore both become ½ in the limit of the critical temperature we conclude that all terms in equation (1.20) diverge with the same exponent α''. The different paths and exponents in the $\Delta\rho^*$-ΔT^*-plane are given in Figure 1.5.

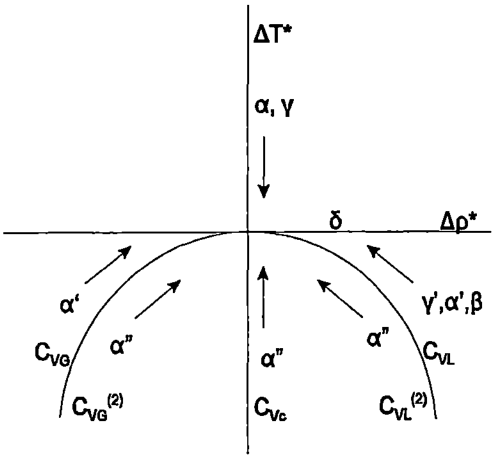


Figure 1.5: Paths and exponents

Two other exponent inequalities can be derived with use of the Yang-Yang relation in the two-phase region where μ and p are only a function of temperature:

$$\rho\bar{C}_V = \frac{C_V}{V} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_\rho - \rho T\left(\frac{\partial^2 \mu}{\partial T^2}\right)_\rho \rightarrow \rho\bar{C}_V = T\frac{d^2p}{dT^2} - \rho T\frac{d^2\mu}{dT^2}$$

(1.21)

After substitution of equation (1.14) into equation (1.20) and comparison of the result with equation (1.21), it can be concluded:

$$T\frac{d^2p}{dT^2} = \frac{\rho_L\rho_G}{\rho_L - \rho_G}(\bar{C}_{VG}{}^{(2)} - \bar{C}_{VL}{}^{(2)}) \qquad T\frac{d^2\mu}{dT^2} = \frac{\rho_G\bar{C}_{VG}{}^{(2)} - \rho_L\bar{C}_{VL}{}^{(2)}}{\rho_L - \rho_G} \tag{1.22}$$

If C_V diverges when approaching the critical point then, according to the Yang-Yang equation, one of the quantities d^2p/dT^2 and $d^2\mu/dT^2$ must also diverge. Therefore, two new power laws are introduced:

$$\frac{d^2\,p}{d\,T^2} \sim |\Delta T^*|^{-\theta_p} \qquad \frac{d^2\,\mu}{d\,T^2} \sim |\Delta T^*|^{-\theta_\mu} \tag{1.23}$$

It follows from equation (1.22) that [6,13]:

$$\theta_p \le \alpha'' + \beta \qquad \theta_\mu \le \alpha'' + \beta \tag{1.24}$$

The scaling hypothesis for thermodynamic properties, to be introduced in Chapter 2 and 3, leads to the following exponent equalities [2]. It is clear that only two thermodynamic exponents can be chosen independently.

$$\begin{aligned} \alpha &= \alpha' = \alpha'' = \theta_p \qquad & \gamma &= \gamma' \\ 2 - \alpha &= \beta(\delta + 1) \qquad & \gamma &= \beta(\delta - 1) \end{aligned} \tag{1.25}$$

1.4 Choice of variables and order parameter

A physical system can be completely described by the internal energy U as a function of entropy S, volume V and number of moles N. For a one-component system this relation reduces to the Gibbs-Duhem equation which only contains variations in *intensive variables* [8]:

$$0 = Nd\mu + SdT - Vdp \qquad (1.26)$$

Internal energy, entropy, mole number, and volume are all *extensive properties,* which satisfy the homogeneity relation:

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \qquad (1.27)$$

$U(S,V,N)$ is called a homogeneous function of it's variables of degree one. In a homogeneous function, one variable can be eliminated by a proper scaling. See Paragraph 1.6. The conventional way of scaling is dividing the conjugate extensive variables by the mole number N, *i.e.* we consider *molar quantities*. The accompanying equation of state is $p(\overline{V},T)$ and the characteristic variables for the Helmholtz free energy are T and $\overline{V}$:

$$d\overline{A} = -\overline{S}dT - pd\overline{V} \qquad (1.28)$$

Another way of scaling is dividing by V, *i.e.* we consider quantities per unit of volume or *densities*. In this case the accompanying equation of state is of the form $\mu(\rho,T)$ and the characteristic variables for the Helmholtz free energy are ρ and T:

$$d(A/V) = -sdT + \mu d\rho \qquad s = S/V \qquad \rho = N/V \qquad (1.29)$$

The first way of scaling is often preferred because of the more direct accessibility of the variables to measurement. However, for real fluids near the critical point a description in terms of $\mu(\rho,T)$ deserves preference for reasons of increased symmetry [2].

The *control or order parameter* is a parameter that reaches a zero value at the critical point. The order parameter is continuous at the critical point, however, its derivative diverges. See Figure 1.1. The concept of order parameter was first introduced when critical behaviour was studied in systems other than fluids [14]. The spontaneous magnetization of a magnetic material diminishes with temperature and disappears at the Curie point. Below the Curie point an ordered state exists in which the atomic spins are at least partially arranged. Above the Curie point no such order exists. The spontaneous magnetization is called the *order parameter*. In uniaxial ferromagnets and in the Ising model, spins can only assume the 'values' up and down and are therefore represented as scalars. The behaviour of a fluid in its weak direction is reminiscent of that of uniaxial ferromagnets. Below the critical point, there are two states of different density corresponding to the states of aligned spins up or down. Above the critical point the density difference has disappeared. Therefore, a scalar order parameter is ascribed to the critical behaviour of fluids. In one-component fluids this order parameter is often assumed to be the density difference between the actual and the critical density. The choice is dictated principally by the observed symmetry of the property with respect to the critical density. The coexisting densities and the chemical potential-density isotherms show respectively a symmetric and antisymmetric behaviour over a wider range than do other choices of variables [3].

1.5 Classical theory

We consider the Helmholtz free energy A as a function of volume V. The slope $(\partial A/\partial V)_T=-p$ must be negative because pressure is always positive. For a one-component fluid it is necessary that the isothermal Helmholtz free energy as a function of volume curves upward. This means that $(\partial^2 A/\partial V^2)_T$ must be positive:

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T = -\left(\frac{\partial p}{\partial V}\right)_T \geq 0 \tag{1.30}$$

This relation equals zero in the critical limit. The derivative $(\partial^2 A/\partial V^2)_T$ is proportional to the inverse of the isothermal compressibility. Therefore, $(\partial^3 A/\partial V^3)_T$ must be zero at the critical point; if it were not, K_T would be negative on one side of the critical isotherm, which would violate mechanical stability [3]. The critical conditions for *three-point contact* are:

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \quad -\left(\frac{\partial^3 p}{\partial V^3}\right)_T \geq 0 \tag{1.31}$$

Critical conditions can also be derived for *(2k+1)-point contact.* The three-point contact leads to a critical isotherm of the third degree. This conclusion follows from the assumption that the Taylor expansion exists, *i.e.* all derivatives of the Helmholtz function (equation of state) exist and the equation of state is analytic in the critical point. The most famous three-point-contact classical equation of state is that of Van der Waals [15]. It was the first successful attempt at formulating an equation of state exhibiting a critical point:

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \tag{1.32}$$

The Van der Waals equation of state is a typical *mean-field equation of state.* Characteristics of mean-field equations are an analytic dependence of the Helmholtz free-energy density or the pressure on volume and temperature while the critical point is characterized by relation (1.31). Van der Waals' approximation, or the mean-field approximation, for the attractive interaction is rigorous in the limit of weak long-range intermolecular forces [2].

For $T>T_c$ the *p(V)*-isotherms decrease monotonically with increasing *V* and they do not violate the criterion of mechanical stability. See Figure 1.6. However, for $T<T_c$, the *p(V)*-isotherms predict a loop in the two-phase region, which does violate the criterion of mechanical stability. The system separates into a liquid and a gas phase according to the *Maxwell construction* of equation (1.33):

$$p_G - p_L = 0 \qquad \mu_G - \mu_L = \int_{\tilde{V}_L}^{\tilde{V}_G} \tilde{V}\,dp = 0 \tag{1.33}$$

Application of the Maxwell equal-area rule eliminates the loop in the two-phase region. However, this construction introduces discontinuities in several thermodynamic properties and eliminates the analyticity of the Van der Waals equation of state [8].

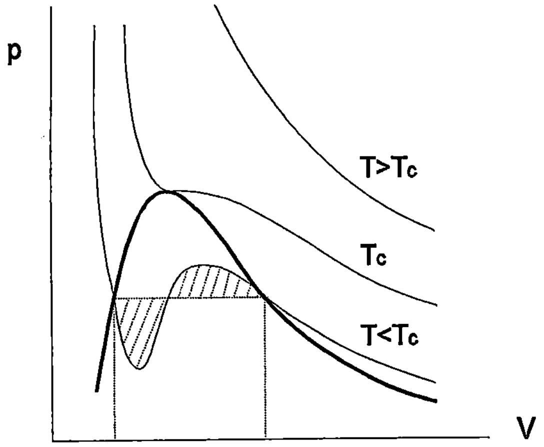


Figure 1.6: Van der Waals-like behaviour and Maxwell construction

The characteristic pattern of the critical anomalies of the classical equations near the critical point can be explored by studying a Taylor series expansion of the equation of state near the critical point [2]. If the power laws also hold for the classical equations of state, the critical exponents and amplitudes can be determined by comparison of the scaling laws and the Taylor series expansion. The expansion procedure is often called the *Landau theory* [16], but in fact it is the work of Van der Waals and Van Laar. We assume that the Helmholtz free-energy density, the pressure, and the chemical potential have a Taylor series expansion in the vicinity of the critical point. The reduced variables are given by equation (1.3) [2]:

$$X^*(\Delta\rho^*,\Delta T^*)=\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{1}{m!}\frac{1}{n!}X_{mn}(\Delta\rho^*)^m(\Delta T^*)^n \qquad (1.34)$$

$$\text{where } X = A,\ p,\ \mu \quad \text{and} \quad X_{mn}=\frac{\partial^{m+n}X^*}{\partial\rho^{*m}\,\partial T^{*n}}$$

The coefficients (derivatives) A_{mn} do completely specify the thermodynamic behaviour of the system. The coefficients p_{mn} and μ_{mn} can be expressed in A_{mn} by use of $\mu^*=(\partial A^*/\partial\rho^*)_T$ and $p^*=\mu^*\rho^*-A^*$:

$$\mu_{mn}=A_{m+1,n} \qquad p_{mn}=A_{m+1,n}+(m-1)A_{mn} \qquad (1.35)$$

The critical conditions for three-point contact are:

$$\begin{array}{lll} A_{20}=A_{30}=0 & \mu_{10}=\mu_{20}=0 & p_{10}=p_{20}=0 \\ A_{40}\geq 0 & \mu_{30}\geq 0 & p_{30}\geq 0 \end{array} \qquad (1.36)$$

The latter three relations follow from the condition of mechanical stability. The relation between p_{mn} and μ_{mn} is:

$$p_{m,n}=\mu_{m,n}+(m-1)\mu_{m-1,n} \quad \text{for} \quad m\geq 1 \qquad (1.37)$$

Using the Taylor series expansions mentioned above, we can give expressions for several thermodynamic properties. These properties are given in Table 1.2. Comparison between the classical expansions in Table 1.2 and the power laws in Table 1.1 gives values for the critical exponents and amplitudes of the behaviour in the limit $\Delta T^*\to 0$, $\Delta\rho^*\to 0$ of the classical three-point contact model for the Van der Waals equation of state [2]:

$$\delta = 3 \qquad \gamma = 1 \qquad \alpha = 0 \qquad D = \frac{p_{30}}{3!} = \frac{3}{2} \qquad \Gamma = p_{11}^{-1} = \frac{1}{6} \qquad \Gamma' = \frac{p_{11}^{-1}}{2} = \frac{1}{12}$$
$$B = \sqrt{\frac{3!\mu_{11}}{\mu_{30}}} = 2 \qquad p_{01} = 4 \qquad p_{02} = \frac{24}{5} \qquad \mu_2 = -\frac{6}{5} \tag{1.38}$$

The exponent $\alpha=0$ means that C_V does not show an anomalous increase in approaching the critical point from within the one-phase region. This conclusion is independent of equation (1.36) and it is general in the classical theory [2]. The classical exponent β can be determined by considering a Taylor series expansion to lowest order in p and μ around the critical point and by recalling that pressure and chemical potential are identical in the coexisting phases:

$$p_{11}(\Delta\rho_L^*)(\Delta T^*) + \frac{1}{6}p_{30}(\Delta\rho_L^*)^3 = p_{11}(\Delta\rho_G^*)(\Delta T^*) + \frac{1}{6}p_{30}(\Delta\rho_G^*)^3$$
$$\mu_{11}(\Delta\rho_L^*)(\Delta T^*) + \frac{1}{6}\mu_{30}(\Delta\rho_L^*)^3 = \mu_{11}(\Delta\rho_G^*)(\Delta T^*) + \frac{1}{6}\mu_{30}(\Delta\rho_G^*)^3 \tag{1.39}$$

According to (1.36) and (1.37), $\mu_{11}=p_{11}$ and $\mu_{30}=p_{30}$. This implies that the relations in (1.39) are identical to lowest order. We can see in Figure 1.7, in which Δp^* is given as a function of $\Delta\rho^*$, that phase separation occurs for $\Delta T^*<0$ ($p_{11}>0$, $p_{30}>0$). For $\Delta T^*<0$, the sum of the contributions (1.39) shows a loop and equation (1.39) has two nonzero solutions. See figure 1.7.

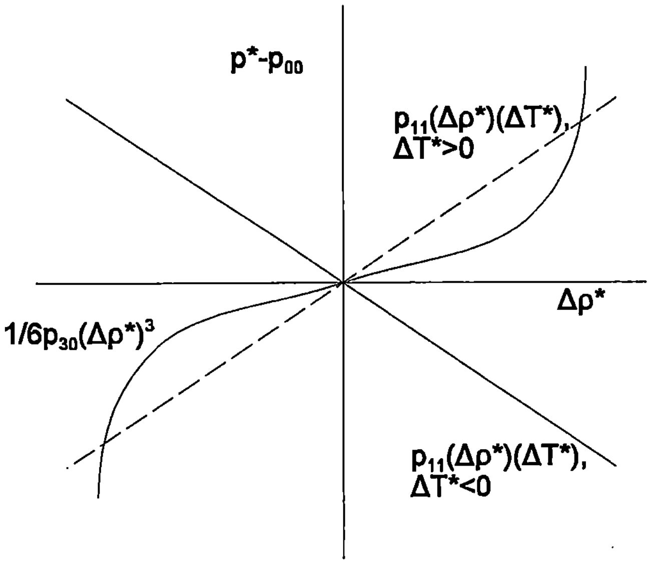


Figure 1.7: Δp^* as a function of $\Delta\rho^*$ in the classical theory

It follows from (1.39) that:

$$\frac{(\Delta\rho_G^* + \Delta\rho_L^*)^2 - (\Delta\rho_G^*)(\Delta\rho_L^*)}{\Delta T^*} = -\frac{6p_{11}}{p_{30}} \tag{1.40}$$

The right part of this equation is independent of T. It can be concluded that to lowest order $\Delta\rho^*_L$ and $\Delta\rho^*_G$ must vary as:

$$\Delta\rho_G{}^* = -B|\Delta T^*|^\beta \quad \Delta\rho_L{}^* = +B|\Delta T^*|^\beta \quad \text{with}$$
$$\beta = \frac{1}{2} \quad \text{and} \quad B = \sqrt{\frac{6p_{11}}{p_{30}}} = \sqrt{\frac{6\mu_{11}}{\mu_{30}}} \tag{1.41}$$

Thus the top of the coexistence curve is quadratic and it is assumed that the top is symmetric with respect to ρ_c. The fundamental postulate of the classical theory is that the Helmholtz free-energy density, pressure, and chemical potential can be expanded into whole powers of $\Delta\rho^*$ and ΔT^*. However, we see in equation (1.41) terms proportional to $|\Delta T^*|^{1/2}$. These terms can be substituted into equations (1.34) and the conditions for coexisting resulting in [17]:

$$\begin{aligned}\Delta\rho_G{}^* &= B_{1G}|\Delta T^*|^{1/2} + B_{2G}|\Delta T^*| + B_{3G}|\Delta T^*|^{3/2} + \ldots.. \\ \Delta\rho_L{}^* &= B_{1L}|\Delta T^*|^{1/2} + B_{2L}|\Delta T^*| + B_{3L}|\Delta T^*|^{3/2} + \ldots..\end{aligned} \tag{1.42}$$

The series expansion of the pressure along the coexistence curve can be obtained by substituting (1.42) into (1.34). The series expansion for μ is identical to the series expansion of the pressure if $p_{m\,n}$ is replaced by $\mu_{m\,n}$. The chemical potentials and pressures of the two coexisting phases must be the same. All coefficients in front of the terms $|\Delta T^*|^{m/2}$ must be identical in the gas and the liquid phase. These constraints result in a large number of conclusions. If we only consider terms up to order $|\Delta T^*|$, we get [8]:

$$p_{Coex}{}^* = p_{00} + p_{01}\Delta T^* \qquad \mu_{Coex}{}^* = \mu_{00} + \mu_{01}\Delta T^* \tag{1.43}$$

It follows from (1.34) for the critical isochore above the critical temperature *($\Delta\rho^*=0$, $\Delta T^*\geq 0$)* that:

$$\begin{aligned} p^*(\Delta\rho^* = 0, \Delta T^* \geq 0) &= p_{00} + p_{01}\Delta T^* + \frac{1}{2}p_{02}(\Delta T^*)^2 + \ldots.. \\ \mu^*(\Delta\rho^* = 0, \Delta T^* \geq 0) &= \mu_{00} + \mu_{01}\Delta T^* + \frac{1}{2}\mu_{02}(\Delta T^*)^2 + \ldots..\end{aligned} \tag{1.44}$$

It follows from (1.43) and (1.44) that the slope of the vapour pressure curve continuously turns to the slope of the critical isochore:

$$\lim_{\substack{\Delta T^*\to 0 \\ \Delta T^*\leq 0}} \frac{dp^*_{Coex}}{dT^*} = \lim_{\substack{\Delta T^*\to 0 \\ \Delta T^*\geq 0 \\ \Delta\rho^*=0}} \left(\frac{\partial p^*}{\partial T^*}\right)_\rho = p_{01} \tag{1.45}$$

The same conclusion holds for the behaviour of μ in the $\mu(T)$-diagram.

Now, we compare the liquid and gas coefficients before the terms $|\Delta T^*|^{3/2}$, $|\Delta T^*|^2$, and $|\Delta T^*|^{5/2}$. The results are given in Table 1.3. The second relation in Table 1.3 is obtained by eliminating B_{2G} and B_{2L} by subtracting the equations for pressure and chemical potential. The only physically realistic solution to this equation is:

$$B_{1L} = -B_{1G} = B = \sqrt{\frac{6p_{11}}{p_{30}}} \tag{1.46}$$

The third relation in Table 1.3 is obtained by eliminating B_{3L} and B_{3G} by subtracting the equations for pressure and chemical potential.

The assumption of symmetry in the top of the coexistence curve (1.41) is justified by equation (1.46). Another result is $B_{2L}=B_{2G}$. With this result, equation (1.42), and equation (1.46), the *diameter of the coexistence curve* is given by:

$$\bar{\rho}^* = \frac{\rho_L^* + \rho_G^*}{2} = 1 + B_2|\Delta T^*| + \ldots.. \qquad (1.47)$$

Asymptotically, this diameter is a linear function of temperature. Therefore, equation (1.47) is called the *law of the rectilinear diameter.*

The coefficients in (1.42) are known and the reduced densities in the Taylor series expansion (1.34) can now be replaced by (1.42) to get thermodynamic properties along the coexistence curve and in the two-phase region as a function of reduced temperature. These thermodynamic properties are given in Table 1.4.

On comparing the relations for the pressure and chemical potential in the two-phase region with the pressure and the chemical potential along the critical isochore (1.44), we conclude that the second order derivatives of pressure and chemical potential along the coexistence curve and the second order derivatives along the critical isochore are not the same. The jump of the second order derivatives in going from the two-phase to the one-phase region is [8]:

$$\frac{p_{11}}{p_{30}^2}\left\{\frac{3}{5}p_{11}p_{40} - 2p_{21}p_{30} + \frac{16}{5}p_{11}p_{30}\right\} \quad \text{or} \quad \frac{\mu_{11}}{\mu_{30}^2}\left\{\frac{3}{5}\mu_{11}\mu_{40} - 2\mu_{21}\mu_{30}\right\} \qquad (1.48)$$

The isochoric heat capacity also makes a jump in going from the two-phase region to the one-phase region. This can be seen by the Yang-Yang relation (1.21):

$$\lim_{\substack{\Delta T^* \to 0 \\ \Delta T^* \le 0}} \frac{C_V^*(0,\Delta T^*)}{T^*} = \lim_{\substack{\Delta T^* \to 0 \\ \Delta T^* \ge 0}} \frac{C_V^*(0,\Delta T^*)}{T^*} + \frac{3p_{11}^2}{p_{30}} \qquad (1.49)$$

Although the second order derivatives d^2p_{Coex}/dT^2, $d^2\mu_{Coex}/dT^2$, and C_{VCoex} are discontinuous in the critical region they stay finite and the critical exponents in the scaling laws are zero:

$$\alpha'' = 0 \qquad \theta_p = \theta_\mu = 0 \qquad (1.50)$$

In the classical theory the critical exponents suffice the following exponent inequalities of Paragraph 1.3 as equalities:

$$\alpha'' + \beta(1+\delta) = 2 \qquad \alpha'' + 2\beta + \gamma' = 2 \qquad \beta(\delta - 1) = \gamma' \qquad (1.51)$$

The followed procedure can be extended to higher orders of $|\Delta T^*|$ and one finds [8]:

$$B_{2iL} = B_{2iG} = B_{2i} \qquad B_{2i-1L} = -B_{2i-1G} = B_{2i-1} \qquad \text{for } i \ge 1$$

$$\Delta\rho_G^* = -B|\Delta T^*|^{1/2} + B_2|\Delta T^*| - B_3|\Delta T^*|^{3/2} + \ldots.. \qquad (1.52)$$

$$\Delta\rho_L^* = +B|\Delta T^*|^{1/2} + B_2|\Delta T^*| + B_3|\Delta T^*|^{3/2} + \ldots..$$

It can be concluded that the difference in coexisting densities,

$$\frac{1}{2}(\rho_L^* - \rho_G^*) = B|\Delta T^*|^{1/2} + B_3|\Delta T^*|^{3/2} + \ldots \qquad (1.53)$$

will in general follow the power law $B|\Delta T^*|^{1/2}$ over a larger range than the separate branches $\Delta\rho_G^*$ and $\Delta\rho_L^*$ in equation (1.52). The diameter of the coexistence curve is given by:

$$\bar{\rho}^* = \frac{1}{2}(\rho_L^* + \rho_G^*) = 1 + B_2|\Delta T^*| + B_4|\Delta T^*|^2 + \ldots\ldots \qquad (1.54)$$

All coefficients in front of the terms $|\Delta T^*|^{m/2}$ must vanish because they are uneven in B_{2i-1} and the constraints $p_L=p_G$ and $\mu_L=\mu_G$ must be satisfied. Concluding; the temperature series expansions of the diameter of the coexistence curve, d^2p_{Coex}/dT^2, $d^2\mu_{Coex}/dT^2$ and the heat capacity C_{VCoex} contain only whole powers of $|\Delta T^*|$ [8].

1.6 Gas-liquid symmetry in the classical theory

The gas and liquid phase become identical in the critical point . It will be obvious that the thermodynamic behaviour in the vicinity of the critical point will be determined by properties that show *symmetry* between the liquid and vapour phase. Firstly, this symmetry is investigated in the classical theory. We have seen that the critical isotherm is asymptotically antisymmetric (Table 1.2, second equation) and the coexistence curve asymptotically symmetric (1.41, 1.46) with respect to the critical isochore ρ_c. For temperatures other than T_c, the classical theory generally predicts no symmetry with respect to ρ_c.

As a first approximation the $\mu(\rho)$-isotherms will be symmetric with respect to the inflection point $\partial^2\mu/\partial\rho^2=(\partial/\partial\rho)(\partial\mu/\partial\rho)=0$. This automatically also holds for derived properties:

$$\text{p}(\rho)\text{ - isotherms with respect to: } \frac{\partial^2 p}{\partial\rho^2} = \left(\frac{\partial}{\partial\rho}\right)\left(\rho\frac{\partial\mu}{\partial\rho}\right) = 0$$

$$\text{compressibility with respect to: } \frac{\partial}{\partial\rho}\left(\rho\frac{\partial p}{\partial\rho}\right) = \left(\frac{\partial}{\partial\rho}\right)\left(\rho^2\frac{\partial\mu}{\partial\rho}\right) = 0 \qquad (1.55)$$

$$\text{p}(\tilde{V})\text{ - isotherms with respect to: } \frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial p}{\partial\rho}\right) = \left(\frac{\partial}{\partial\rho}\right)\left(\rho^3\frac{\partial\mu}{\partial\rho}\right) = 0$$

In general, the geometric place of the symmetry points is given by $(\partial/\partial\rho)(\rho^n\partial\mu/\partial\rho)=0$ and becomes a straight line in the ΔT^*-$\Delta\rho^*$-plane in the vicinity of the critical point. We can calculate these lines, for example the line of maximum $(\partial\rho/\partial\mu)_T$:

$$\Delta\rho^* = -\frac{\mu_{21}}{\mu_{30}}\Delta T^* = -\frac{p_{21}-p_{11}}{p_{30}}\Delta T^* \qquad (1.56)$$

These lines do in general not coincide with the critical isochore $\Delta\rho^*=0$. Below the critical point the lack of symmetry is revealed by the finite slope, $B_2=\mu_{21}/\mu_{30}-3\mu_{11}\mu_{40}/5\mu_{50}^2$, of the diameter of the coexistence curve (1.54).

There exist two symmetry conditions. The *weak symmetry condition*, $\mu_{21}=0$, makes the chemical potential antisymmetric with respect to the critical isochore and the *strong symmetry condition*, $\mu_{21}=0$ and $\mu_{40}=0$, makes the diameter of the coexistence curve asymptotically coincide with the critical isochore and makes that the jump in C_V is connected with a jump in $(\partial^2p/\partial T^2)_\rho$ and not in $(\partial^2\mu/\partial T^2)_\rho$. These considerations can be applied to the equation of state of Van der Waals. The equation of Van der Waals satisfies the weak symmetry condition [8]. See Figure 1.8.

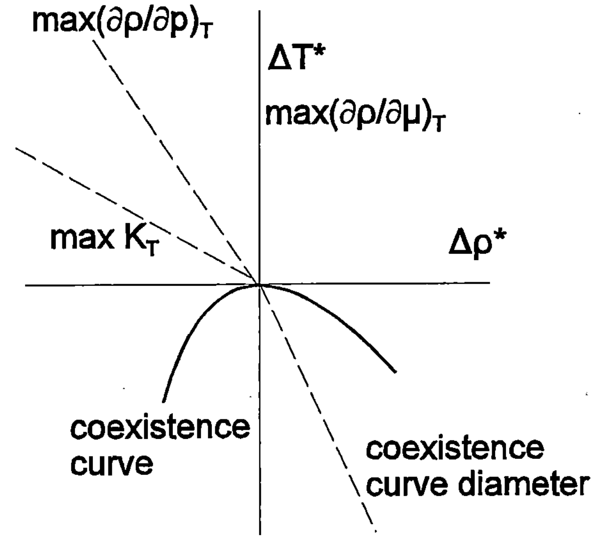


Figure 1.8: Asymptotic behaviour of the symmetry lines according to the Van der Waals equation of state

1.7 Generalized homogeneous functions

A function *f(u)* of the variable *u* is called a homogeneous function of its variable if it satisfies relation (1.57) for all values of the parameter λ.

$$f(\lambda u) = g(\lambda)(u) \qquad (1.57)$$

This means that the value of the function in an arbitrary point λu_0 is connected with the value of the function in the reference point u_0 by a change of scale. The concept of homogeneity can be extended to generalized homogeneous functions of more variables. A function *f(u,v)* of the two variables *u* and *v* is called a generalized homogeneous function of its variables if it satisfies relation (1.58) for two fixed exponents a_u and a_v and for all values of the parameter λ:

$$f(\lambda^{a_u}u, \lambda^{a_v}v) = \lambda f(u,v) \qquad (1.58)$$

A generalized homogeneous function can always be reduced to the form (1.58) by a proper redefinition of λ. The advantage of the homogeneity of a property is the possibility to deduce a scaling law; the dependence on the two variables can be reduced to the dependence on one new scaled variable by an appropriate change of scale:

$$\frac{f(u,v)}{u^{1/a_u}} = f\left(1, \frac{v}{u^{a_v/a_u}}\right) \qquad (1.59)$$

Thus, the generalized homogeneous function satisfies a simple power law along any line $v/u^{av/au}=B$:

$$f(u,v) = f(B,1)u^{1/a_u} \qquad (1.60)$$

The coefficient *f(B,1)* is a constant coefficient. Along the special lines *u=0* and *v=0* the function behaves as:

$$f(0,v) = f(0,1)u^{1/a_v} \qquad f(u,0) = f(1,0)u^{1/a_u} \qquad (1.61)$$

To formulate the scaling property of the classical equation the equation of state $\mu(\rho,T)$ is chosen. The Taylor series expansion for the three-point contact model to lowest order reads:

$$\Delta\mu^* = \mu^* - \mu_c^* - \mu_{01}\Delta T^* + \mu_{11}(\Delta T^*)(\Delta\rho^*) + \frac{1}{3!}\mu_{30}(\Delta\rho^*)^3 + \ldots \qquad (1.62)$$

This equation can be rearranged as:

$$\Delta\mu^* = D(\Delta\rho^*)^\delta\left(1 + \frac{1}{x_0}\frac{\Delta T^*}{|\Delta\rho^*|^{1/\beta}}\right) \qquad \frac{\Delta\mu^*}{(\Delta\rho^*)^\delta} = D\left(1 + \frac{x}{x_0}\right) \qquad x = \frac{\Delta T^*}{|\Delta\rho^*|^{1/\beta}} \quad (1.63)$$

Hence to lowest order, $\Delta\mu^*$ does indeed satify the homogeneity property (1.58) with $a_\rho=1/\delta$ and $a_T=1/(\beta\delta)$ [2].

1.8 Incorrect classical description of the critical region

Unfortunately, the classical equations do not predict correctly the asymptotic shape of the coexistence curve and the critical isotherm of real fluids because classical critical exponents differ from the experimental ones [2, 3, 18]. The classical critical isotherm has a cubic shape with horizontal inflection point. The exponent δ equals 3 for all equations of state that can be expanded at the critical point and have two derivatives zero. The exponent β equals $1/2$ and the coexistence curve has a parabolic top. The heat capacity C_V remains finite at the critical point and shows a jump on crossing the phase boundary. The exponent γ for the isothermal compressibility K_T equals 1. The correlation length in the classical theory of Ornstein and Zernike diverges with an exponent $\nu=1/2$, so that ξ^2 diverges as the compressibility [19].

For real fluids the coexistence curve is flatter than parabolic with a roughly cubic shape with critical exponent $\beta=0.326$. The heat capacity C_V shows a weak divergence with an exponent $\alpha=0.11$. The value of the exponent γ for the isothermal compressibility K_T equals 1.24; a strong divergence. The critical isotherm is flatter than it is in the classical theory with an exponent $\delta=4.8$. The exponent for the correlation length is slightly larger than in the classical case.

The classical or mean-field approximation for the attractive interaction is rigorous in the limit of weak long-range intermolecular forces. In real fluids, however, the attractive forces are usually not long-ranged. This is the reason why the mean-field theories fail to represent the observed thermodynamic behaviour near the critical point [2].

The classical equations are limited with respect to scaling. The quantity $\Delta\mu^*$ (1.62) equals $\mu^*(\rho,T)-\mu^*(\rho_c,T)$ above T_c to linear order in ΔT^*. It also equals $\mu^*(\rho,T)-\mu^*_{Coex}$ because the saturation chemical potential μ^*_{Coex} and the chemical potential $\mu^*(\rho_c,T)$ along the critical isochore have continuous slopes (1.45). It is clear that the scaled equation (1.63) is valid both in the one-phase region above and below T_c to linear order in ΔT^*. However, this argument can not be extended to include higher order terms in ΔT^* since the second order derivative of $\mu^*(\rho_c,T)$ is discontinuous at the critical point. In other words, if higher order terms are included in (1.62), the feature of homogeneity is lost. Thus, although the classical equations of state obey a scaling law up to lowest order, the second order derivative, and consequently the specific heat, in general does not scale even in lowest order [2]. This failure of the classical description is a result of the assumption of analyticity of the thermodynamic properties in the critical point.

Chapter 2: Renormalization Group Theory

The incorrectness of the classical equations of state in the vicinity of the critical point goes together with the critical anomalies or singularities in the critical region:

- The divergence of the correlation length ξ makes a local analysis (at the critical point) impossible.
- The divergence of ξ makes it impossible to do any analysis which assumes that the system of size l is homogeneous on a scale $l \ll L$. This is the failure of the classical or mean-field theories, in which the interactions between the elementary constituents are replaced by an effective homogeneous exterior influence depending only on the statistical properties of the system.
- The correlation length, ξ, coincides with the size of the inhomogeneities of the microscopic distribution so that its divergence makes it impossible to treat the statistical fluctuations perturbatively starting from a macroscopic description using only statistical averages.
- It is difficult to handle singular quantities. The state functions can not be expressed in the form of analytic expansions in $(\theta-\theta_c)$. The succesive terms become very large as the critical point θ_c is approached and convergence of the expansion becomes slower. In the limit of the critical point all terms in the expansion must be taken into account.

A new theory must be designed that is able to describe the thermodynamic properties in the critical region.

2.1 Difference between critical and non-critical systems

To understand scaling laws, the principle of the correlation length, and the different approach of the near-critical region by the Renormalization Group Theory, we must clarify the differences between critical and non-critical systems. Physical phenomena can be roughly divided into two schematic classes illustrated in Figure 2.1:

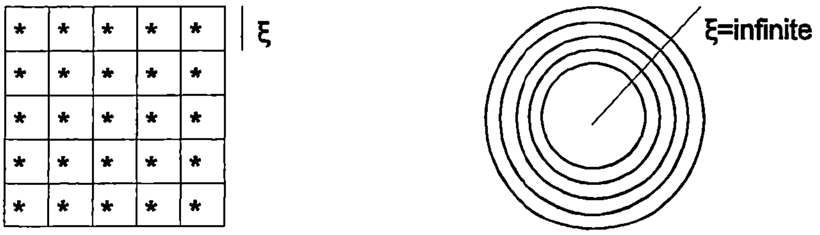


Figure 2.1: The checkerboard-type and the balloon-type system

The checkerboard-type system, which resembles non-critical systems, is invariant under spatial translations of vectors of length ξ. The system with identical squares of size ξ looks homogeneous when observed with a minimum yardstick $a>\xi$. The global structure of the system on a scale $L \gg \xi$, does not reveal the microscopic structure on a scale $\lambda \ll \xi$. The physical interpretation of this is that the range, ξ, of the statistical correlations between the elementary constituents (squares) is too weak to generate collective macroscopic effects: the subsystems act as statistically

independent identical subsystems. To know the state and the properties of the whole checkerboard, it is sufficient to study the state of one subsystem with characteristic length ξ. This characteristic length separates the microscopic structure inside the squares from the macroscopic structure of the global system. In the local microscopic analysis of a square, the quantities associated to scales greater than ξ are constant and play the role of parameters. In the global (macroscopic) analysis, the influence of the microscopic fluctuations is only perceptible through averages of properties which play the role of homogeneous deterministic parameters [1].
The balloon-type system is typical for critical systems. The fundamental invariance of these systems is scale invariance under simultaneous scaling of the amplitudes of the different quantities and lengths. Thus, critical systems have a self-similar structure throughout a large range of scales without any characteristic length, except for the natural bounds and a minimal scale at which a different formalism is to be used. If there would be a characteristic scale, $\xi>0$, it must coincide with its dilations, $k\xi$, because of the invariance under different scalings. So, the characteristic scale must be infinite. This characteristic length, also called *correlation length*, diverges at the critical point, revealing the organization of the microscopic fluctuations giving rise to a perceptible macroscopic phenomenon visible even in the global structure.
These systems behave like a balloon with a pattern as pictured in Figure 2.1. Blowing up the balloon dilates and deformes the pattern, but does not modify its nature nor the topological properties of its structure. To identify the pattern, it is necessary to make a global analysis of the physical system since knowledge of a sample does not suffice to reproduce it completely. No subsystem is statistically independent of the others. Any fluctuation of the pattern is reflected on every scale, up to the global structure. However, an analysis can be done on every scale, as long as the action of a change of scale on the statistical properties and on the state functions is known [1].

As mentioned, the correlation length in the vicinity of the critical point becomes much longer than the range of the intermolecular forces. The long-range nature of the critical fluctuations causes the singular part of the Helmholtz free energy to become a generalized homogeneous function of its variables [20]. Systems having the same invariance properties under transformation, whether of scale or associated to another symmetry will belong to the same universality class [1].
The idea of universality means: the critical singularities do not depend on those parameters in the hamiltonian that characterize the microscopic nature of the system on a length scale of the order of the intermolecular distances, but depend only on some gross features of the system such as the dimensionality of the system and the number of components of the order parameter. These ideas have been given a firm theoretical basis by the Renormalization Group Theory of critical phenomena [21].

Renormalization refers to an operation, based on scaling transformations, meant to be iterated and designed to reduce critical divergences and to obtain scaling laws for critical phenomena. The most interesting question relative to critical systems is how the short-range physical couplings generate a phenomenon perceptible on a large scale. The mechanism is often called *domino* or *snowball effect*; an initially localized perturbation has an effect on the whole of the system. The analysis of the system must be global and must not deal with the microscopic details, but with the way in which they cooperate. The different scales of the system must be related to each other in order to make the scale invariances explicit. Finally, the analysis should be detached from the specific details of the system, in order to give universal results which should be the same for any system in the universality class; the universality of the results make it possible to link qualitative observations of the critical phenomena, which are sufficient to identify its universality class, to quantitative results such as critical exponents and universal functions.

The aims of renormalization are thus:

- to prove the existence of the scaling laws
- to give expressions for the critical exponents (and critical amplitudes if needed)
- to show their universal nature and to determine the associated universality class.

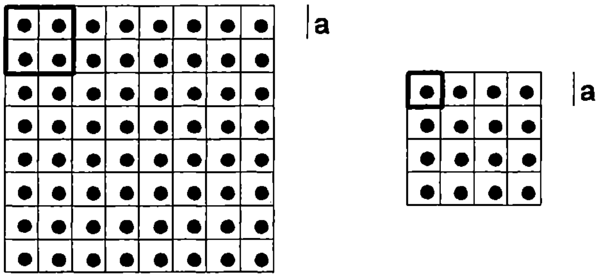
2.2 Terminology

To describe the Renormalization Group Theory we need to define some terms.

- Once a *physical system* ***S*** has been modeled, each of its states on which it is observed is specified by a point of space, possibly a *function space*, called its *phase space* χ. *The structure rule* Φ is the set of ingredients which must be added to the definition of a system in order to describe its equilibrium, its reaction to applied constraints and so on, for example the hamiltonian of a system.
- The *thermodynamic limit of a spatially extended system* corresponds to the following conditions. The linear size L of the system can be considered infinite on the scale of the elementary constituents, so that we can observe the divergence of the range of their statistical correlations. The boundary effects are negligible, thus we can imagine a possible invariance by translation, choose the origin in space arbitrarily and eliminate the non-universal features related to the form of the system. Once the global quantities of the system are calculated, taking the thermodynamic limit consists in dividing them by L^d to reduce the quantities per unit volume, then letting L tend to infinity at a constant density (d is the dimensionality of the system).

2.3 Description of the Renormalization Group Theory

The first step of the renormalization method is to specify the space Φ of structure rules, which are functions φ defined on the phase space χ of the physical system **S**. The renormalization operator R, acting on Φ, shifts the analysis to the space Φ. The renormalization does not transform the realizations of a system in its phase space χ, but transforms its structure rule $\phi \in \Phi$. This shift of the analysis of the space χ to the space Φ is what gives universal results. R relates to each of its fixed points $\phi^* \in \Phi$ all the elements ϕ whose images $[R^n \phi]_{n\geq 0}$ converge to ϕ. The set Φ^* of these elements is a universality class, associated to the typical representative ϕ^*, which is a fixed point of R and thus scale invariant. The critical properties of the elements of Φ^* are related to the characteristics of the operator R and its linearization $DR(\phi^*)$. At each iteration, information contained in the small-scale structures is lost because it is absorbed in the averages or in the local integrations used in the coarse-grainings. Thus, the mean idea of the renormalization is the simultaneous modification of the number of degrees of freedom, reduced by an arbitrary factor $k>1$ by a decimation operation, and of the structure rule $\varphi \in \Phi$. Renormalization selects only those microscopic mechanisms which have repercussions on the higher scales. A simplified version of the decimation operation is given in Figure 2.2.



Initial system **Renormalized system**

Figure 2.2: Decimation operation of a critical system **S**

The systems in Figure 2.2 have a *resolution* or *minimum scale* a at which they are observed. The resolution is large enough for the grain to be considered as pointlike, *i.e.* without internal structure. The range λ of the direct physical interactions between the elementary constituents is the distance a. The result of the use of the minimum scale a, defining the microscopic scale, greater than or equal to λ is to describe the system, so that only the nearest-neighbour elementary constituents interact directly. Depending on the self-similarity of the physical system **S**, the decimation procedure (renormalization) starts with a tiling by macro-cells (coarse-graining) identical to the framed one in Figure 2.2. This procedure reveals the organization of the constituents at the scale $a \cdot n$. It continues with a local average over each macro-cell and ends by contracting the lengths by a factor k in order to preserve the minimal scale a. In this case $k=2$. The number of degrees of freedom is reduced by a factor of k^d, which is equal to 4 in this case. If the minimal scale a is fixed and the number of apparent degrees of freedom is N, the renormalization iterated n times $(n \to \infty)$ makes it possible to describe self-similar systems with initial number Nk^{nd} of degrees of freedom $(Nk^{nd} \to \infty)$.

Scale changes adapted to the value of *k* ensure the preservation of the physical invariants of the system, and weaken its critical nature by reducing the correlation length by a factor *k* and the amplitude of the critical divergences. The renormalization operator, labeled by *k*, is devised so that the scale invariance of the system is expressed by the invariance of its structure rule $\phi = R_k\phi$. The fixed points of R_k are thus typical critical systems.

S is a physical system with extent proportional to *N*. ***S*** has a structure rule ϕ and can be described by a global state function $X(N,\phi)$. The renormalization of ***S*** is given by:

$$N \to N/k \qquad \phi \to Q_k\phi \qquad X \to R_kX \tag{2.1}$$

The renormalization must satisfy:

$$X(N/k, Q_k\phi) = R_k[X(N,\phi)] \qquad X(N) = T_k[X(N/k)] \tag{2.2}$$

The transformation T_k is given by:

$$T_kX(.,\phi) \equiv R_k^{-1}[X(.,Q_k\phi)] \tag{2.3}$$

The point can equal every irrelevant parameter. The dependence of *X* on *N* follows by induction:

$$\forall N_0, p \in N \quad X(k^pN_0,\phi) = R_k^{-p}[X(N_0, Q_k^p\phi)] = [T_k^pX](N_0,\phi) \tag{2.4}$$

The thermodynamic limit $N \to \infty$ is transferred to the iteration of T_k:

$$\lim_{N\to\infty} X(N,\phi) = \lim_{p\to\infty} R_k^{-p}[X(N_0, Q_k^p\phi)] = \lim_{p\to\infty}[T_k^pX](N_0,\phi) \tag{2.5}$$

If this limit exists, its value $X_\infty(\phi)$ does not depend on N_0 and is a fixed point of T_k. The study of the asymptotic dependence on *N* of the state function $X(N,\phi)$ of a particular system ***S*** as $N \to \infty$, is replaced by the study of the asymptotic flow generated by the transformation T_k in the function space $\{X(.)\}$. As a result, the universality of the result in automatically proved, since each result comes with the set $\{X(.)\}$ of functions and thus of systems to which it applies. The physical interpretation of the renormalization associated to R_k and Q_k ensures that the group-theoretic relations $R_{k1} \circ R_{k2} = R_{k1k2}$ and $Q_{k1} \circ Q_{k2} = Q_{k1k2}$ are satisfied whenever the renormalizations by the factors k_1 and k_2 are well defined. If the dependence of R_k and Q_k with respect to *k* can be computed explicitly, we can use $R_k^p = R_kp$ and $Q_k^p = Q_kp$ to write [1]:

$$\lim_{N\to\infty} X(N,\phi) = \lim_{N\to\infty} R_N^{-1}[X(N_0, Q_N\phi)] = \lim_{N\to\infty}[T_NX](N_0,\phi) \tag{2.6}$$

At each iteration, renormalization reduces the range $\xi(\boldsymbol{S})$ of the statistical correlations in ***S*** by a factor *k*. Moreover:

- If $\xi(\boldsymbol{S}) < \infty$, then after *j* iterations for sufficiently large *j*, it will bring ***S*** to a non-critical system $R^j\boldsymbol{S}$, since the scale $k^j\xi(\boldsymbol{S})$ of its correlations is then of the (microscopic) order of the minimum scale *a* of the description.
- If $\xi(\boldsymbol{S}) = \infty$, it will transform ***S*** (critical) into other exactly critical models, from which the specific details having no macroscopic consequences are progressively eliminated. This reveals the self-similar structures of ***S*** and causes the structure rule $R^n\phi$ to approach a fixed point ϕ^* of *R*; then $\xi^* = \infty$, so that ϕ^* is associated to a typical critical system.

2.4 Ising model and lattice gas

The Ising model is a theoretical model to describe the magnetic phenomena in solid matter. It was formulated for the ferromagnetic phase transition in solids in which the assumption of the long-range forces implicit in the classical or mean-field theories was dropped [22]. The model posseses a critical point in which the Helmholtz free energy is not analytic. The behaviour of the magnetism M as a function of T for a ferromagnet in the limit of zero magnetic field H is given in Figure 1.1. At low temperatures spontaneous magnetization occurs. The spontaneous magnetization decreases at increasing temperature and vanishes in the critical point, which is called the Curie point, $H=0$ and $M=0$.

In the Ising model, the magnetic spins are placed on a regular array, one spin at each site, which may either point upwards or downwards. In the simplest form of the model, the interactions between spins are limited to nearest neighbours only. These interactions may be ferromagnetic, when the lowest energy state is that of parallel spins on neighbouring sites, or antiferromagnetic, when it is energetically favourable for neighbouring spins to line up in an antiparallel configuration. The *1*-dimensional Ising model gives no correct results. However, the *2*-dimensional model does [23]. The Ising model can serve as a model for a variety of phase transitions, for example the gas-liquid phase transition [24]. The renormalization procedure is not restricted to lattice systems. Most calculations based on the renormalization group theory have been performed for the so-called Landau-Ginzburg-Wilson model. This model is a generalization of the Ising-like systems in which the spin variable is no longer assiociated with discrete lattice sites but is replaced by a continuous spin function $\sigma(x)$.

The rigorous translation of the Ising model into a model for a gas on a lattice was formulated by Lee and Yang [25]. The generalization of the Ising model, called the Ising-like spin system, is given here [26]. An Ising-like spin system is a lattice system in which the spin variable σ_i may assume an arbitrary number of values. According to statistical mechanics, the Helmholtz free energy of a system can be calculated using the canonical partition function:

$$A_S = -kT\ln(Z_S) \qquad Z_S(T,H,N_S) = \sum_{\{\sigma_i\}} \exp\left(\frac{J}{kT}\sum_{\langle i,j\rangle}\sigma_i\sigma_j + \frac{H}{kT}\sum_i \sigma_i\right) \tag{2.7}$$

For a description of the phase transition we have to consider the Helmholtz free energy per spin, $\tilde{A}_s=A_s/N$, which has a well defined value in the thermodynamic limit $N_S\rightarrow\infty$. The other thermodynamic properties follow from differentiation of the Helmholtz free energy per spin:

$$\begin{aligned} &d\tilde{A}_s=-\tilde{S}dT-\tilde{M}dH \qquad \tilde{C}_M = \tilde{C}_H - T\left(\frac{\partial M}{\partial T}\right)_H^2 \frac{M_0}{\chi_T} \qquad \tilde{M} = -\left(\frac{\partial \tilde{A}_s}{\partial H}\right)_T \\ &\tilde{C}_H = T\left(\frac{\partial \tilde{S}}{\partial T}\right)_H = -T\left(\frac{\partial^2 \tilde{A}_s}{\partial T^2}\right)_H \qquad \chi_T \equiv \frac{1}{M_0}\left(\frac{\partial M}{\partial H}\right)_T = -\frac{1}{\tilde{M}_0}\left(\frac{\partial^2 \tilde{A}_s}{\partial H^2}\right)_T \end{aligned} \tag{2.8}$$

The Renormalization Group Theory can be applied to this example by considering equation (2.7). The function in the exponent is called the *generalized hamiltonian* H_t. We consider the reduced Helmholtz free energy per spin:

$$\tilde{A}_s = -\frac{A_s}{N_s \cdot k_b \cdot T} = \ln \sum_{\{\sigma_i\}} \exp(H_t) \qquad (2.9)$$

In this case the hamiltonian depends on a number of parameters, such as temperature, field, and number of states of the spin variable. These parameters may be indicated by:

$$\{K\} = K_1 K_2 \ldots\ldots \qquad (2.10)$$

For a spin system with N_s lattice sites, one may attempt to calculate the free energy from relation (2.9) by first summing only over groups that are within cells of length l, where l is measured in terms of the lattice constant. The result may be interpreted in terms of the properties of a new spin system for which the lattice sites correspond to the cells of the original lattice. The reduced free energy of the new spin system may be written as:

$$\tilde{A}_s' = \tilde{A}_s\{K'\} = \ln \sum_{\{\sigma_i'\}} \exp H_t\{K'\} \qquad (2.11)$$

The summation is to be conducted over all possible values of the spin variables σ_i' of the new spin system. The hamiltonian $H_t\{K'\}$ will be determined by a new set of values K' of the parameters of the hamiltonian. The Renormalization Group Transformation is given by:

$$\{K'\} = R_l\{K\} \qquad (2.12)$$

The reduced free energy of the new spin system is related to the reduced free energy of the original system by:

$$\tilde{A}_s\{K\} = l^{-d}\tilde{A}_s\{K'\} \qquad (2.13)$$

When the system is not at the critical point but close to it, the correlation length is large but not infinite. Upon iteration of the renormalization transformation the trajectory in the space of the parameters of the hamiltonian will approach a fixed point K^* as long as the length scale remains smaller than ξ and will move away from the fixed point when the length scale becomes larger than ξ:

$$\{K^*\} = R_l\{K^*\} \qquad (2.14)$$

In the vicinity of the critical point the transformation may be presented by a linear approximation:

$$K'_\alpha - K_\alpha^* = \sum_\beta \left(\frac{\partial K'_\alpha}{\partial K_\beta}\right)_{K^*} (K_\beta - K_\beta^*) \qquad (2.15)$$

The eigenvalues of the matrix $(\partial K'_\alpha/\partial K_\beta)_{K^*}$ are denoted by $l^{y\alpha}$, and the corresponding eigenfunctions or scaling fields by u_α. The transformation in the vicinity of the critical point is:

$$u_{\alpha'} = l^{y_\alpha} u_\alpha \qquad (2.16)$$

It follows from (2.13) and (2.14) that the reduced free energy as a function of its scaling fields satisfies a generalized homogeneous relation:

$$\tilde{A}_s(u_1, u_2, \ldots) = l^{-d}\tilde{A}_s(\lambda^{y_1}u_1, \lambda^{y_2}u_2, \ldots) \qquad (2.17)$$

This result holds for the singular part of the reduced free energy. In addition there is a regular (classical) contribution due to the summation over the short-range interactions. The scaling fields with $l^{y\alpha}>1$ are called relevant and the scaling fields with $l^{y\alpha}<1$ are called irrelevant. Upon iteration of the transformation (2.17), the singular part of the Helmholtz free energy in the vicinity of the critical point will assume the same form independent of the starting variables of the irrelevant parameters. Therefore, systems whose hamiltonians differ only with respect to the irrelevant scaling fields belong to the same universality class.

Onsager found an analytical solution for the *2*-dimensional Ising model with *H=0* [23]. One striking result is that the second derivative of the Helmholtz free energy to the temperature does not exist in the Curie-point. This is in contradiction with the assumption of the classical theory that assumes the free energy to be analytic in the critical point. The *3*-dimensional model can not be solved but there is a lot of numerical information, obtained by analysis of series expansions. The exponents β, δ, γ, γ', α, and α' can be calculated from the eigenvalues of the linearized renormalization group transformation respectively for the coexistence curve, the critical isotherm, the susceptibility, and the heat capacity:

$$\beta = \frac{5}{16} \qquad \delta = 5 \qquad \gamma = \gamma' = \frac{5}{4} \qquad \alpha = \alpha' = \alpha'' = \frac{1}{8} \qquad \theta_p = \alpha \qquad \theta_\mu = 0 \tag{2.18}$$

These values are estimated values. They are expected to be rational. The values of the exponents differ from the values in the classical theory. The difference can be explained by the fact that classical theory assumes long-range interactions and the Ising model short range interactions. Exponent-value estimates for the Landau-Ginzburg-Wilson theory are [27]:

$$\beta = 0.320 \pm 0.015 \quad \gamma = 1.241 \pm 0.002 \quad \nu = 0.627 \pm 0.01 \quad \eta = 0.021 \pm 0.02 \tag{2.19}$$

An agreement between the classical theory and the Ising model is that they both satisfy the inequalities of Rushbrooke and Griffiths as equalities.

The canonical partition function (2.7) is invariable under inverting the magnetic field, however the magnetization *M* changes sign. Also:

$$-H(-M,T) = H(M,T) \tag{2.20}$$

The curve of spontaneous magnetization is symmetric with respect to the "*critical isochore*" *M=0*. The equation of state H(M,T) satisfies the following scaling law in the vicinity of the Curie point [28,29]:

$$\frac{H}{M|M|^{\delta-1}} = Dh\left(\frac{x}{x_0}\right) \qquad x = \frac{\Delta T^*}{|M/M_0|^{1/3}} \tag{2.21}$$

The scaling function $h(x/x_0)$ is known numerically for the *3*-dimensional Ising model. Lee and Yang tried to apply the non-classical results of the Ising model to the gas-liquid phase transition by means of the so-called lattice gas model. It is possible to consider the grand-canonical partition function for this case. We consider *N* identical molecules with mass *m* in a volume *V*. The grand-canonical partition function of this system is:

$$\Xi(T,V,\mu) = \sum_{N=0}^{\infty} \exp\left(\frac{\mu N}{kT}\right) \frac{1}{N!\,\Lambda^{3N}} \int_V d\vec{r}_1 \ldots \int_V d\vec{r}_N \exp\left(-\frac{E}{kT}\right) \qquad \Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2} \tag{2.22}$$

The thermodynamic properties follow from differentiation of:

$$pV = kT\ln(\Xi) \tag{2.23}$$

However, the partition functions are too complicated to calculate. The grand-canonical partition function can be simplified by the lattice gas model. We devide de volume *V* up into N_S cells of volume v_0 and assume that the potential energy *E* is composed additively by the sum of the energies of interaction of pairs of molecules. Every cell can contain one molecule at most, *i.e.* the interaction energy for two molecules in one cell is ∞. The interaction energy for two molecules in neighbouring cells is $-\epsilon$ and for other pairs zero. The constants ϵ and v_0 are adaptable parameters that can be identified with the critical temperature and the critical density of the real gas. We hope to find the same simple symmetry behaviour as in the Ising model. The grand-canonical partition function for the lattice gas is given by:

$$\Xi(T,V,\mu) = \sum_{\tau_i} \exp\left(\frac{\varepsilon}{kT} \sum_{\langle i,j \rangle} \tau_i \tau_j + \frac{\mu - kT\ln(\Lambda^3 / v_0)}{kT} \sum_i \tau_i \right) \tag{2.24}$$

This form is analogous to the form of the grand-canonical partition function of the Ising model. This analogy can be made exact by relating the variables of the Ising model to the variables of the lattice gas:

$$\frac{\varepsilon}{4} = J \qquad \Delta\mu = \mu + \frac{\varepsilon q}{2} - kT\ln\left(\frac{\Lambda^3}{v_0}\right) = 2H \tag{2.25}$$

Results of the lattice gas are: in contrast to the classical theory the chemical potential in the lattice gas does not show anomalous behaviour on the critical isochore and all derivatives of the chemical potential are continuous in the critical point. We conclude from the Yang-Yang equation (1.21) that the divergence of C_V in the two-phase region is connected with a divergence in the second order derivative of the vapour pressure curve. The chemical potential is, in analogy with (2.20), antisymmetric with respect to the critical isochore $\Delta\rho^*=0$:

$$-\Delta\mu^*(-\Delta\rho^*, \Delta T^*) = \Delta\mu^*(\Delta\rho^*, \Delta T^*) \tag{2.26}$$

This means that the diameter of the coexistence curve coincides with the critical isochore. Another consequence is that the compressibillity of the lattice gas is a symmetric function of $\Delta\rho^*$. The pressure constains a symmetric and an antisymmetric term. The critical exponents for the lattice gas equal the ones for the Ising model given in (2.18). A scaled equation of state can be made in analogy with relation (2.21):

$$\frac{\Delta\mu^*}{\Delta\rho^* |\Delta\rho^*|^{\delta-1}} = Dh\left(\frac{x}{x_0}\right) \qquad x = \frac{\Delta T^*}{|\Delta\rho^*|^{1/\beta}} \tag{2.27}$$

The importance of the Ising model is that it can serve as a model for a variety of phase transitions [30]. The analogy between the Ising model and the lattice gas can be extended to models with interactions between non-neighbouring cells. All three-dimensional lattice gases belong to the same universality class. Both the ferromagnetic and the antiferromagnetic phase transitions can be described by changing the sign of the nearest-neighbour interaction. If spins pointing upward are replaced by particles *A* and spins pointing downward by particles *B*, a model for phase transitions in binary solids is obtained. Finally, the Ising model can be used as a model for the gas-liquid transition [24]. The rigorous translation of the Ising model into a model for a gas on a lattice was formulated by Lee and Yang [25]. Decorated lattice gases are obtained from the ordinary lattice gas by creating interstitial sites and allowing molecules occupying those interstitial sites to interact with molecules on adjacent primary sites. Doing so, the particle-hole symmetry is broken, which makes the lattice gas a more realistic fluid. An important feature of the decorated lattice gases is that their hamiltonian can be mapped onto that of a *spin-½* Ising model [31]. In the application to fluids, the decorated lattice gas has suggested the form of the transformation from physical to scaling variables. It has also been used in the description of dilute mixtures. However, there is no closed form of the Ising model and therefore, the use of the decorated lattice gas is limited to preferred curves as the coexistence curve, $H=0$.

Chapter 3: Homogeneous functions and scaling laws

3.1 Universality

The key idea in the development of scaled descriptions for the critical behaviour of fluids and fluid mixtures is that of critical-point universality.
To characterize the behaviour of the thermodynamic properties of systems near a critical point, systems are grouped into universality classes. Systems within one universality class have the same universal critical exponents and scaling functions. Specifically, fluids are expected to belong to the *3*-dimensional Ising-like systems (*3*-dimensional systems with a *1*-dimensional order parameter and with short-range forces) for which the universal quantities have been calculated with considerable accuracy. Many detailed theoretical predictions have become available for the Ising-like universality class, the major part by the RG-Theory of critical phenomena applied to spin systems. See Chapter 2.

The lattice gas has a perfect antisymmetry with respect to the critical isochore when μ is considered as a function of ρ, while this symmetry property is lacking in any other set of variables. However, for real fluids we do not a priori know which variables are to be preferred in describing critical behaviour. Such a choice can be based on empirical considerations. The shape of the coexisting curve can be studied by plotting either the coexisting volumes or the coexisting densities as a function of temperature. This has been done for argon and it is seen that there is a clear preference for a description in terms of $\mu(\rho,T)$ rather than $p(\tilde{V},T)$ while in contrast to the $p(\tilde{V},T)$-isotherms the $\mu(\rho,T)$-isotherms are remarkably antisymmetric with respect to ρ_c [3]. The property $\rho^{*2}K_T^{*}=(\partial\rho^{*}/\partial\mu^{*})_T$ as a function of ρ also shows symmetry with respect to the critical density [8]. We conclude that the antisymmetry of $\Delta\mu^{*}$ in the lattice gas also holds for real gases in the vicinity of the critical point.
If the chemical potential is indeed antisymmetric with respect to the critical isochore, as in the lattice gas, then the chemical potential along the critical isochore can be written as [8]:

$$\mu(\rho_c,T)=\frac{1}{2}\left(\mu(\rho_c+\Delta\rho,T)+\mu(\rho_c-\Delta\rho,T)\right) \qquad (3.1)$$

both above and below the critical temperature. The chemical potential will be regular in the one-phase region (maybe without coexistence curve), which results together with equation (3.1) in the conclusion that $\mu(\rho_c,T)$ will be regular even for $T=T_c$. In practice, this antisymmetry is only approximately valid and it is difficult to say something about the behaviour of the higher derivatives of $\mu(\rho_c,T)$. We assume in deriving scaling laws that the derivatives $(\partial\,\mu(\rho_c,T)/\partial T)_\rho$ and $(\partial\,^2\mu(\rho_c,T)/\partial T^2)_\rho$ vary continuously. The analyticity of μ on the critical isochore gives the possibility of scaling to a higher order in ΔT^{*} than is possible for the classical equations and it gives the possibility of scaling the specific heat C_V. Thus, if the assumption of scaling is to be tested on numerical data for the lattice gas, it is advisable to consider $\mu(\rho,T)$ instead of $p(\tilde{V},T)$ [8].

The slope of the line through the coexisting specific heats C_V^*/T as a function of reduced density equals $d^2\mu/dT^2$ and the intercepts of these lines equal d^2p/dT^2. The first derivative does not vary in a temperature range of 10 %, while the latter derivative shows an appreciable increase [32A]. In the lattice gas $d^2\mu/dT^2$ would be constant, while d^2p/dT^2 would diverge weakly like C_V. Therefore, we identify u and v in relation (1.58) with ΔT^* and $\Delta\rho^*$. The observation that the thermodynamic properties in the vicinity of the critical point follow power laws along the critical isochore, the critical isotherm, and the coexistence curve leads to the assumption that the properties are generalized homogeneous functions of ΔT^* and $\Delta\rho^*$ in the vicinity of the critical point. We assume that the singular part of the Helmholtz free-energy density A^*_{sing} is symmetric and $\Delta\mu^*$ is antisymmetric in $\Delta\rho^*$. A rough guideline for the range of symmetry is $\Delta\rho^*=\pm 0.25$. The symmetry relations ignore the difference between the critical isochore and the rectilinear diameter when applied below T_c.

Experimentally found critical exponents are [33A]:

$$\begin{aligned} &\alpha = 0.10 \pm 0.04 \quad \beta = 0.355 \pm 0.007 \\ &\gamma = 1.19 \pm 0.03 \quad \delta = 4.35 \pm 0.10 \end{aligned} \tag{3.2}$$

Within the accuracy of the measurements the critical exponents satisfy the following relations:

$$\begin{aligned} &\alpha = \alpha' = \alpha'' = \theta_p \qquad && \alpha + 2\beta + \gamma = 2 \\ &\gamma = \gamma' && \alpha + \beta(\delta + 1) = 2 \end{aligned} \tag{3.3}$$

The description of the thermodynamic behaviour in the vicinity of the critical point is based on three assumptions [8];

- The chemical potential is antisymmetric with respect to the critical isochore in the vicinity of the critical point.
- The critical exponent θ_μ equals zero.
- The critical exponents satisfy the exponent equalities (3.3).

3.2 Postulate for the homogeneity of the Helmholtz free-energy density

The description of the thermodynamic behaviour in the vicinity of the critical point by generalized homogeneous functions was first made by Widom [34A].

The assumptions mentioned in Paragraph 3.1 lead to the following description of the Helmholtz free-energy density A^*:

$$A^* = A_0^*(T^*) + \rho^* \mu^*(\rho_c, T^*) + A_{sing}^*(\Delta T^*, \Delta\rho^*) \tag{3.4}$$

A_{sing}^* is a symmetric function of $\Delta\rho^*$ which follows from $(\partial A_{sing}^*/\partial\Delta\rho^*)_T = \Delta\mu^*$. The term $A_0(T^*)$ is an analytic background term, which depends on T. Because $\mu(\rho_c, T)$ is assumed to be a regular function, all critical anomalies are accomodated in the term A_{sing}^*. In analogy with relation (1.58) we assume this term to be a generalized homogeneous function of ΔT^* and $\Delta\rho^*$ in the one-phase region:

$$A_{sing}^*(\lambda^{a_T}\Delta T^*, \lambda^{a_\rho}\Delta\rho^*) = \lambda A_{sing}^*(\Delta T^*, \Delta\rho^*) \tag{3.5}$$

This postulate results in the power laws and exponent equalities in Table 3.1 and equation (3.3). The postulate is based on the known properties of the lattice gas.

However, since the lattice gas is a highly artificial model of a fluid, the assumption of homogeneity and the choice of variables for real fluids remain empirical postulates. The homogeneity property of A_{sing}^* means that the derivatives of A_{sing}^* to $\Delta\rho^*$ or ΔT^* also are generalized homogeneous functions of $\Delta\rho^*$ and ΔT^*. After differentiation and redefining Λ we get the results of Table 3.1 [90].

The exponents a_T and a_ρ can be expressed in the known exponents:

$$a_T = \frac{1}{(\delta+1)} = \frac{\beta}{2-\alpha} \qquad a_\rho = \frac{1}{\beta(\delta+1)} = \frac{1}{2-\alpha} \tag{3.6}$$

We can make a scaling law with the scaling variable x in analogy with (1.60):

$$\frac{A_{sing}^*}{|\Delta\rho^*|^{\delta+1}} = A_{sing}^*(x,1) \quad \text{with} \quad x = \frac{\Delta T^*}{|\Delta\rho^*|^{1/\beta}} \tag{3.7}$$

The coexistence curve can be described by defining:

$$x_0 = B^{-1/\beta} \qquad \text{or} \qquad B = x_0^{-\beta} \qquad \text{with} \quad -x_0 = x \tag{3.8}$$

The accompanying scaled expressions of the derivatives of A_{sing}^* can be found in Table 3.2. We can rewrite equation (3.4) as:

$$A^* = A_0^*(T^*) + \rho^*\mu^*(\rho_c, T^*) + |\Delta\rho^*|^{\delta+1} Da\left(\frac{x}{x_0}\right) \quad \text{with} \quad Da\left(\frac{x}{x_0}\right) = A_{sing}^*(x,1) \tag{3.9}$$

In the same way:

$$\mu^* = \mu^*(\rho_c, T^*) + \Delta\rho^*|\Delta\rho^*|^{\delta-1} Dh\left(\frac{x}{x_0}\right) \quad \text{with} \quad Dh\left(\frac{x}{x_0}\right) = \Delta\mu^*(x,1) \tag{3.10}$$

The functions *a(y)* and *h(y)* are coupled via the following relation [36A, 33]:

$$\beta h(y) = -ya'(y) + \beta(\delta+1)a(y) \qquad a'(y) = da/dy \tag{3.11}$$

The scaling function $h(x/x_0)$ determines the equation of state $\Delta\mu^*(\Delta\rho^*, \Delta T^*)$. If the equation of state is known we can calculate the singular part of the Helmholtz free-energy density by solving (3.11). The other thermodynamic properties can be calculated from relation (3.9) and (3.10) by differentiation. They are given in Table 3.3.

We see from (Table 3.3, relation 7) and (Table 3.3, relation 11) that the anomalous contribution to C_V/T in the two-phase region indeed diverges as d^2p/dT^2.

The anomalous contributions along every curve of constant x vary as a power law as can be seen in Table 3.3. The curves of constant x in the ΔT^*-$\Delta\rho^*$-plane are indicated schematically in Figure 3.1. The curve with $x = -x_0$ is the coexistence curve, with $x=\infty$ the critical isochore and with $x=0$ the critical isotherm. Universality predicts that, for example, scaling plots of $\Delta\mu^*/(\Delta\rho^*)|\Delta\rho^*|^{\delta-1}$ versus x/x_0 must coincide for different fluids with proper choice of D and x_0. [3, 33]. This has been done for the quantum gas ^4He, the noble gas Xe, the more-atomic gas CO_2, and the polar gas H_2O [3]. Indeed, all scaled chemical potentials coincide on one curve; these gases approximately satisfy the principle of universality. In practice, the scaled equation of state (3.10) can describe results in the following temperature and density range around the critical point [8]:

$$|\Delta\rho^*| \leq 0.25 \qquad 5\cdot 10^{-4} \leq |\Delta T^*| \leq 3\cdot 10^{-2} \tag{3.12}$$

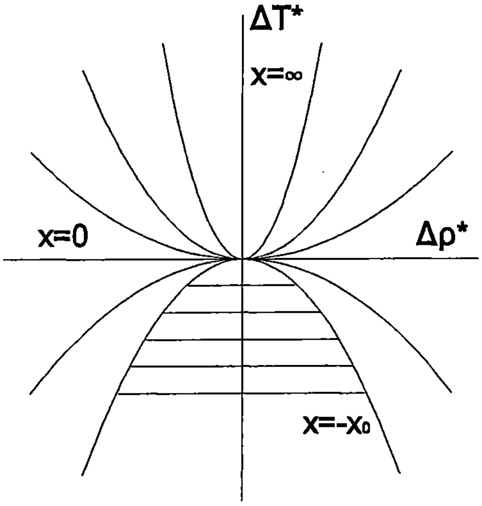


Figure 3.1: Curves of constant x in the Δρ*-ΔT*-plane

3.3 Scaled equations of state

The scaled equation of state as a function of *h(y)* is given by equation (3.10). The question is how *h(y)* looks like. The function *h(y)* has the following boundary values:

$$h(-1)=0 \qquad h(0)=1 \qquad h(\infty)=\infty \tag{3.13}$$

The first boundary value makes $\Delta\mu^*$ equal to zero on the coexistence curve. The second boundary value makes that the amplitude *D* can be identified with the amplitude of the power law (Table 1.1). The last boundary value follows from the observation that the compressibility remains finite along the critical isochore. Mechanical stability and thermal stability require two other constraints [8]:

$$\beta\delta h(y) \geq y\frac{dh(y)}{dy} \qquad a''(y) \leq 0 \tag{3.14}$$

Finally, one expects $\Delta\mu^*$ to be analytic everywhere in the one-phase region with exception of the critical point and maybe the coexistence curve. The function *h(y)* can be expanded in a power law around every value y_1 in the interval $-1<y_1<\infty$. For little *y*:

$$h(y) = 1+\sum_{n=1}^{\infty} h_n y^n \tag{3.15}$$

$\Delta\mu^*$ must also be analytic along the critical isochore for $\Delta T^*>0$. Therefore, *h(y)* is expected to have the following expansion around $y=\infty$:

$$h(y) = \sum_{n=1}^{\infty} \eta_n y^{\beta(\delta+1-2n)} \tag{3.16}$$

Up till now, it is not possible to find a closed expression for *h(y)*. An approximation is the so-called MLSG-equation, which results in the following equation of state [37A, 38A]:

$$h_{MLSG}(y) = (1+y)\left(\frac{1+E_2(1+y)^{2\beta}}{1+E_2}\right)^{\frac{\gamma-1}{2\beta}}$$

$$\Delta\mu^* = \Delta\rho^*|\Delta\rho^*|^{\delta-1}E_1\left(1+\frac{x}{x_0}\right)\left(1+E_2\left(1+\frac{x}{x_0}\right)^{2\beta}\right)^{\frac{\gamma-1}{2\beta}} \quad \text{with} \quad E_1 = \frac{D}{(1+E_2)^{\frac{\gamma-1}{2\beta}}} \qquad (3.17)$$

This equation of state describes experimental results in the density and temperature range (3.12) rather well [8, 33A]. However, it has two disadvantages. While the equation satisfies the analyticity requirement for small values of *y*, it does only reproduce the first two terms in the series expansion (3.16) for large values of *y*. Secondly, the equation can not be integrated to yield a closed form for the function *a(y)* [39A, 40A].

The problems of the MLSG-equation can be overcome by replacing the physical parameters $\Delta\rho^*$ and ΔT^* by parametric variables r and θ [16, 41A]. The parameter θ indicates the position at a curve of constant r and r indicates the distance from the critical point. An advantage of this approach is that all critical anomalies are described by power laws as a function of r while the dependence on θ remains analytical. All anomalies are limited to $r=0$. The curves of constant x in Figure 3.2 become curves of constant θ. A transformation between physical and parametric variables is given by [8]:

$$\Delta T^* = rT(\theta) \qquad \Delta\rho^* = r^{\beta}M(\theta) \qquad \Delta\mu^* = r^{\beta\delta}H(\theta) \qquad (3.18)$$

The quantities $x=\Delta T^*/|\Delta\rho^*|^{1/\beta}=T(\theta)/|M(\theta)|^{1/\beta}$ and $\Delta\mu^*/(\Delta\rho^*|\Delta\rho^*|^{\delta-1})=H(\theta)/(M(\theta)^*|M(\theta)|^{\delta-1}$ are both a function of θ and not of r. As a consequence, equation (3.18) satisfies the scaling law (3.10). We can also satisfy the asymptotical antisymmetric behaviour of $\Delta\mu^*$ with respect to $\Delta\rho^*$ by requiring that $M(\theta)$ and $H(\theta)$ are antisymmetric functions and $T(\theta)$ is a symmetric function of θ:

$$-M(-\theta) = M(\theta) \qquad -H(-\theta) = H(\theta) \qquad T(-\theta) = T(\theta) \qquad (3.19)$$

The transformation is fixed if we specify the functions $T(\theta)$ and $M(\theta)$. The result of the transformation, as given in Figure 3.2, can be obtained by [8]:

$$T(\theta) = 1-b^2\theta^2 \qquad M(\theta) = k\theta \qquad H(\theta) = a(\theta)\theta(1-\theta)^2$$

$$a(-\theta) = a(\theta) \qquad k = \left(\frac{b^2-1}{x_0}\right)^{\beta} \qquad (3.20)$$

The function *a* is an unknown function that is symmetric according to equation (3.19). The constant b^2 is still to be specified. Yet, the equation of state can be fixed by determining $a(\theta)$ instead of $h(y)$. One can calculate the parameters r and θ using $\Delta\rho^*$ and ΔT^* for a given value of b. Subsequently, the experimentally derived values of $\Delta\mu^*/(r^{\beta\delta}\theta(1-\theta)^2)=a(\theta)$ can be plotted against θ [8]. The function $a(\theta)$ is almost independent of θ for suitable values of the parameter b and can be approximated by a mean value a [33A]. This approximation is called the *linear model* [16]:

$$\Delta T^* = r\left(1-b^2\theta^2\right) \qquad \Delta\rho^* = kr^{\beta}\theta \qquad \Delta\mu^* = ar^{\beta\delta}\theta(1-\theta)^2 \qquad (3.21)$$

The description with the linear model has about the same quality as the description with the MLSG-equation (3.17). The advantages of the linear model are the analyticity in the one-phase region and the possibility to obtain closed expressions for thermodynamic functions due to the possibility of analytical integration. The coefficients of the power laws in terms of constants and the thermodynamic parametric functions for the linear model are given in Table 3.4 and Table 3.5.

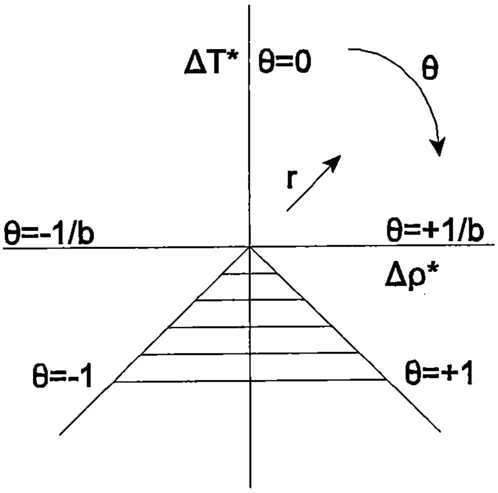


Figure 3.2: Curves of constant θ in the Δρ*-ΔT*-plane

The linear model (3.21) can be extended by taking *a* as a constant and extending the second relation in (3.21) to $\Delta\rho^{*}=r^{\beta}\theta(k+k'\theta^{2})$ to get the *cubic model* [42A] or by extending the third relation in (3.21) to $\Delta\mu^{*}=r^{\beta\delta}\theta(1-\theta^{2})(a+a'\theta^{2})$ to get the *quintic model.* The linear model does not describe the 3-dimensional Ising model very well but the cubic model does [8].

3.4 Consequences of universality of critical behaviour

The scaled equations of state are only suitable candidates for a universal equation of state if the number of adjustable parameters is restricted to two. This means that E_2 and the critical exponents in the MSLG equation (3.17), must have universal values if E_1 and x_0 are the adjustable parameters. In practice E_2 is small and roughly the same for a number of fluids [2]. In the parametric linear model, b_1 must be kept at a constant value while k_1 and a_1 are the adjustable parameters. Schofield *et al.* proposed the following value for b_1 [16, 32]:

$$b_1^2 = \frac{\delta - 3}{(\delta - 1)(1 - 2\beta)} \qquad (3.22)$$

With this choice for b_1^2, the singular part of the specific heat reduces to:

$$\frac{C_{V\text{sing}}^*}{T^*} = \frac{A^+}{\alpha} r^{-\alpha} = a_1 k_1 \frac{(1-2\beta)\gamma(\gamma-1)(\delta-1)}{2\alpha(\delta-3)} r^{-\alpha} \qquad (3.23)$$

The model with this value for b_1 is called the *restricted linear model* or *special linear model*. The special linear model gives a rather good description of values of chemical potentials derived from experimental results [8]. In this way we can also get a restricted version of the MSLG equation [33]. We get the *restricted cubic model* or *special cubic model* by the following choices for b_2^2 and c [34]:

$$b_2^2 = \frac{3}{3 - 2\beta} \qquad c = \frac{2\beta\delta - 3}{3 - 2\beta} \qquad (3.24)$$

The restricted cubic model does yield a satisfactory representation of the equation of state for the 3-dimensional Ising model, however with different choices for b_2^2 and c [35, 36, 37].

The hypothesis of universality can also be investigated for fluids with the MSLG equation or the parametric equations. This has been done for ^{3}He [38, 39], ^{4}He [40], Xe [41], CO_2 [42], H_2O [43-46], and O_2 [47]. The experimental data could be fitted on the same equation of state, in this case the restricted linear model. The range of the fit in which the critical exponents are compatible with the 'universal' values and the accompanying critical exponents are given below [48].

$$\begin{array}{lll} 5\cdot10^{-4} \le |\Delta T^*| \le 3\cdot10^{-2} & |\Delta\rho^*| \le 0.25 & \alpha = 0.10 \pm 0.04 \\ \beta = 0.355 \pm 0.007 & \gamma = 1.19 \pm 0.03 & \delta = 4.35 \pm 0.10 \end{array} \qquad (3.25)$$

These exponent values are very similar to the ones found by other authors. More recent theoretical values for the critical exponents for the universality class of Ising-like systems are [49]:

$$\alpha = 0.110 \pm 0.003 \quad \beta = 0.326 \pm 0.002 \quad \gamma = 1.239 \pm 0.002 \quad \delta = 4.80 \pm 0.02 \qquad (3.26)$$

If we assume universality between fluids, the equation of state in the range and with the exponents as given above can be imposed to other fluid date to find the remaining two adjustable parameters [2]. The hypothesis of universality also implies universality for the amplitude ratios Γ/Γ', $\Gamma D B^{\delta-1}$, $A^+/A^-_{//}$, $A\Gamma/B^2$, and $\Gamma D B^{\delta-1}$ so that only two amplitudes are independent of each other. A survey of the experimental evidence for universal asymptotic critical behaviour can be found in a number of reviews [50-53, 54-57].

Some questions are raised by experiments. According to the hypothesis of universality, fluids, the Ising model, and the Landau-Ginzburg-Wilson model belong to the same universality class. However, the critical exponents of the fluids exceed the values of the other two members of the class (2.18, 2.19). The picture of universality of fluid critical behaviour has to be challenged as soon as, for at least one fluid, a different critical exponent is found. Such experimental challenges do exist; (SF_6) $\beta=0.34$, (^{3}He) $\gamma=1.14/1.22$. It has been noted for SF_6 that the exponent β decreases with temperature range [58]. Sufficiently close to the critical point, $|\Delta T^*| \leq 10^{-4}$, the critical exponents do approach Ising-like values [59]. As a consequence, it must be concluded that corrections to asymptotic scaling must be present in the entire temperature range. The corrections may vary from fluid to fluid causing the deviations from universality of the apparent critical exponents [2].

3.5 Fluid critical behaviour

The thermodynamic scaling laws, as given in Table 3.3, in terms of the field variables p, μ, and T result in the pressure:

$$p^* = p^*_{sing}(\Delta\mu^*, \Delta T^*) + \rho^* \Delta\mu^* - A_0^*(T^*) \qquad p^*_{sing}(\Delta\mu^*, \Delta T^*) = |\Delta T^*|^{2-\alpha} f\left(\frac{\Delta\mu^*}{|\Delta T^*|^{\beta\delta}}\right) \quad (3.27)$$

The renormalization theory of critical phenomena indicates that the singular part of the pressure, which is analogous to the free energy of a spin system, will in general have the form [60, 61]:

$$p^*_{sing}(u_h, u_t) = |u_t|^{2-\alpha} f\left(\frac{u_h}{|u_t|^{\beta\delta}}\right) \quad (3.28)$$

The scaling fields u_t and u_h are analytic functions of μ^* and T^*:

$$u_h = (\mu^* - \mu_c^*) - c_1 \Delta T^* + .. \qquad u_t = \Delta T^* - c_2(\mu^* - \mu_c^*) + .. \qquad \mu_c^* = \mu^*(\rho_c, T_c) \quad (3.29)$$

The term $\Delta\mu^* - A_0^*(T^*)$ is an analytic background term that can be made general resulting in a new scaled equation for the pressure [2]:

$$p^* = |u_t|^{2-\alpha} f\left(\frac{u_h}{|u_t|^{\beta\delta}}\right) + \sum_i \sum_j p_{ij} (\Delta T^*)^i (\mu^* - \mu_c^*)^j \qquad p_{00} = p_c^* = 1 \qquad p_{01} = \rho_c^* = \quad (3.30)$$

Suppose that the scaling fields u_h and u_t are properly defined and that the scaling hypothesis (3.28) is made. This hypothesis will only be valid in a limited range around the critical point. Away from the critical point, corrections to scaling have to be made. The RG-theory also provides estimates of the sizes and forms of the correction terms beyond the asymptotic range. Instead of retaining only the scaling fields u_h and u_t in (2.17, 3.28), also irrelevant scaling fields must be retained [60, 62]:

$$p^*_{sing}(u_h, u_t, u_1, u_2, ...) = |u_t|^{2-\alpha} f\left(\frac{u_h}{|u_t|^{\beta\delta}}, u_1|u_t|^{\Delta_1}, u_2|u_t|^{\Delta_2}, ...\right) \quad (3.31)$$

The procedure for applying the Wegner expansion (3.31) to fluids near the gas-liquid critical point was proposed by Ley-Koo and Green. They assumed an analogy between the grand-canonical partition function of a fluid and the canonical partition function of a spin system as is known to exist for the lattice gas [63, 64, 2].

Unlike the relevant scaling fields, the irrelevant scaling fields do not approach zero at the critical point and scale with the so-called gap exponents. These exponents are expected to be universal. Estimates for the 3-dimensional Ising model are Δ_1=0.50 and Δ_2=1.5 [65]. The irrelevant scaling fields do not contribute to the critical anomalies but they lead to corrections to the asymptotic scaling laws. Universality of the correction-to-scaling functions also implies the ratios of all correction-to-scaling amplitudes to be universal. Experimental values for the amplitude ratios of the first correction term are [66-71, 49]:

$$\frac{A_1}{\Gamma_1} = 0.9 \pm 0.1 \qquad \frac{B_1}{\Gamma_1} = 0.5 \pm 0.2 \qquad \frac{\xi_1}{A_1} = 0.6 \pm 0.1 \qquad \frac{\xi_1}{\Gamma_1} = 0.7 \pm 0.1 \qquad (3.32)$$

Accurate determination of the correction to scaling amplitudes requires further research [49].

As mentioned, optical experiments at $|\Delta T^*|<10^{-4}$ have shown that in that range the fluid critical exponents approach Ising-like values. The optical data can be reconciled with data in more conventional ranges by using a Wegner expansion with sufficient terms. Ley-Koo and Green fitted the difference of coexisting densities of SF_6 with a simple power law $B|\Delta T^*|^{\beta}$. The exponent $\beta=0.327\pm0.003$ was restricted to the range $|\Delta T^*|<7\cdot10^{-4}$. A temperature range $|\Delta T^*|<2\cdot10^{-2}$ already required 3 terms in the Wegner expansions [62]. If they had imposed the Ising-like value for $\beta=0.312$, suggested from series expansions, the asymptotic range would even have been smaller and more correction terms would have been required. However, a value of β slightly larger than 0.312 is supported by optical experiments [59], by calculations on the basis of the renormalization theory [27], and by other investigators [65].

Sengers and Levelt Sengers use a scaled thermodynamic potential for fluids in terms of other reduced variables (1.4). The reduced pressure is given by [4]:

$$\tilde{p} = \tilde{p}_0(\tilde{T},\tilde{\mu}) + |u_t|^{\beta(\delta+1)} f_0(x) + u_1 |u_t|^{\beta(\delta+1)+\Delta} f_1(x) \qquad (3.33)$$

At the critical point:

$$\Delta\tilde{T} = 0 \qquad \Delta\tilde{\mu} = 0 \qquad (3.34)$$

The analytic background functions for the chemical potential and the pressure can be expanded around their values at the critical point in powers of reduced temperature, reduced temperature, and reduced chemical potential:

$$\tilde{\mu}_0(\tilde{T}) = \tilde{\mu}_c + \sum_{i=1}^{3} \tilde{\mu}_i (\Delta\tilde{T})^i \qquad \tilde{p}_0(\tilde{T},\tilde{\mu}) = 1 + \sum_{i=1}^{3} \tilde{p}_i (\Delta\tilde{T})^i + \Delta\tilde{\mu} + \tilde{p}_{11}(\Delta\tilde{T})(\Delta\tilde{\mu}) \qquad (3.35)$$

The scaling fields u_t, u_h and u_1 are analytic functions of reduced temperature and reduced chemical potential:

$$u_h = \Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_0(T) \qquad u_t = \Delta\tilde{T} + c\Delta\tilde{\mu} \qquad c = \text{const.} \qquad \mu_1 \approx \text{const.} \qquad (3.36)$$

The system-dependent constant c in the effective scaling field u_t accounts for the mixing of the variables for non-symmetric systems. The potential satisfies the following differential equation from which expressions for the different thermodynamic properties can be calculated:

$$d\tilde{p} = \tilde{U} d\tilde{T} + \tilde{\rho} d\tilde{\mu} = \left(\tilde{U} + \tilde{\rho}\frac{d\tilde{\mu}_0}{d\tilde{T}}\right) d(\Delta\tilde{T}) + \tilde{\rho}\, d(\Delta\tilde{\mu}) \qquad (3.37)$$

To describe the thermodynamic properties as functions of both temperature and density one needs a form for the scaling functions $f_i(x)$ in equation (3.33). A parametric description is needed to describe the universal scaling functions f_0 and f_1 because non-analyticities in the one-phase region away from the critical point are to be avoided. The commonly used transformation is [4]:

$$u_h = r^{\beta\delta} a\theta(1-\theta^2) \qquad u_t = r(1-b^2\theta^2) \qquad a = \text{const.} \qquad b = \text{const.} \qquad (3.38)$$

By the approximation of Schofield [32] (linear model) and the generalization of the linear model approximation to the first correction-to-scaling term by Balfour *et al.* [72], the scaled fundamental equation is completely specified:

$$\Delta\tilde{p} = a r^{\beta(\delta+1)}\left[k_0 p_0(\theta) + r^{\Delta} k_1 p_1(\theta)\right] \qquad p_i(\theta) = p_{0i} + p_{2i}\theta^2 + p_{4i}\theta^4 \qquad \text{for} \quad i = 0,1 \qquad (3.39)$$

The coefficients p_{ij} are functions of β, δ, Δ and b^2 [4]. Higher order models such as the cubic and quintic models with corrections to scaling have also been considered [55, 2, 73, 36]. The system-dependent constants that determine the scales of the fields u_t, u_h and u_1 are given by the coefficients a, k_0, and k_1. Universality of the scaling functions also implies the constant b^2 to be universal. Sengers and Levelt Sengers adopt the value $b^2=1.3757$ to reproduce the universal amplitude ratios [4]. The scaled equation of state with corrections to scaling (3.39) has been applied to experimental data of H_2O, D_2O, Ethylene, Isobutane and CO_2. It gives a correct physical representation in a density range of approximately 30 % above and below the critical density at temperatures up to about 6 % above T_c and down to temperatures below T_c where the vapour and liquid densities begin to differ by more than 30 % from ρ_c.

3.6 Weak and strong directions and divergences

The theory of Griffiths and Wheeler leads to a classification of the types of divergences to be expected in certain thermodynamic derivatives. The simplest form of the theory describes a one-component fluid in terms of its field variables with p and T as the independent and μ as the dependent variable. The dependent variable is called *potential* [2].

The pressure, chemical potential, and temperature are equal in both coexisting phases. Therefore, the two-phase surface in the space formed by the intensive variables p, T, and μ reduces to a coexistence line. The slopes $(\partial p/\partial T)_\mu=s$ and $(\partial p/\partial \mu)_T=\rho$ vary discontinuously when the coexistence line is crossed. Therefore, this coexistence line is a fault in the thermodynamic surface with different slopes on both sides. The difference between the slopes decreases at higher temperatures and vanishes at the critical point. The tangent to this coexistence line in the critical point is called the *special* or *weak direction* [2, 8]. The weak field measures the distance from T_c along the coexistence curve. The exponents α and γ are defined on this path. This direction refers to variables that are distinct in the coexisting phases. Griffiths and Wheeler called such variables *densities* and examples are volume, density, enthalpy, and entropy. Besides the path of constant volume, also the paths of constant enthalpy and entropy have the same critical slope as the coexistence line in the p-T-plane.

The projections of the coexistence line in the p-T-plane and the μ-T-plane are given in Figure 3.3. The special direction in the μTp-space satisfies the following equations:

$$p-p_c=c_1(T-T_c) \qquad \mu-\mu_c=c_2(T-T_c) \tag{3.40}$$

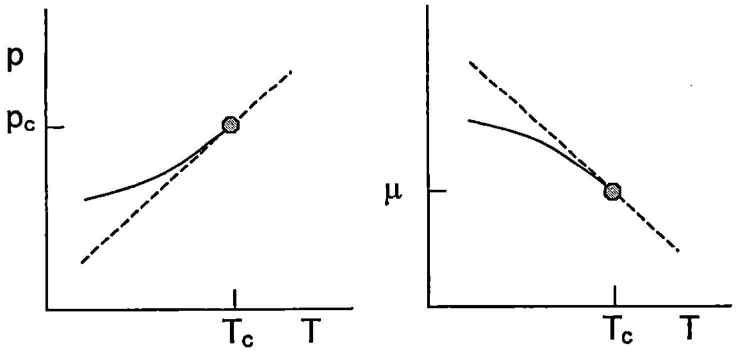


Figure 3.3: Projections of the special direction

The coefficients c_1 and c_2 are given by the equation of Clapeyron. The slope of the tangent to the coexistence curve equals the slope of the critical isochore in the critical point [8]:

$$c_1 = \lim_{\substack{T\to T_c \\ T\le T_c}} \frac{S_V - S_L}{V_V - V_L} = \lim_{T\to T_c}\left(\frac{dp}{dT}\right)_{Coex} = \lim_{\substack{T\to T_c \\ V=V_c}}\left(\frac{\partial p}{\partial T}\right)_V$$

$$c_2 = \lim_{\substack{T\to T_c \\ T\le T_c}} \frac{s_V - s_L}{\rho_V - \rho_L} = \lim_{T\to T_c}\left(\frac{d\mu}{dT}\right)_{Coex} = \lim_{\substack{T\to T_c \\ \rho=\rho_c}}\left(\frac{\partial \mu}{\partial T}\right)_p \qquad \rho_c c_2 = c_1 - s_c \tag{3.41}$$

The property s_c is the entropy density at the critical point. According to Griffiths and Wheeler, the special direction is the only direction that characterizes the properties of the phase transition at the critical point [74]. Therefore, the singular character of the thermodynamic functions will depend on the way in which the critical point is approached. Approaching the critical point in a direction that is asymptotically parallel to the special direction or approaching the critical point in a direction that crosses the special direction changes the singular behaviour. Any path that intersects the special or weak direction in the p-T-plane is called *strong*. The strong scaling field measures departure from the coexistence curve in field space. All strong directions have the same singular behaviour. Examples are the critical isotherm, the critical isobar, the critical iso-chemical potential curve, and the so-called gravity curve. This direction refers to variables that are equal in the coexisting phases. Griffiths and Wheeler called such variables *fields* and examples are pressure, temperature, and chemical potential. The following derivatives show divergences with the same critical exponent:

$$-\left(\frac{\partial^2\mu}{\partial T^2}\right)_p = \frac{\tilde{C}_p}{T} \qquad -\left(\frac{\partial^2\mu}{\partial p^2}\right)_T = \tilde{V}K_T \tag{3.42}$$

If we change the role of p and T in the second order derivatives of $\mu(p,T)$, the singular behaviour does not change, while the co-ordinate axes of p and T both cross the special direction [8].

In the ρ-T-plane the strong and the weak direction are reversed. Curves of constant volume, enthalpy, and entropy intersect the coexistence curve at the critical point, while the isotherm, isobar, iso-chemical potential curve, and gravity curve are tangent to the coexistence curve.

The values of the critical exponents depend on the dependent and independent variables chosen and on the path of approach to the critical point, *i.e.* along a weak or a strong direction. The dependence of the exponent value of the path of approach is *called exponent renormalization*. If, for example, the path of approach of the compressibility is the critical isobar instead of the critical isochore, the critical exponent is renormalized from γ to $\gamma/(\beta\delta)$ or from 1.24 to 0.79. Likewise, the exponent α is renormalized from α to $\alpha/(\beta\delta)$. See for exponent renormalizations of the isothermal compressibility and the isochoric heat capacity Table 3.6 [3]:

Table 3.6: Path dependence of divergences

					Exponent value	
Property	Diverg.	Path	Diverg.	Exponent	Classical	Non-classical
$K_T^*(\Delta T^*)$	s	Crit. Isochore	w	γ	1	1.239
$K_T^*(\Delta T^*)$	s	Crit. Isobar	s	$\gamma/(\beta\delta)$	2/3	0.792
$K_T^*(\Delta\rho^*)$	s (I)	Crit. Isotherm	s	$\gamma/(\beta\delta)$	2/3	0.792
$K_T^*(\Delta\rho^*)$	s (II)	Crit. Isotherm	s	γ/β	2	3.8
$C_V^*(\Delta T^*)$	w	Crit. Isochore	w	α	0	0.110
$C_V^*(\Delta T^*)$	w	Crit. Isobar	s	$\alpha/(\beta\delta)$	0	0.070
$C_V^*(\Delta\rho^*)$	w (I)	Crit. Isotherm	s	$\alpha/(\beta\delta)$	0	0.070
$C_V^*(\Delta\rho^*)$	w (II)	Crit. Isotherm	s	α/β	0	0.337

The second order derivatives $-(\partial^2\mu/\partial T^2)_p=(\partial S/\partial T)_p=C_p/T$, $-(\partial^2\mu/\partial p^2)_T=-(\partial V/\partial p)_T=V/K_T$, and $(\partial^2\mu/(\partial p\partial T))=(\partial V/\partial T)_p=V\alpha_p$ diverge strongly at the critical point. These derivatives are called *susceptibilities*. A susceptibility is a response of a density to a change in the conjugate field, with other fields held constant [19]. It is concluded that second derivatives of the dependent field variable (potential) with respect to the independent fields, which are first derivatives of densities with respect to fields, *in directions that are oblique to the coexistence surface (strong field)* are strongly divergent. In other words; any path on which a field such as pressure, temperature or chemical potential is kept constant intersects the coexistence curve in μ-T-space. Second derivatives of the potential $p(T,\mu)$ along such directions diverge strongly [49]. By using the thermodynamic identity (3.43)

$$\left(\frac{\partial V}{\partial T}\right)_{Coex}=\left[\left(\frac{\partial p}{\partial T}\right)_{Coex}-\left(\frac{\partial p}{\partial T}\right)_V\right]\left(\frac{\partial V}{\partial p}\right)_T \tag{3.43}$$

and by showing that the direction $V=V_c$ is asymptotically the same as that of the coexistence curve, Griffiths and Wheeler conclude that second derivatives of the dependent variable with respect to the independent ones or first derivatives of a density to a field variable, taken *along the coexisting curve,* which is the weak direction, are in fact derivatives in which a density is kept constant. These derivatives diverge weakly at the critical point [2]. For example the adiabatic compressibility $K_s=-1/V(\partial V/\partial p)_S$ and the isochoric heat capacity $C_V=T(\partial S/\partial T)_V$ diverge weakly. These derivatives are finite in the classical theory. Derivatives of densities with respect to densities at constant field, or of fields with respect to fields at constant density are generally well behaved and finite at the critical point. For example $(\partial S/\partial V)_T=(\partial p/\partial T)_V$. The latter derivative is the slope of the vapour pressure curve, which is known to have a finite limiting slope at the critical point [19].

3.7 Asymmetry in the compressibility and the coexistence curve diameter

The theory of the special direction can be used to show the asymmetry of the compressibility and the coexistence curve diameter with respect to the critical density. Up till now, the compressibility along the coexistence curve was symmetrical with respect to the critical density, and it could be approached by the relation in Table 1.1. The difference in compressibility between liquid and vapour is given by $\Delta_{LV}(\partial\rho/\partial\mu)_T$. The asymptotic behaviour of this term will be determined by the first non-symmetric correction term in the expansion for the compressibility. Sengers used the following relations to determine the first non-symmetric correction term [8]:

$$\begin{gathered}\left(\frac{d\mu}{dT}\right)_{Coex}^{2}\Delta_{LV}\left(\frac{\partial\rho}{\partial\mu}\right)_T-\Delta_{LV}\left(\frac{\partial s}{\partial T}\right)_\mu=2\left(\frac{d\mu}{dT}\right)_{Coex}\left(\frac{d\Delta_{LV}\rho}{dT}\right)+\left(\frac{d^2\mu}{dT^2}\right)_{Coex}\Delta_{LV}\rho\\ \Delta_{LV}\left(\frac{\partial\rho}{\partial\mu}\right)_T=\Delta_{LV}\left(\frac{\partial^2 p}{\partial\mu^2}\right)_T\qquad\Delta_{LV}\left(\frac{\partial s}{\partial T}\right)_\mu=\Delta_{LV}\left(\frac{\partial^2 p}{\partial T^2}\right)_\mu\end{gathered} \tag{3.44}$$

The derivatives $(d\mu/dT)_{Coex}$ and $(d^2\mu/dT^2)_{Coex}$ remain finite and continuous in the critical point [8]. The latter two relations in equation (3.44) have the same singular character while the role of μ and T can be interchanged in the second order derivatives of $p(\mu,T)$ without changing the singular behaviour. It follows that the compressibility difference diverges as:

$$\Delta_{LG}\left(\frac{\partial\rho}{\partial\mu}\right)_T\propto\left|\Delta T^*\right|^{-1+\beta} \tag{3.45}$$

The compressibility on both sides of the coexistence curve becomes:

$$\begin{aligned}\left(\frac{\partial \rho_L{}^*}{\partial \mu^*}\right)_T &= \Gamma'|\Delta T^*|^{-\gamma} + \Gamma_{2L}|\Delta T^*|^{-1+\beta} + .. = \frac{1}{2\mu_{11}}|\Delta T^*|^{-1} + \frac{3\mu_{40}}{20\mu_{11}\mu_{30}}\sqrt{\frac{6\mu_{11}}{\mu_{30}}}|\Delta T^*|^{-1/2} + .. \\ \left(\frac{\partial \rho_G{}^*}{\partial \mu^*}\right)_T &= \Gamma'|\Delta T^*|^{-\gamma} + \Gamma_{2G}|\Delta T^*|^{-1+\beta} + .. = \frac{1}{2\mu_{11}}|\Delta T^*|^{-1} - \frac{3\mu_{40}}{20\mu_{11}\mu_{30}}\sqrt{\frac{6\mu_{11}}{\mu_{30}}}|\Delta T^*|^{-1/2} + ..\end{aligned} \qquad (3.46)$$

The second parts of the relations are the classical relations for the compressibility. From the classical parts of relation (3.46) it can be seen that the first non-symmetrical correction terms indeed diverge as in relation (3.45).

Mermin and Rehr show the behaviour of the coexistence curve diameter using the following identity for the specific-heat density in the two-phase area [13,8]:

$$\frac{c_V(\rho,T)}{T} = \frac{d\bar{s}}{dT} + \frac{d\mu}{dT}\frac{d\bar{\rho}}{dT} + (\bar{\rho}-\rho)\frac{d^2\mu}{dT^2} \qquad (3.47)$$

The properties $\bar{\rho}$ and $\bar{s}$ are the diameter of the coexistence curve and the diameter of the entropy density for the coexisting phases. Relation (3.47) can be simplified by taking $\rho=\bar{\rho}$. The specific heat diverges along every path as $|\Delta T^*|^{-\alpha}$. See Table 1.1. Mermin and Rehr consider the function $p(\mu,T)$ as a function of the points in the μ-T-area. They choose a coordinate transformation $X=X(\mu,T)$ and $Y=Y(\mu,T)$ with one of the coordinate axes asymptotically parallel to the coexistence curve, *i.e.* asymptotically parallel to the special direction. The transformation has the following properties:

- The functions $X=X(\mu,T)$ and $Y=Y(\mu,T)$ are regular functions of μ and T,
- the inverse transformations $\mu(X,Y)$ and $T(X,Y)$ also exist,
- curves of constant X are asymptotically parallel to the coexistence line,
- lines with constant Y cut the coexistence line with a finite angle.

The hypothesis of Griffiths and Wheeler states that the singular behaviour of the second derivatives of $p(X,Y)$ can not depend on the choice of Y if it cuts the coexistence line. The relation $dp=sdT+\rho d\mu$ as a function of $X(\mu,T)$ and $Y(\mu,T)$ averaged over the coexisting phases reads [8]:

$$\left(\frac{\partial \bar{p}}{\partial X}\right)_Y = \bar{s}\left(\frac{\partial T}{\partial X}\right)_Y + \bar{\rho}\left(\frac{\partial \mu}{\partial X}\right)_Y \qquad (3.48)$$

The left term is the diameter of the coexisting values of $(\partial p/\partial X)_Y$. The derivative with respect to Y, along the coexistence line, X=*constant*, reads:

$$\frac{\partial^2 \bar{p}}{\partial X \partial Y} \approx \left[\frac{d\bar{s}}{dT}\left(\frac{\partial T}{\partial X}\right)_Y + \frac{d\bar{\rho}}{dT}\left(\frac{\partial \mu}{\partial X}\right)_Y\right]\left(\frac{\partial T}{\partial Y}\right)_X \qquad (3.49)$$

Both sides of equation (3.49) have the same divergence. It is also clear that both terms on the right side must have the same divergence. This can be seen by setting $Y=T$ and $Y=\mu$ and by realizing that both lines Y=*constant* cut the special direction. It follows from (3.49) that the coexistence curve diameter behaves as:

$$\frac{d\bar{\rho}}{dT} \propto |\Delta T^*|^{-\alpha} \qquad \bar{\rho}^* - 1 = C|\Delta T^*|^{1-\alpha} + ... \qquad (3.50)$$

The behaviour of the coexistence curve diameter is schematically given in Figure 3.4.

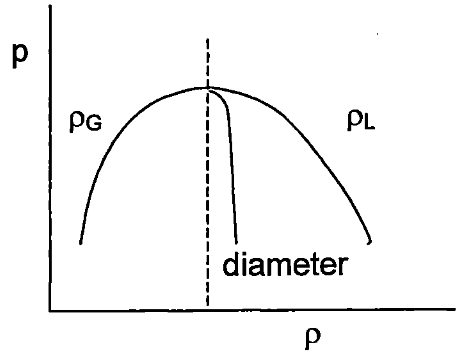


Figure 3.4: Coexistence curve diameter

3.8 Critical phenomena in fluid mixtures

Van der Waals first described the generalization of one-component critical anomalies to critical anomalies in mixtures for the classical model in 1891 [75]. Griffiths and Wheeler generalized the one-component theory for the non-classical case in 1970 [63]. Here a short description of the generalized theory for the non-classical case is given.

Griffiths and Wheeler gave a description of the critical phenomena in fluid mixtures by developing the geometry of the critical region in the space of the field variables. Their work was inspired by studies of symmetric critical systems subjected to additional fields and studies of decorated lattice gases [49]. The critical behaviour of a binary- or multi-component mixture is in general a generalization of the one-component fluid critical behaviour. This is a requirement of the critical-point universality because it states that the critical behaviour of a *n*-component fluid must be in the same universality class as that of one-component fluids and the Ising model [49].

A fluid mixture of n components in the one-phase region has $n+1$ thermodynamic degrees of freedom. In the two-phase region there are n degrees of freedom because all field variables are equal in both phases. The thermodynamic states with two coexisting phases form a n-dimensional surface in the $(n+1)$-dimensional space. The critical condition requires the coexisting phases to become identical resulting in one less degree of freedom; the n-dimensional surface terminates in a $(n-1)$-dimensional critical surface.

The simplest mixture is a binary system, *i.e.* n=2. To describe critical phenomena in fluid mixtures, it is convenient to choose a potential, which is itself a field, and a function of $n+1$ independent field variables. In the binary case the independent variables f_2, p, and T, where $f_2=exp(\mu_1/(k_BT))$, can be chosen. The chemical potentials are exponentiated as to avoid their divergence at $x=0$ and $x=1$. Other valid potentials are $\mu_1(p,T,\mu_2)$, $\mu_2(\Delta,p,T)$, and $p(\mu_1,\mu_2,T)$ [3]. The variable Δ is given by $\Delta=-\mu_2+\mu_1$.

For a binary mixture, the *2D*-coexistence surface terminates in a *1D*-critical line. The liquid-vapour critical points are called *plait points*. There is also a possibility that two liquid phases of different composition coexist. This gives rise to another coexistence surface terminating in a critical line. The critical points on the critical liquid-liquid line are called *consolute* points [2].

In the one-component fluid, the critical point could be approached along the special direction determined by the coexistence curve, or along the strong direction, which is at an angle with the special direction. As mentioned before, in multi-component mixtures three directions exist; the one intersecting the coexistence surface, the one in the coexistence surface but not parallel to the critical line, and the one asymptotically parallel to the critical line or critical surface. In binary fluids critical lines are smooth curves in field space and therefore we expect derivatives taken in this direction to be non-divergent. For this direction a new type of exponent renormalization occurs. This type of renormalization is called *Fisher-renormalization*. On such a path, where two densities are kept constant, the exponents γ, δ, and β are renormalized by a factor $1/(1-\alpha)$ [3]. Examples of such derivatives are the adiabatic compressibility and the isochoric heat capacity, both at constant composition:

$$\left(\frac{\partial^2\mu_2}{\partial p^2}\right)_{Sx} = \left(\frac{\partial V}{\partial p}\right)_{Sx} = -VK_{Sx} \qquad -\left(\frac{\partial^2\mu_2}{\partial T^2}\right)_{Vx} = \left(\frac{\partial S}{\partial T}\right)_{Vx} = \frac{C_{Vx}}{T} \tag{3.51}$$

These derivatives diverge weakly for one-component fluids and in general remain finite for mixtures. Derivatives of densities with respect to densities at two constant fields remain, in analogy with one-component fluids, finite. An example is the partial molar volume:

$$\left(\frac{\partial V}{\partial x}\right)_{pT} = -\left(\frac{\partial V}{\partial p}\right)_{Tx}\Bigg/\left(\frac{\partial x}{\partial p}\right)_{VT} = VK_{Tx}\Bigg/\left(\frac{\partial x}{\partial p}\right)_{VT} \tag{3.52}$$

Both derivatives on the right side diverge weakly but the ratio remains finite. Exceptions occur when $x=0$ or $x=1$, where the compressibility of the solvent becomes strongly divergent. Also, near critical lines, densities vary linearly with densities on paths where two fields are kept constant [3]. See also Chapter 5, Dilute mixtures.

In analogy with the one-component fluid a derivative of a density with respect to a field with one field and one density constant is taken along a path asymptotically parallel to the coexistence curve and diverges weakly:

$$\begin{aligned} &\left(\frac{\partial^2\mu_2}{\partial p^2}\right)_{Tx} = \left(\frac{\partial V}{\partial p}\right)_{Tx} = -VK_{Tx} \qquad -\left(\frac{\partial^2\mu_2}{\partial T^2}\right)_{px} = \left(\frac{\partial S}{\partial T}\right)_{px} = C_{px}/T \\ &\left(\frac{\partial^2 p}{\partial \mu_1{}^2}\right)_{T\rho_2} = \left(\frac{\partial \rho_1}{\partial \mu_1}\right)_{T\rho_2} \qquad \left(\frac{\partial^2 p}{\partial \mu_2 \partial T}\right)_{\rho_1} = \left(\frac{\partial \rho_2}{\partial T}\right)_{\rho_1} \end{aligned} \tag{3.53}$$

These derivatives diverge with an exponent α along the weak path, in the coexistence surface *intersecting the critical line*. They remain finite in the classical case. In general properties that diverge strongly in one-component fluids only diverge weakly in binary mixtures of constant composition or constant molar density of one of the components.

In analogy with the one-component theory, a derivative of a density with respect to a field with two fields constant intersects the coexistence surface and is taken in a strong direction. The potential $\mu_2(\Delta,p,T)$ leads to the strongly diverging second order derivatives:

$$\left(\frac{\partial^2\mu_2}{\partial \Delta^2}\right)_{pT} = \left(\frac{\partial x}{\partial \Delta}\right)_{pT} \qquad \left(\frac{\partial^2\mu_2}{\partial p^2}\right)_{\Delta T} = -VK_{T\Delta} \qquad -\left(\frac{\partial^2\mu_2}{\partial T^2}\right)_{p\Delta} = \left(\frac{\partial S}{\partial T}\right)_{p\Delta} = \frac{C_{p\Delta}}{T} \tag{3.54}$$

This potential is preferred for the description of consolute points of virtually incompressible binary liquids. The accompanying order parameters are x and S or V and S [3]. These derivatives diverge with an exponent γ along the weak path and with a renormalized exponent $\gamma/(\beta\delta)$ along a strong path, in analogy with the one-component fluid. As $x \to 0$, the potential $\mu_1(\Delta,p,T)$ goes over smoothly into $\mu(p,T)$.

Another useful thermodynamic potential is $p(\mu_1,\mu_2,T)$ with the accompanying densities:

$$\rho_1 = \left(\frac{\partial p}{\partial \mu_1}\right)_{\mu_2 T} \qquad \rho_2 = \left(\frac{\partial p}{\partial \mu_2}\right)_{\mu_1 T} \qquad s = \left(\frac{\partial p}{\partial T}\right)_{\mu_1\mu_2} \tag{3.55}$$

Where ρ is a molar density and s is the entropy per unit volume. This potential is preferred by symmetry arguments for the description of the gas-liquid critical point of fluid mixtures. Since a liquid-liquid and a gas-liquid critical line can go over continuously into each other, it is clear that the two extreme forms of the order parameter, mole fraction and density, must somehow be mixed [3]. Leung and Griffiths use the mixture density as the order parameter [3]. Some of the second order derivatives associated with this potential are:

$$\left(\frac{\partial^2 p}{\partial \mu_1^2}\right)_{\mu_2 T} = \left(\frac{\partial \rho_1}{\partial \mu_1}\right)_{\mu_2 T} \quad \left(\frac{\partial^2 p}{\partial \mu_2^2}\right)_{\mu_1 T} = \left(\frac{\partial \rho_2}{\partial \mu_2}\right)_{\mu_1 T} \quad \left(\frac{\partial^2 p}{\partial \mu_1 \partial \mu_2}\right)_{T} = \left(\frac{\partial \rho_1}{\partial \mu_2}\right)_{\mu_1 T} = \left(\frac{\partial \rho_2}{\partial \mu_1}\right)_{\mu_2 T} \qquad (3.56)$$

These derivatives play a major role in the Kirkwood-Buff theory of supercritical solubility. As $x \rightarrow 0$, the potential goes over smoothly into the potential $p(\mu, T)$ for a one-component fluid.

The strongly diverging behaviour of the osmotic susceptibilities can be explained in the following manner. Before the limit of mechanical stability is reached, fluid mixtures become materially unstable. Splitting into two phases of different composition lowers the free energy. For the isothermal Helmholtz free energy to remain concave upwards (1.30), a $n \cdot n$-determinant of second order derivatives must remain positive [3]:

$$\mathrm{Det}(A) = A_{VV}A_{xx} - A_{Vx}^2 = -\left(\frac{\partial p}{\partial V}\right)_{xT}\left(\frac{\partial^2 G}{\partial x^2}\right)_{pT} \geq 0 \qquad (3.57)$$

G is the molar Gibbs free energy. According to the classical theory, $(\partial p/\partial V)_{xT}$ is finite and nonzero in a mixture and the criticality condition $(\partial^2 G/\partial x^2)_{pT}=0$ follows from (3.57). The last step must be taken care of while in the case of dilute mixtures in the vicinity of the solvent's critical point, $(\partial p/\partial V)_{xT}^{-1}$ shows a strong divergence and in the case of critical azeotropy $(\partial p/\partial V)_{xT}=0$. Useful relations between the derivatives of the chemical potential and the Gibbs free energy are the following susceptibilities:

$$\begin{aligned} \left(\frac{\partial x_1}{\partial \mu_1}\right)_{pT} &= -\left(\frac{\partial x_2}{\partial \mu_1}\right)_{pT} = \left\{x_2\left(\frac{\partial^2 G}{\partial x_2^2}\right)_{pT}\right\}^{-1} \\ \left(\frac{\partial x_2}{\partial \mu_2}\right)_{pT} &= -\left(\frac{\partial x_1}{\partial \mu_2}\right)_{pT} = \left\{x_1\left(\frac{\partial^2 G}{\partial x_1^2}\right)_{pT}\right\}^{-1} = \left\{(1-x_2)\left(\frac{\partial^2 G}{\partial x_1^2}\right)_{pT}\right\}^{-1} \end{aligned} \qquad (3.58)$$

Because $\{(\partial^2 G/\partial x^2)_{pT}\}^{-1}$ diverges strongly at the critical line (3.57), the *osmotic susceptibilities* in (3.58) diverge strongly at the critical line or surface of the mixture as long as x_1 and x_2 are non-zero. The osmotic susceptibilities in the mixture are the equivalents of the compressibility in the one-component fluid.

Another strong diverging derivative is $(\partial x/\partial p)_{T\sigma}$, which is the isothermal increase of mole fraction of solute with pressure in the presence of a pure phase of the solute that effectively keeps the chemical potential constant. This is the phenomenon of *supercritical solubility* [19].

There are exceptions to the general rules mentioned in this paragraph when the critical surface or the coexistence surface has a special direction with respect to the co-ordinate axes.

3.9 Scaling laws for mixtures

Leung and Griffiths developed a method for describing the critical behaviour of binary fluids with a constant critical line in terms of scaling laws [76]. The dependent field variable is the pressure p and the independent variables are the temperature T and the chemical potentials μ_1 and μ_2 of the two components. Two new variables Θ and ζ are defined which are related to the fugacities, or the chemical potentials, of both components in the following manner:

$$\Theta = c_1 f_1 + c_2 f_2 \qquad \zeta = \frac{c_2 f_2}{\Theta} \tag{3.59}$$

C_1 and c_2 are two arbitrary constants related to the zeros of μ_1 and μ_2. The critical line can be characterized by $T_c(\zeta)$. The intersection of the coexistence surface with a plane ζ=*constant* defines a coexistence curve that terminates in a point on the critical line (but it can be extended into the one-phase region). For $\zeta=0$ and $\zeta=1$ this intersection reproduces the coexistence curves for the pure components 1 and 2. See Figure 3.5.

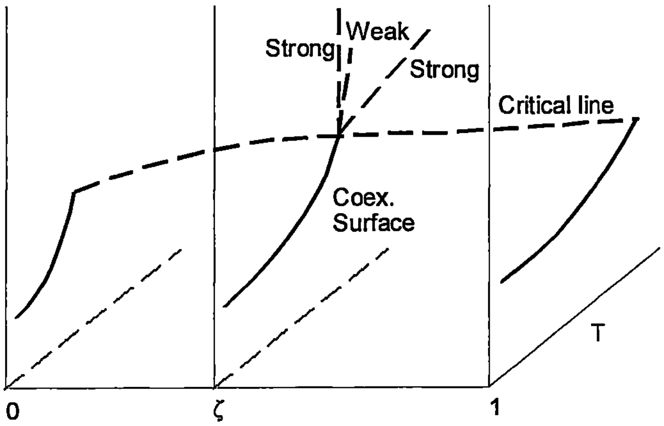


Figure 3.5: Thermodynamic surface of the Leung-Griffiths potential

The behaviour of the mixture with ζ=*constant* is completely analogous to the behaviour of a one-component fluid. In the ζ=*constant*-plane a new coordinate system can be chosen with the weak variable $\tau=T-T_c(\zeta)$ and the strong variable $h=\ln(\Theta/\Theta_\sigma)$, where $\Theta_\sigma(\zeta,\tau)$ is the value of Θ on the coexistence curve for ζ and τ. The variables τ and h are closely related to ΔT^* and $\Delta\mu^*$ in the scaling laws for one-component fluids. The pressure at ζ=*constant* can be written as the sum of the regular background term $p_{reg}(\zeta,\tau,h)$, which is an analytic function of its variables, and a singular term $p_{sing}(\zeta,\tau,h)$ which satisfies the same scaling law in terms of τ and h as the singular part of a one-component fluid in terms of ΔT^* and $\Delta\mu^*$ (3.27). $P_{sing}(\zeta,\tau,h)$ also contains a factor which is a smooth factor of ζ to interpolate between the scaled equations of state of the pure components. The theory of Leung and Griffiths is an application of the geometric considerations of Griffiths and Wheeler. The theory has been applied successfully to equation-of-state data near the critical line of ^{3}He-^{4}He mixtures. The theory has also been generalized for an arbitrary smooth critical line connecting the critical points of the pure components. This method has been applied successfully to the systems CO_2-C_2H_6, SF_6-C_3H_8, and C_3H_8-C_8H_{18} [77].

Also a generalization of the one-component potential $\Delta\tilde{p}$ by introducing another Leung-Griffiths potential $\omega=\omega(\nu_1, \nu_2, \varphi)$ can be made [49]:

$$\omega = p/T \qquad \nu_1 = \mu_1/(RT) \qquad \nu_2 = \mu_2/(RT) \qquad \varphi = 1/(RT) \tag{3.60}$$

The densities conjugate to ν_1, ν_2, and φ are the number densities ρ_1, ρ_2, and the energy density u respectively. In this case, the singular part of the potential, $\Delta\omega=\omega-\omega_0$, is assumed to have the same dependence on the strong field h and the weak field τ for given ζ as the potential $\Delta\tilde{p}$ of the one-component fluid. At this point, the critical behaviour of all thermodynamic derivatives can be deduced. Several Jacobians with corresponding asymptotic behaviour can be deduced. Thermodynamic properties near the critical point are proportional to ratios of these Jacobians. Some Jacobians with accompanying physical properties and asymptotic behaviour are given in Table 3.7 [76].

Table 3.7: Asymptotic behaviour of characteristic Jacobians

Jacobian	Structure	Property	Structure	ζ=0,1	$\zeta\neq$0,1
$E=\frac{\partial(u\rho x)}{\partial(h\tau\zeta)}$	$s\cdot w+\zeta(1-\zeta)s\cdot w$	$C_{Vx}\propto E/F$	$\frac{s\cdot w+\zeta(1-\zeta)s\cdot w}{s+\zeta(1-\zeta)s\cdot w}$	w	f
$F=\frac{\partial(\varphi\rho x)}{\partial(h\tau\zeta)}$	$s+\zeta(1-\zeta)s\cdot w$	$K_{Tx}\propto F/G$	$\frac{s+\zeta(1-\zeta)s\cdot w}{f+\zeta(1-\zeta)s}$	s	w
$G=\frac{\partial(\omega\varphi x)}{\partial(h\tau\zeta)}$	$f+\zeta(1-\zeta)s$	$(\partial V/\partial x)_{pT}\propto K/G$	$\frac{1}{f+\zeta(1-\zeta)s}$	s	f
$K=\frac{\partial(\rho\omega\varphi)}{\partial(h\tau\zeta)}$	s	$(\partial p/\partial x)_{VT}\propto K/F$	$\frac{s}{s+\zeta(1-\zeta)s\cdot w}$	f	w^{-1}
$L=\frac{\partial(\omega\rho x)}{\partial(h\tau\zeta)}$	$s+\zeta(1-\zeta)s\cdot w$	$(\partial x/\partial\mu)_{pT}\propto G/U$	$[f+\zeta(1-\zeta)s]\zeta(1-\zeta)$	0	s
$U=\frac{\partial(\nu\rho\varphi)}{\partial(h\tau\zeta)}$	$1/(\zeta(1-\zeta))$				

f=finite nonzero, w-1=weak zero, w=weak, s=strong

By defining $\tau'=l(\zeta)\tau$ and $\Delta\omega=q(\zeta)\pi(h,\tau')$, where $l(\zeta)$ and $q(\zeta)$ are truncated polynomials in ζ, the same parametric form can be used as for one-component fluids (3.21, 3.38) [49]:

$$h=r^{\beta\delta}a\theta(1-\theta^2) \qquad \tau'=r(1-b^2\theta^2) \qquad \pi(h,\tau')=r^{\beta(\delta+1)}p(\theta) \qquad (3.61)$$

This simple parametric form does not incorporate mixing of variables and corrections to scaling.

Theory predicts that in mixtures near the critical line, C_{px} and K_{Tx} diverge weakly, C_{Vx} remains finite, and the slope of the isochore-isopleth is confluent with the critical line. However, in practice K_{Tx} appears to remain finite while C_{Vx} appears to diverge. The Leung-Griffiths method is able to predict the size of the region where the theoretical mixture effects are to be seen. The Jacobian F determines the character of both C_{px} and K_{Tx} and has strong divergences for $\zeta=0,1$ but a $s\cdot w$ divergence at intermediate values of ζ. Thus, the mixture character of the fluid will become manifest as the $s\cdot w$-term dominates the s-term, with the largest opportunity at $\zeta=1/2$. In many cases this does not happen in experimentally accessible ranges, resulting in neither a finite limiting value of C_{Vx} nor a weak divergence in K_{Tx} [49].

There are also other cases in which a competition between a weak divergence and a constant or slowly varying term is only won in an experimentally inaccessible range. The Leung-Griffiths model is from the point of view of application not attractive because it can not predict the critical locus, it has many adjustable parameters, and the model is changed when the zero-points of energy and entropy are redefined [49].

The theory of Griffiths and Wheeler applies to all kinds of critical points in fluid mixtures. However, the specific theory of Leung and Griffiths can not be applied in the vicinity of the consolute points of partially miscible binary liquids. The theory of the gas-liquid critical point can be changed to also describe the critical phenomena near the critical point of a binary liquid by using the fundamental differential relation at constant pressure $(\Delta=\mu_1-\mu_2)$:

$$d\mu_2 = -SdT - xd\Delta \qquad (3.62)$$

On comparing this relation with $-dp=-sdT-\rho d\mu$ for a one-component fluid, it can be concluded that the behaviour of the fundamental equation $\mu_2(T,\Delta)$ for binary liquids at constant p near the critical mixing point is analogous to that of $p(T,\mu)$ near the critical point of a one-component fluid. The concentration or mole fraction x is now the order parameter, analogous to the magnetization of a ferromagnet near the Curie point and the density of a fluid near the gas-liquid critical point [2]. Some thermodynamic properties showing analogous behaviour are listed in Table 3.8:

Table 3.8: Analogy between plait points and consolute points

	'One-component'	'Binary liquid at constant *p*'
Fundamental Equation	$p(T,\mu)$	$\mu_2(T,\Delta)$
Order parameter	$\rho=(\partial p/\partial\mu)_T$	$x=-(\partial\mu_2/\partial\Delta)_{Tp}$
Coexistence curve	$\rho(T)$	$x(T)$
Equation of state	$\mu(\rho,T)$	$\Delta(x,T)$
Susceptibility (strongly divergent)	$\chi_T=(\partial^2 p/\partial\mu^2)_T$	$\chi_T=-(\partial^2\mu_2/\partial\Delta^2)_{Tp}$
Specific heat (weakly divergent)	$C_V/V=T(\partial^2 p/\partial T^2)_\rho$	$C_{px}=-T(\partial^2\mu_2/\partial T^2)_{xp}$

Now, the critical exponents α, β, γ and δ respectively represent the power law behaviour of $C_{px}(T)$, the composition difference between the coexisting phases as a function of temperature, the osmotic susceptibility as a function of temperature and the critical isotherm of μ_2 as a function of concentration. A comprehensive review of critical exponent values for binary fluids has been given by Scott [78]. The coexistence curve of the isobutyric acid-water system can be described by a simple power law $B|\Delta T^*|^\beta$ in the range $|\Delta T^*|<6\cdot 10^{-3}$ with $\beta=0.328\pm0.004$. Coexistence curve data of the carbondisulphide-nitromethane system in terms of a three term Wegner expansion yield a leading exponent $\beta=0.316\pm0.008$ [79]. The exponent for the aniline-cyclohexane system assumed the constant value $\beta=0.328\pm0.007$ in the range $|\Delta T^*|<10^{-2}$ [80]. The osmotic susceptibility and also the exponent γ can be determined by measuring the intensity of scattered light [81]. Using light scattering data, a value of 1.23±0.02 was found for γ [82]. Other light scattering measurement data for the system 3-methylpentane-nitroethane gave $\gamma=1.240\pm0.014$ within the range $|\Delta T^*|<3\cdot 10^{-3}$ [83]. The close agreements between the experimentally found values of β and γ for binary liquids and the ones calculated by the renormalization group theory (2.18, 2,19) do support the hypothesis of universality for critical behaviour of binary liquids. The asymptotic power laws of binary liquids in the critical region seem to hold over a larger temperature range than in fluids near the gas-liquid critical point [2].

Chapter 4: Critical fluctuations and correlation functions

4.1 Correlation functions and correlation length

When a system is in the vicinity of the critical point, its thermodynamic states are accompanied by large fluctuations in the order parameter. The large compressibility or equivalently, the flatness of the Helmholtz free energy surface near the critical point makes it possible for density fluctuations to be generated at low cost in free energy [19]. A fluid near the gas-liquid critical point exhibits large density fluctuations and a binary liquid near the critical mixing point exhibits large concentration fluctuations, which are correlated in space. Here a description is given for the fluctuations near the gas-liquid critical point. The description for a binary liquid can be obtained if density is replaced by concentration.

The fluctuations of the number of particles *N*, in a given volume *V*, can be calculated by the grand canonical ensemble. The probability of finding *N* particles in a volume *V* is [8]:

$$P(N)=\frac{\exp(\mu N/k_BT)}{\Xi}Z(T,V,N)=\frac{\exp\left(\frac{\mu N-A}{k_BT}\right)}{\Xi} \qquad (4.1)$$

The mean number of particles and the fluctuations in *V* are:

$$<N>=\sum_{N=0}^{\infty}NP(N)=k_BT\left(\frac{\partial \ln(\Xi)}{\partial\mu}\right)_{T,V}=V\left(\frac{\partial p}{\partial\mu}\right)_T=V\rho$$

$$<(N-<N>)^2>=<N^2>-<N>^2= \qquad (4.2)$$

$$\sum_{N=0}^{\infty}N^2P(N)-\left[\sum_{N=0}^{\infty}NP(N)\right]^2=(k_BT)^2\left(\frac{\partial^2\ln(\Xi)}{\partial\mu^2}\right)_{T,V}=k_BTV\left(\frac{\partial\rho}{\partial\mu}\right)_T=k_BTV\rho^2K_T$$

According to equation (4.2), the fluctuations indeed increase with increasing compressibility. These fluctuations can be analysed by *ρ(r)*, which gives the particle density at a specific position *r*. Thus, *ρ=<ρ(r)>*, and *N=∫ρ(r)dr*. According to the density fluctuations, the number of particles in the vicinity of a given molecule will not equal the mean number. The magnitude and the spatial character of the fluctuations are described by the so-called correlation functions *G(r-r')* and *H(r-r')*, which measure the joint probability of finding a molecule in the volume element *dr'* for a given molecule in volume element *dr* minus the average number of pairs. In other words, they describe the local density at a distance *r* from a molecule fixed at the origin of *r*. The function *ρG(r)* describes the density and the function *ρH(r)=ρ[G(r)-1]* describes the excess density, both compared to the average density at a distance *r* from a molecule [19]:

$$\rho^2G(|r-r'|)=<\{\rho(r)-\rho\}\{\rho(r')-\rho\}>=<\rho(r)\rho(r')>-\rho^2 \qquad (4.3)$$

The brackets indicate an equilibrium average over the canonical ensemble. The particles are not correlated at very large intermolecular distances [8]:

$$\lim_{r\to\infty}G(r)=0 \qquad (4.4)$$

At liquid-like low-temperature states, these correlation functions show pronounced oscillations indicating the arrangement of several shells of neighbours around a molecule. The range of the correlations in the vicinity of the critical point is well beyond the range of molecular interaction. The structure of the first few shells is largely unaffected. Component-specific properties that depend on local structure only will not show critical anomalies. It follows that due to the increased range of the correlations the detailed behaviour of the component-specific forces is no longer relevant [19].

The distance over which the particles are correlated depends on the size of the fluctuations:

$$<(N-<N>)^2>=<\int\{\rho(r)-\rho\}dr\int\{\rho(r')-\rho\}dr'>=\int dr\int dr'\{<\rho(r)\rho(r')>-\rho^2\}= \qquad (4.5)$$

$$\rho^2\int G(|r-r'|)drdr'=V\rho^2\int G(r)dr$$

The zeroth moment of the correlation function is related to the symmetrized isothermal compressibility χ_T by the fluctuation theorem [84]. This theorem is a result of equations (4.4) and (4.5):

$$k_BT\chi_T=\rho^2\int G(r)dr \qquad \chi_T=\rho^2K_T \qquad \text{or} \qquad k_BT\chi_T=\rho+\rho^2\int H(r)dr \qquad (4.6)$$

It is known that the compressibility diverges strongly at the critical point and, therefore, the integral of *G(r)* must diverge. However, the correlation function is finite everywhere and the only way the integral can diverge is by *G(r)* becoming long-ranged. In approaching the critical point the correlation function develops a long *tail* [19].

Several properties can be expressed in the intermolecular potential $\varphi(r)$ and the correlation function *G(r)*. For example the residual internal energy:

$$U^r=\int G(r)\varphi(r)dr \qquad (4.7)$$

For short-ranged intermolecular potentials, $\varphi(r)$ has decayed to zero in the region of *r* where the tail develops. Therefore, U^r is determined by the short-range part of *G(r)*. This implies that U^r has no conspicuous critical effects in the classical theory. In the non-classical theory something subtle happens with the short-range behaviour of *G(r)*, while the first derivative of the internal energy, C_V, has a weak anomaly. This phenomenon is called a *(1-α)-anomaly*, while the property is expected to have a temperature dependence of $(T-T_c)^{1-\alpha}$. This means that the properties remain finite at the critical point, but their first derivatives diverge weakly [3].

Instead of *G(r)* it is more convenient to consider its Fourier transform, the following static structure factor [2]:

$$\chi(\Delta\rho^*,\Delta T^*;k)=\frac{\rho^2}{k_BT}\int\exp(ikr)G(\Delta\rho^*,\Delta T^*;r)dr \qquad (4.8)$$

$$\chi(\Delta\rho^*,\Delta T^*;0)=\chi(\Delta\rho^*,\Delta T^*)$$

This static structure factor can be measured as a function of the wave number *k*, or distance *r*, since it is directly proportional to the intensity of scattered electromagnetic radiation as a function of scattering angle [81, 85]. The dimensionless structure factor is defined as:

$$\chi^*=\frac{p_c}{\rho_c^2}\chi \qquad (4.9)$$

The correlation length, ξ, which is a measure of the tail mentioned above, characterizes the correlation function *G(r)*:

$$\xi^2=\frac{1}{2d}\frac{\int r^2G(r)dr}{\int G(r)dr}=-\lim_{k\to 0}\left(\frac{\partial\ln\chi(k)}{\partial k^2}\right)_{\Delta\rho^*\Delta T^*} \qquad (4.10)$$

The parameter *d* is the dimensionality of the system. Typical values for ξ in a fluid such as CO_2 are 1.3 nm (10 K from T_c) and 5.5 nm (1 K from T_c). These values are to be compared with the location of the minimum in the curve of the intermolecular potential at 0.45 nm, the molecular size of 0.4 nm, and the intermolecular distance of 0.55 nm at ρ_c [19].

The correlation length, which diverges at the critical point, is a function of density and temperature. Along the coexistence curve *($\Delta\rho^*=\Delta\rho_{Coex}$, $\Delta T^*\leq 0$)* and the critical isochore *($\Delta\rho^*=0$, $\Delta T^*\geq 0$)* the correlation length respectively behaves as:

$$\xi(\Delta\rho_{Coex}{}^*,\Delta T^*)=\xi_0'\left|\Delta T^*\right|^{-\nu'} \qquad \xi(0,\Delta T^*)=\xi_0(\Delta T^*)^{-\nu} \qquad (4.11)$$

These relations can be used for the 3-dimensional Ising model, the lattice gas, gases and liquids [8].

The amplitude ξ_0 is of the order of molecular size. Typical values for simple molecules are in the range of 0.1 to 0.3 nm [3].

The exponent η is introduced to specify the nature of the dependence of the correlation function on the distance parameter *r*. The following relation for the correlation function holds at the critical point [12]:

$$G_c(r)=G(0,0;r)\propto r^{-d+2-\eta} \qquad \text{or} \qquad \chi(0,0;k)\propto k^{\eta-2} \qquad (4.12)$$

The analogue in the Ising model is the spin-spin correlation function [8]. The exponent η is zero in the classical theory of Ornstein and Zernike, however it is known to be non-zero for the lattice models with short-range interactions. Near but not at the critical point *H(r)* or *G(r)* behaves as [19]:

$$G(r)\propto \exp\left(\frac{-r/\xi}{r}\right) \qquad (4.13)$$

Estimates for the correlation-function critical exponents, respectively by series expansion of the 3-dimensional Ising model [86, 87] and the Landau-Ginzburg-Wilson model [27], are:

$$\nu=0.638\pm^{0.002}_{0.008} \qquad \eta=0.041\pm^{0.006}_{0.003} \qquad (4.14)$$

$$\nu=0.627\pm 0.01 \qquad \eta=0.021\pm 0.02$$

Experimental exponent values for neon and argon are *$\eta=0.11\pm0.03$* and *$\eta=0.10$ ±0.05* [88]. These values are very different from the Ising-like values. In the classical theory, *$\nu=1/2$* or *$\gamma/2$*.

Using heuristics the following exponent equality has been proposed [89]:

$$\nu=\frac{d+2}{4(d-1)} \qquad d\leq 4 \qquad (4.15)$$

4.2 Homogeneity postulate for the symmetrized correlation function

In Chapter 3 it was assumed that the chemical potential difference is an odd and the compressibility is an even function of the density $\Delta\rho^*$. The correlation function can be symmetrized by multiplying by ρ^2/k_BT. It is assumed that the symmetrized correlation function is a generalized homogeneous function of its variables for large values of *r* [8]:

$$G_s(\lambda^{b_\rho}\Delta\rho^*,\lambda^{b_T}\Delta T^*;\lambda^{b_r}r)=\lambda G_s(\Delta\rho^*,\Delta T^*;r) \qquad G_s=\frac{\rho^2}{k_BT}G \qquad (4.16)$$

Kadanoff first formulated this postulate for the correlation function of the 3-dimensional Ising model [20, 90]. The postulate follows from the RG-theory in the same way as for the Helmholtz free energy. Now, according to (4.8), (4.10), and (4.16), we expect that also the structure factor and the correlation length will be even functions of $\Delta\rho^*$ and will be generalized homogeneous functions of their variables near the critical point for wavenumbers k small relative to the inverse molecular interaction range [2]:

$$\chi(-\Delta\rho^*,\Delta T^*;k)=\chi(\Delta\rho^*,\Delta T^*;k) \qquad \xi(-\Delta\rho^*,\Delta T^*)=\xi(\Delta\rho^*,\Delta T^*)$$

$$\chi^*(\lambda^{b_\rho}\Delta\rho^*,\lambda^{b_T}\Delta T^*;\lambda^{b_k}k)=\lambda\chi^*(\Delta\rho^*,\Delta T^*;k) \tag{4.17}$$

$$\xi(\lambda^{-b_\rho/b_k}\Delta\rho^*,\lambda^{-b_T/b_k}\Delta T^*)=\lambda\xi(\Delta\rho^*,\Delta T^*)$$

We expect that the correlation function or structure factor has the same structure for the real gas and the Ising model because the Ising model and the real gas belong to the same universality class. However, it is to be expected that exponent values for real fluids will differ from exponent values calculated from the Ising model [2]. In the limit $k\to 0$, the homogeneity postulate for the thermodynamic functions is recovered if the exponents b_ρ and b_T are identified with [2]:

$$b_\rho=-\frac{\beta}{\gamma}=-\frac{1}{\delta-1} \qquad b_T=-\frac{1}{\gamma} \tag{4.18}$$

Along the coexistence curve $(\Delta\rho^*=\Delta\rho_{Coex}, \Delta T^*\leq 0)$ and the critical isochore $(\Delta\rho^*=0, \Delta T^*\geq 0)$ the following scaling laws hold for the correlation length:

$$\begin{aligned}\xi(0,\Delta T^*)&=\xi(0,1)(\Delta T^*)^{-b_k/b_T}=\xi_0|\Delta T^*|^{-\nu}\\ \xi(\Delta\rho_{Coex}{}^*,\Delta T^*)&=\xi(B,-1)|\Delta T^*|^{-b_k/b_T}=\xi_0{}'|\Delta T^*|^{-\nu'}\end{aligned} \tag{4.19}$$

Thus, $\nu=\nu'=b_k/b_T$ and the homogeneity postulate of the static structure factor in terms of the critical exponents reads:

$$\chi^*(\lambda^{-\beta/\gamma}\Delta\rho^*,\lambda^{-1/\gamma}\Delta T^*;\lambda^{-\nu/\gamma}k)=\lambda\chi^*(\Delta\rho^*,\Delta T^*;k) \tag{4.20}$$

Taking $\lambda=k^{-\gamma/\nu}$ yields the exponent relation $\gamma=\nu(2-\eta)$ [12]. Equation (4.20) can be scaled to become a function of only two variables by taking $\lambda^{\beta/\gamma}=\Delta\rho^*$:

$$\chi^*(\Delta\rho^*,\Delta T^*;k)=|\Delta\rho^*|^{-\gamma/\beta}\chi^*(1,x;y) \qquad x=\frac{\Delta T^*}{|\Delta\rho^*|^{1/\beta}} \qquad y=k|\Delta\rho^*|^{-\nu/\beta} \tag{4.21}$$

In the limit $k\to 0$:

$$\chi^*(\Delta\rho^*,\Delta T^*;0)=|\Delta\rho^*|^{-\gamma/\beta}D^{-1}X(x/x_0) \tag{4.23}$$

Where $X(x/x_0)=[\delta h(x/x_0)-(x/\beta x_0)h'(x/x_0)]^{-1}$ is the scaling function introduced in Table 3.3. The scaling law for the correlation length is given by:

$$\xi(\Delta\rho^*,\Delta T^*)=|\Delta\rho^*|^{-\nu/\beta}\xi_{0,c}\Xi(x/x_0) \qquad [\xi_{0,c}\Xi(x/x_0)]^2=-\lim_{y\to 0}\left(\frac{\partial\ln\chi^*(1,x;y)}{\partial y^2}\right) \tag{4.24}$$

The factor $\xi_{0,c}$ is the amplitude of the power law for the correlation length along the critical isotherm. It follows from (4.23, 4.24) that the scaling law for the structure factor (4.21) can be written in the following form:

$$\chi^*(\Delta\rho^*,\Delta T^*;k)=\chi^*(\Delta\rho^*,\Delta T^*)Y(x/x_0;k\xi) \tag{4.25}$$

As stated before, the structure factor can be determined as a function of ξ and k by measuring the intensity of scattered light as a function of temperature and scattering angle. The scattering angle and k are related via the Bragg relation. If the scattered light intensity, $I(k)\propto\chi(k)$, (divided by $I(0)$) is plotted as a function of $k\xi$, it follows from the scaling law (4.25) that data obtained along a curve of constant x, such as the critical isochore, critical isotherm, and coexistence curve, should collapse onto the same curve. Good results are obtained for the binary liquid 3-methylpentane-nitroethane at the critical concentration as a function of temperature [91].

The hypothesis of universality of thermodynamic behaviour near the critical point as formulated in Chapter 2 and 3, when extended to the correlation length, asserts that for all systems which differ only with respect to irrelevant parameters in the hamiltonians, the scaling function $\chi^*(1,x;y)$ (4.21) will be the same, except for three adjustable parameters D, x_0, and $\xi_{0,c}$ (or ξ_0), which define the scale of χ^*, x and y [92, 93]. Thus, *the hypothesis of three-scale-factor universality* predicts that not only the function $h(x/x_0)$ for the equation of state, but also the scaling functions $Y(x/x_0;k\xi)$ and $\Xi(x/x_0)$ for the structure factor and the correlation length will be the same for all systems within one universality class [2].

To be able to reduce the critical exponents for the correlation length from experimental data and to make a quantitative analysis of the hypothesis of universality, an explicit functional form of the correlation scaling function $Y(x/x_0;k\xi)$ as a function of $y=k\xi$ must be known. Different equations for small and large values of y have been suggested [12, 94, 94-98]. However, neither equation both accommodates the amplitudes of the leading terms for small and large values of y. The following model is proposed for the 3-dimensional Ising model [36]:

$$Y\left(\frac{x}{x_0};y\right)=\frac{\left(1+\Phi^2y^2\right)^{\eta/2}}{1+\psi y^2}\left[1-\Lambda+\Lambda\frac{\left(1+\psi y^2/4\right)}{2\ln(\Omega)}\ln\left(\frac{\Omega^2+\psi y^2/4}{1+\psi y^2/4}\right)\right]$$

$$\psi\left(\frac{x}{x_0}\right)=\frac{1+\eta\Phi^2/2}{1-(\Lambda/4)[1-(\Omega^2-1)/(2\Omega^2\ln(\Omega))]} \qquad (4.26)$$

Φ, Λ and Ω are universal functions of x/x_0. Unfortunately, this model does not correctly describe the higher order terms in y. Bray proposed a scattering function for the 3-dimensional Ising model in zero field (critical isochore in the lattice gas) implementing higher order terms in y [99]. His scattering function reproduces the known 2-dimensional Ising model values for all $k\xi$ to within 0.03 % [2]:

$$Y^{-1}(\infty;y)=1+y^2f\left(\frac{y^2}{9}\right)/f\left(-\frac{1}{9}\right) \qquad f(z)=\frac{2}{\pi}\sin\left(\frac{\pi\eta}{2}\right)\int_{w_0}^{\infty}\frac{wF(w)\,dw}{w^2+z\,w^n}$$

$$F(w)=\frac{P+Q\cot(\pi\eta/2)}{P^2+Q^2} \qquad P(w)=1-\frac{C_2}{(3w)^{(1-\alpha)/\nu}}\sin\left(\frac{\pi}{2\nu}\right)+\frac{C_3}{(3w)^{1/\nu}}\cos\left(\frac{\pi}{2\nu}\right) \qquad (4.27)$$

$$Q(w)=\frac{C_2}{(3w)^{(1-\alpha)/\nu}}\cos\left(\frac{\pi}{2\nu}\right)-\frac{C_3}{(3w)^{1/\nu}}\sin\left(\frac{\pi}{2\nu}\right)$$

The constants C_2 and C_3 must be the same for all systems within one universality class. When $k\xi<<1$, higher order terms in y can be neglected to give:

$$\chi(k)=\chi(0)/(1+k^2\xi^2) \qquad (4.28)$$

Thus, if the inverse scattering intensity $I^{-1}(k)\propto\chi^{-1}(k)$ is plotted as a function of k^2, the data for different densities and temperatures must have the same slope [100, 101, 85]. The intercept is proportional to the inverse compressibility $\chi^{-1}(0)$ and the ratio of slope over intercept yields the square correlation length ξ^2. Using this method, the correlation length has been determined experimentally for ^{3}He [102], ^{4}He [103, 104], Ar [105], etc. This has also been done for a number of binary liquids [82, 106, 78].

Experimental values for ν are 0.63±0.04 for gases as well as binary liquids. By using γ-values from zero-angle scattering data, and ν-values, the exponent η can be calculated from the Fisher equation. Typical values are $\eta=0.07\pm0.04$ for CO_2 [107] and $\eta=0.03\pm0.03$ for SF_6 [108]. Exponent values for η are very sensitive to the adopted values for ν and γ. In order to obtain more reliable information, the intensity of scattered light needs to be measured over a wider range of $k\xi$-values. Exponent values over a wider range of $k\xi$-values are $\eta=0.016\pm0.014$ with $\nu=0.625\pm0.005$ for the system 3-methylpentane-nitroethane [83]. These exponent values are in good agreement with the exponent values of the Landau-Ginzburg-Wilson model (2.19). This supports the validity of the universality hypothesis for the correlation function. The exponent estimates by series expansions of the 3-dimensional Ising model (2.18) are in bad agreement with the experimental results.

Singular thermodynamic behaviour is characterized by two critical exponents among the thermodynamic exponents α, β, γ and δ, while the long-range behaviour of the correlation function is characterized by the exponents ν and η. If the singular part of the system is completely determined by the long-range character of the correlation function there exists a relation between the thermodynamic exponents and the correlation-function exponents. Widom derived such a relation introducing the dimensionless quantity:

$$Q^d \equiv \frac{|A_{sing}/V|\xi^d}{k_B T_c} = \frac{p_c |A_{sing}{}^*|\xi^d}{k_B T_c} \qquad (4.30)$$

This quantity is expected to remain finite at the critical point. Along each curve of constant x, $A_{sing}{}^*$ and ξ respectively vary as $|\Delta T^*|^{2-\alpha}$ and $|\Delta T^*|^{-\nu}$, which implies the relation [109/110]:

$$\nu d = 2 - \alpha = \beta(\delta + 1) \qquad (4.31)$$

Together with the Fisher exponent relation and other exponent relations the following exponent relation is obtained:

$$\frac{2-\eta}{d} = \frac{\delta - 1}{\delta + 1} \qquad (4.32)$$

In contradiction to the thermodynamic exponent relations, this relation contains the dimensionality d. The former two exponent relations are the so-called *hyperscaling relations*, which are expected to be valid for sufficiently long-range correlation functions ($d \geq 4$). These relations are satisfied for the 2-dimensional and the 3-dimensional Ising model. The validity of the hyperscaling relations is implicitly assumed in the RG-theory of critical phenomena and, therefore, they are automatically satisfied by the numerical estimates of the Landau-Ginzburg-Wilson model (2.19). Unfortunately, they are not satisfied within error by the series expansion estimates of the 3-dimensional Ising model (2.18) [27].

As stated before, the scaling function for the structure factor is a universal function of the scaling variables $\Delta T^*/|\Delta\rho^*|^{\beta}$ (x) and $k|\Delta\rho^*|^{-\gamma/\beta}$ (y) except for the scaling factors or amplitudes D, x_0 and $\xi_{0,c}$. The number of independent scaling factors can be reduced by one by the hypothesis of *two-scale-factor universality*. Q is assumed to be a universal function of the thermodynamic scaling variable x/x_0 [111]. Now, a relation can be obtained between the scaling factors D and $\xi_{0,c}$ by substituting the following scaled expressions for $A_{sing}{}^*$ and ξ in equation (4.30) yielding:

$$A_{sing}{}^* = |\Delta\rho^*|^{(2-\alpha)/\beta} D a(x/x_0) \qquad \xi = |\Delta\rho^*|^{-\nu/\beta}\xi_{0,c}\Xi(x/x_0) \qquad \rightarrow$$

$$\frac{p_c}{k_B T_c} D\xi_{0,c}{}^d = \text{universal constant} \qquad (4.33)$$

This relation also follows from the RG-theory [112]. The hypothesis of two-scale-factor universality can be investigated by comparing the experimental values for C_V and ξ for different fluids at the same $\Delta\rho^*$ and ΔT^* [112, 113]; universality of Q also implies the combination $\xi^d|\Delta T^*|^2 C_V/V$ to be universal [113]. The hypothesis of two-scale-factor universality presupposes that the experimental data for different fluids can be represented by a power law with universal exponents. For the gas-liquid critical point, the range of simple asymptotic scaling is restricted to $|\Delta T^*|\leq 10^{-4}$. Unfortunately, there are too little experimental correlation-length data in this range to investigate the validity. However, using estimates for the correlation length amplitude ξ_0 for different components and estimates for the effective fluid exponents, the two-scale-factor universal constant along the critical isochore, $Q(\infty)$, can be calculated for different components. The correlation length on an absolute basis was not known with an accuracy better than 10 %. Nevertheless, the two-scale-factor universal constant seemed to be remarkably constant for 5 gases, approximately $Q(\infty)=0.46$ [2]. Other relationships between thermodynamic amplitudes and the amplitude ξ_0 of the correlation length are [114-116, 68]:

$$\xi_0\left(\frac{Ap_c}{k_B T_c}\right)^{1/3}=0.27\pm 0.01 \qquad \xi_0\left(\frac{B^2 p_c}{\Gamma k_B T_c}\right)^{1/3}=0.7\pm 0.1 \tag{4.34}$$

4.3 Correlation length and equation of state

By adopting the universal value $Q(\infty)=0.46$ and the equation-of-state parameters for different gases we can calculate an effective correlation-length amplitude ξ_0. However, in order to calculate correlation-length amplitudes for densities other than the critical density a functional form of the scaling function $\Xi(x/x_0)$ must be introduced. This has been tried for the 3-dimensional Ising model by Tarko and Fisher [36]. The required analyticity properties of ξ in the one-phase region away from the critical point can be automatically ensured by a parametric representation:

$$\Delta T^*=r(1-b^2\theta^2) \qquad \Delta\rho^*=kr^{\beta}\theta(1+c\theta^2) \qquad \xi=\xi_0 r^{-\nu}g(\theta) \tag{4.35}$$

The function $g(\theta)$ is an analytic function of θ which must be even in θ. The linear model is identified with $c=0$ and the cubic model with $c\neq 0$. In order to reproduce the power law amplitudes along the critical isochore and the coexistence curve $g(\theta)$ must satisfy the boundary conditions [2]:

$$g(0)=1 \qquad g(\pm 1)=\xi_0'/\xi_0 \tag{4.36}$$

The ratio ξ_0'/ξ_0 is 0.51 for the 3-dimensional Ising model [36]. For fluids the following values were derived $\xi_0'/\xi_0=0.49\pm 0.05$ [117] and $\xi_0'/\xi_0=0.45\pm 0.1$ for ^4He [103]. Another approach is to relate the correlation length to the isothermal compressibility (4.24):

$$\xi=\xi_0 R(\theta)(\Gamma^{-1}\chi_T^*)^{1/(2-\eta)} \tag{4.37}$$

Where R is a universal function of x/x_0 and, hence, a universal function of the parametric variable θ. On the critical isochore and the coexistence curve it is equal to:

$$R(0)=1 \qquad R(\pm 1)=\frac{\xi_0'}{\xi_0}\left(\frac{\Gamma}{\Gamma'}\right)^{1/(2-\eta)} \tag{4.38}$$

For the 3-dimensional Ising model $R(\pm 1)=1.17$ [36]. An experimental value for R can be calculated using the argon data of Lin and Schmidt; $R(\pm 1)=1.17\pm 0.03$ [105, 2]. This value is in good agreement with the theoretical value for the Ising model.

4.4 Correlation functions in mixtures

The correlation function of a one-component fluid, $H(r)$, is generalized to a correlation function $H_{ij}(r)$. In analogy with the one-component fluid, $\rho_i H_{ij}(r)$ measures the excess of the (molar) density of molecules of type i at a position r, compared to the average, if a molecule of type j is at the origin. The integral of the correlation function over all space

$$H_{ij} = \int H_{ij}(r)dr \qquad (4.39)$$

relates to the susceptibilities in the following way:

$$RT\chi_{ij} = RT\left(\frac{\partial \rho_i}{\partial \mu_j}\right)_{T\mu_{k\neq j}} = \rho_i\rho_j H_{ij} + \delta_{ij}\rho_j \qquad (4.40)$$

The function δ_{ij} is the Dirac delta function. For a binary mixture the following relations hold:

$$RT\chi_{11} = RT\left(\frac{\partial \rho_1}{\partial \mu_1}\right)_{T\mu_2} = RT\left(\frac{\partial^2 p}{\partial \mu_1^{\,2}}\right)_{T\mu_2} = \rho_1^{\,2}H_{11} + \rho_1$$

$$RT\chi_{22} = RT\left(\frac{\partial \rho_2}{\partial \mu_2}\right)_{T\mu_1} = \rho_2^{\,2}H_{22} + \rho_2 \qquad (4.41)$$

$$RT\chi_{12} = RT\left(\frac{\partial \rho_1}{\partial \mu_2}\right)_{T\mu_1} = RT\left(\frac{\partial \rho_1}{\partial \mu_1}\right)_{T\mu_2} = \rho_1\rho_2 H_{12}$$

All osmotic susceptibilities on the left side diverge strongly (3.56) and, in analogy with a pure fluid, all integrals of the correlation functions diverge. This means that the correlation function must become long-ranged because $H_{ij}(r)$ remains finite. In the first shells, no effects of criticality are expected, except that leading to the weak non-classical $(1-\alpha)$-behaviour. For a mixture in a fixed thermodynamic state in the vicinity of the critical point there is only one correlation length ξ and all $H_{ij}(r)$ decay with that correlation length:

$$H_{ij}(r) \propto \frac{\exp(-r/\xi)}{r} \qquad (4.42)$$

This relation holds for large values of r and a finite value of ξ. The correlation length diverges as in the pure fluid, $\xi(\rho_c)=\xi_0|\Delta T^*|^{-\nu}$, but additional constraints need to be specified, namely one or more fields to be kept constant. The amplitude ξ_0 is yet a function of the composition of the mixture. In the case of dilute binary mixtures, the osmotic susceptibility $(\partial\rho_1/\partial\mu_1)_{T\mu_2}$ approaches $(\partial\rho/\partial\mu)_T=\rho^2K_T$, where K_T is the compressibility of the pure solvent. The 'mixed' osmotic susceptibilities approach zero. See also Chapter 5, Dilute Mixtures.

Better known susceptibilities, such as the osmotic susceptibility $(\partial x_1/\partial\mu_1)_{pT}$, have more complicated relations to the correlation function integrals [118].

Chapter 5: Dilute mixtures

5.1 Taylor series expansions for dilute mixtures

An understanding of the critical behaviour of dilute mixtures is of importance in the experimental study of one-component fluids while no fluid is absolutely pure and impurity effects are largest at the critical point. The work of Krichevskii in the USSR in the 1960s gives much information about dilute mixtures [119]. Wheeler gives information about the divergence of the partial molar properties of the solute in the decorated lattice gas [120].

As has been done for the one-component fluid, the critical behaviour of some thermodynamic properties in mixtures are calculated using Taylor series expansions of the molar Helmholtz free energy, $A(V,T,x)$. For dilute mixtures, the classical Helmholtz free energy is expanded around the critical point of the solvent. The molar Helmholtz free energy can be separated into three parts [3]:

- A finite analytic residual part, $A_{res}(V,T,x)$, which represents a difference between the real mixture and the ideal gas at the same V and T.
- An analytic part $A(T)$, which is not analytic at T=0 K.
- A perfect-gas volume dependence, $RTln(V)$ and an ideal mixing term $RT\{xln(x)+(1-x)ln(1-x)\}$.

The solvent ideal mixing term is not well behaved at the mixture critical point at x=*0,1* and is subtracted from the molar Helmholtz free energy before expansion takes place. In the following text x stands for the solute and A_{321} stands for:

$$A_{321}=\left(\frac{\partial^6 A}{\partial V^3 \partial T^2 \partial x}\right) \qquad (5.1)$$

The expansions for the molar Helmholtz free energy, pressure, isothermal compressibility, and chemical potentials are given in equation. A superscript c means that the derivative is evaluated at the critical point of the solvent. The double quoting indicates that the ideal mixing term is subtracted. The double quoting has been omitted in all cases in which derivatives of A and A'' are identical. ΔV means V-V_c, ΔT means T-T_c. The variables have not been made dimensionless.

$$A''(V,T,x)=A''^{c}+A_{100}{}^{c}\Delta V+A''_{010}{}^{c}\Delta T+A''_{001}{}^{c}x+A_{110}{}^{c}\Delta V\Delta T+A_{101}{}^{c}\Delta Vx+$$
$$A_{210}{}^{c}\Delta V^2\Delta T/2+A_{201}{}^{c}\Delta V^2x/2+....+A_{400}{}^{c}\Delta V^4/24+....$$

$$p=-A_{100}=-A_{100}{}^{c}-A_{110}{}^{c}\Delta T-A_{101}{}^{c}x-A_{210}{}^{c}\Delta V\Delta T-A_{201}{}^{c}\Delta Vx-A_{400}{}^{c}\Delta V^3/6+....$$

$$(VK_T)^{-1}=A_{200}=A_{210}{}^{c}\Delta T+A_{201}{}^{c}x+A_{400}{}^{c}\Delta V^2/2+.... \qquad (5.2)$$

$$\Delta=\mu_2-\mu_1=A''_{001}{}^{c}+A_{101}{}^{c}\Delta V+A''_{002}{}^{c}x+A_{201}{}^{c}\Delta V^2/2+....+RT\ln(x)-RT\ln(1-x)+....$$

$$\mu_1=A''^{c}+A''_{010}{}^{c}\Delta T+V_cp-A_{101}{}^{c}\Delta Vx-A_{400}{}^{c}\Delta V^4/8+....-RTx+....$$

$$\mu_2=A''^{c}+A''_{001}{}^{c}+A_{101}{}^{c}\Delta V+(A''_{010}{}^{c}+A''_{011}{}^{c})\Delta T+A''_{002}{}^{c}x+V_cp+....+RT\ln(x)+....$$

For dilute mixtures, the leading behaviour of μ_1 is the same as that of p. For μ_2, the $RTln(x)$-term dominates, while the term $A_{101}{}^{c}\Delta V$ is of lower order than the pressure.

5.2 Initial slope of the critical line

This slope is obtained from the expansion of the molar Helmholtz free energy (5.2). The initial rise of the critical temperature due to the admixture of the second component can be calculated using expansions for A_{200}, A_{101}, and A_{002}, for little x, and the relation for the determinant of A [121]:

$$\mathrm{Det}(A) = (A_{201}{}^{c}x + A_{210}{}^{c}\Delta T)\frac{RT_c}{x} - (A_{101}{}^{c})^2 = 0 \rightarrow \left.\frac{dT}{dx}\right|^{c}_{CRL} = \frac{(A_{101}{}^{c})^2 - A_{201}{}^{c}RT_c}{RT_c A_{210}{}^{c}} \qquad (5.3)$$

The subscript *CRL* stands for the critical line. The initial pressure increase, $dp/dx\,/^{c}_{CRL}$, is obtained from the temperature slope (5.3) by means of the thermodynamic identity [122]:

$$\left.\frac{dp}{dx}\right|^{c}_{CRL} = \left(\frac{\partial p}{\partial x}\right)^{c}_{VT} + \left.\frac{dp}{dT}\right|^{c}_{Coex}\left.\frac{dT}{dx}\right|^{c}_{CRL} = -A_{101}{}^{c} - A_{110}{}^{c}\left.\frac{dT}{dx}\right|^{c}_{CRL} \qquad (5.4)$$

Shifts of T_c and p_c due to addition of an impurity are asymptotically linear in x. Shifts of density-like variables are of higher order [19]. The subscript *Coex* stands for coexistence curve. The derivative $dp/dT\,/^{c}_{Coex}$ stands for the slope of the vapour pressure curve of the pure solvent at the critical point, which equals the slope of the critical isochore [123].

The term $A_{101}{}^{c}=(\partial p/\partial x)^{c}_{VT}$ in equation (5.4) plays an important role in the geometry of the critical line. It also plays other important roles in the critical behaviour of dilute mixtures. It can be seen from equation (5.4) that the value of this derivative can be determined from the initial slopes of the critical lines together with the limiting slope of the vapour pressure curve.

With use of equation (5.3) and (5.4) it follows:

$$\left.\frac{dp}{dT}\right|^{c}_{CRL} = -A_{110}{}^{c} - A_{101}{}^{c}\Big/\left.\frac{dT}{dx}\right|^{c}_{CRL} \qquad (5.5)$$

In the p-T-plane the slope of the critical line differs from that of the vapour pressure curve or the critical isochore, $A_{110}{}^{c}$, by an amount $-A_{101}{}^{c}/(dT/dx\,/^{c}_{CRL})$. The sign of the term $A_{101}{}^{c}$ determines whether the critical line in the p-T plane takes off in the half-plane below the vapour pressure curve or in the half-plane above the vapour pressure curve. $A_{101}{}^{c}$ is positive if the pressure drops when some solvent molecules are replaced by solute molecules at constant V and T. In this case the critical line takes off in the lower half-plane. If such a pressure drop takes place, the solute is less volatile than the solvent. If the pressure rises on increasing the mole fraction of the solute, $A_{101}{}^{c}$ is negative and the solute is more volatile than the solvent. The critical line takes off in the half-plane above the vapour pressure curve and its extension irrespective of the sign of $dT/dx\,/^{c}_{CRL}$ [3].

Gases far above their critical point have critical lines that start in the upper half-plane. The upper region consists of two categories divided by the ideal gas. The ideal gas, with zero interaction energy and zero excluded volume, forms a vertical line in the p-T-plane. On the right side of the ideal gas line are the gases with weak interactions but non-negligible excluded volume, such as He and H_2 in near-critical steam [124, 125]. On the left side are gases with somewhat stronger interactions and larger excluded volumes, such as N_2, O_2, CO_2, and NH_3 in near-critical steam [124, 126]. The critical lines of electrolytes in near-critical steam are almost indistinguishable from the extension of the vapour pressure curve but they run in the lower half-plane of the P-T-plane [127]. It is clear that the term $A_{101}{}^{c}=(\partial p/\partial x)^{c}_{VT}$ plays an important role in the geometry of the critical line for dilute near-critical mixtures.

5.3 Dew-Bubble curve

Assume that a mixture has a gas-liquid critical line connecting the critical points of the two components. Consider the *V-x* plane. The difference between normal mixtures and dilute mixtures is the disappearance of the tilt of the tie lines, and the shift of the mixture critical point to an extremum in composition. See Figure 5.1. If the solute is less volatile then the critical solvent (or involatile), isothermal addition of the solute causes a phase separation because the solute is (far) below its critical point. At higher temperatures the mixture critical point and the two-phase region move away from the x=*0*-axis and the extremum. In the case of isothermal addition of a volatile to a critical solvent, no phase split occurs while the solute is far above its critical point. By lowering the temperature, however, a phase split slips across the x=*0*-axis [3]. In the *p-x*-plane the two cases mentioned above are mirror images of each other.

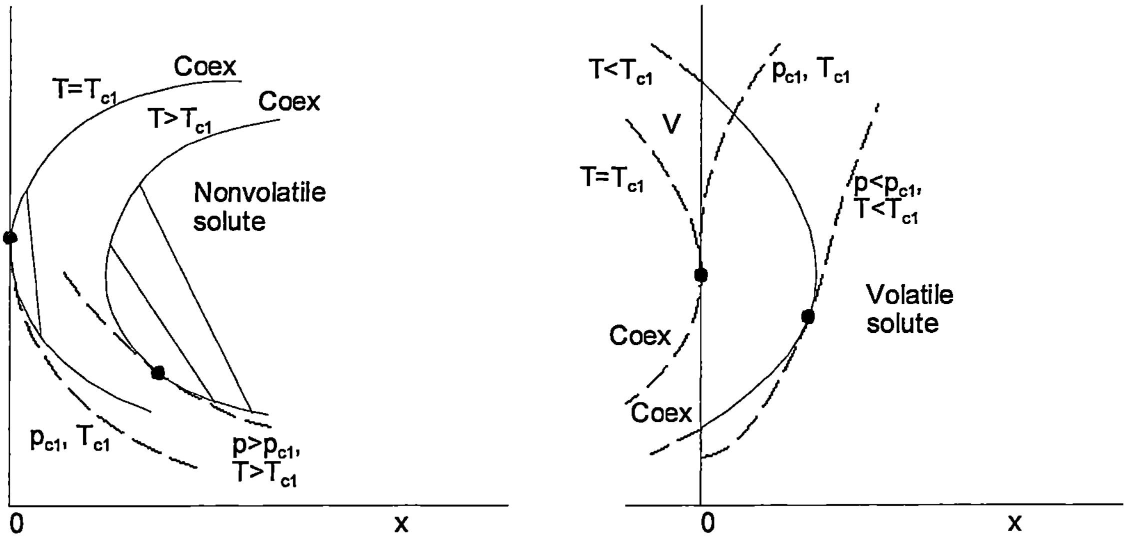


Figure 5.1: isothermal dew-bubble point curves near the critical point of the solvent

In general, the compositions of coexisting gas and liquid phases are quite different. This is not true for dilute mixtures. Tie lines become vertical in approaching the solvent critical point. The width of the tie lines measured in density co-ordinates is similar to that of pure fluids. However, the width measured in *x* co-ordinates shrinks must faster than in pure fluids [19]. Therefore, the isothermal dew-bubble point curve in *p-x*-space is narrowed in dilute mixtures and the transition from a supercritical case with a smooth curve to a sub-critical case where the dew and bubble curves meet at an angle occurs via a so-called *bird's beak* or *cusp* [3, 19]. See Figure 5.2B. The limiting slope of the bird's beak equals the limiting slopes of the dew and bubble point curves. Using the equalities of the pressure and chemical potential of the solute in the liquid and the vapour phase, Levelt Sengers derived that the difference of the molar fractions of the solute in the liquid and vapour phase, x_L-x_V, varies as $x^{3/2}$. Therefore, this difference disappears more rapidly than the individual *x*-values. She found that $-A_{101}{}^{c}x$ is both the leading term for the pressure on the dew and bubble point side at the critical temperature of the solvent. Also, the dew and bubble curves have a joint slope given by the quantity $-A_{101}{}^{c}=(\partial p/\partial x)^{c}{}_{VT}$. The same results are obtained for non-classical critical behaviour [3]. This slope can be estimated for dilute mixtures for which the dew and bubble curves are available. The derivative $A_{101}{}^{c}$ can be estimated by the average of the slopes of the dew and the bubble curves.

Literature values are –20 MPa for the system cyclopentane in carbon dioxide [128] and –15 MPa for propane in methane [129, 130].

5.4 Partial molar properties

Characteristics of the partial molar properties of the solute near the critical point of the solvent are the divergences. They were found experimentally by Kirchevskii [119]. Rozen worked out the critical behaviour for a classical equation of state [131]. Wheeler demonstrated the divergences for a non-classical decorated lattice gas model [120].

The *total* volume V_t, enthalpy H_t, Gibbs free energy G_t, and heat capacity C_{Pt} of a fluid are extensive properties that change with composition at constant temperature and pressure. If the extensive property is given by F_t, then the partial molar property and the partial molar properties in terms of mole fractions are given by:

$$\bar{F}_i = \left(\frac{\partial F_t}{\partial n_i}\right)_{pTn_{j\neq i}} \qquad \bar{F}_1 = F - x\left(\frac{\partial F}{\partial x}\right)_{pT} \qquad \bar{F}_2 = F + (1-x)\left(\frac{\partial F}{\partial x}\right)_{pT} \tag{5.6}$$

For one mole F_t equals F. The partial molar properties at x_i are obtained by drawing a tangent to the F-x-isotherm-isobar at $x=x_i$ and reading off the intercepts with the axes $x=0$ and $x=1$. The behaviour of the partial molar properties can be explained by the volume as an example. In Figure 5.2A, the volume of a mixture of an involatile solute and a solvent at its critical temperature and the critical isotherm-isobar are given. Addition of an involatile solvent causes a phase split. At the critical temperature of the solvent, the coexistence curve opens up at $x=0$. The critical point is on the $x=0$-axis, so that the tie lines near $x=0$ are almost vertical. This can also be seen in Figure 5.1. For an involatile solute, the pressure decreases along the coexistence curve as x increases while the solute is (far) below its critical temperature. Therefore, the critical isotherm-isobar is confined to the liquid-like one-phase region. It is clear that at the critical point of the solvent, the tangent to the critical isotherm-isobar will be vertical and the intercept defining the partial molar volume of the solute tends to -∞. Also, in going from a normal mixture to a dilute mixture, the derivative $(\partial V/\partial x)_{pT}$ goes over from a finite slope at the plait point to an infinite slope [3, 19].

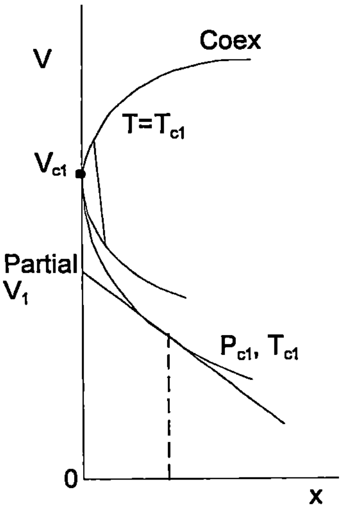


Figure 5.2A: Volume versus mole fraction

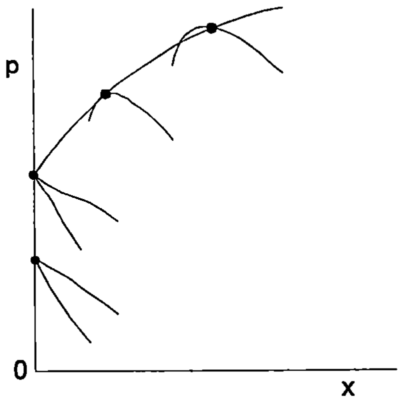


Figure 5.2B: Bird's beak

Another method to explain the divergence of the partial molar volume of the solute is by referring to the thermodynamic identity:

$$\left(\frac{\partial V}{\partial x}\right)_{pT} = -\left(\frac{\partial V}{\partial p}\right)_{Tx}\left(\frac{\partial p}{\partial x}\right)_{VT} = -VK_{Tx}\left(\frac{\partial p}{\partial x}\right)_{VT} = -\frac{A_{101}}{A_{200}} \tag{5.7}$$

The derivative A_{101} is finite in the classical theory, and A_{200} is nonzero in the mixture. Thus $(\partial V/\partial x)_{pT}$ is finite in the mixture, including at the critical line. However, as x tends to 0 or 1, K_{Tx} tends to K_T and the derivative $(\partial V/\partial x)_{pT}$ becomes proportional to the strongly diverging compressibility of one of the pure components. As a consequence, partial molar volumes diverge as the solvent's compressibility at the critical point of the solvent. An almost identical reasoning holds for the partial molar enthalpy [3]. The nature of the divergences of the partial molar volume of the solute on other paths than that of infinite-dilution can be found by expanding the two derivatives in the right part of equation (5.7):

$$\left(\frac{\partial V}{\partial x}\right)_{pT} = -\frac{A_{101}}{A_{200}} = \frac{-A_{101}{}^{c} + \ldots}{A_{201}{}^{c}x + A_{210}{}^{c}\Delta T + A_{400}{}^{c}\Delta V^2/2 + \ldots} \tag{5.8}$$

This equation makes clear that the way the denominator approaches zero will depend on the path of approach of the critical point. As mentioned, at infinite dilution the term $A_{201}{}^{c}x$ disappears and the denominator is the expansion of the inverse compressibility of one of the pure fluids.

On the critical line, T and V initially vary linearly with x (5.3) so that the term in δV^2 is of higher order. It follows from (5.3) and (5.8) that for small values of x:

$$\left(\frac{\partial V}{\partial x}\right)_{pT} = \frac{-RT_c}{A_{101}{}^{c}}\frac{1}{x} \tag{5.9}$$

By equation (5.6), the partial molar volume of the solute diverges as x^{-1}. The partial molar volume of the solvent reaches the value $V_c+RT_c/A_{101}{}^{c}$, which is finite but not equal to V_c. Along the coexistence curve at $T=T_c$, δV^2 varies linearly with x and the two terms in the denominator of equation (5.8) are of the same order. Using relation (5.8) and the condition for the coexistence curve, the following relation can be derived:

$$\left(\frac{\partial V}{\partial x}\right)_{pT} = \frac{-A_{101}{}^{c}}{A_{201}{}^{c} + 3(A_{101}{}^{c})^2/RT_c}\frac{1}{x} \tag{5.10}$$

The partial molar volume of the solute diverges as x^{-1} and the partial molar volume of the solvent reaches the value $V_c-A_{101}{}^{c}/(A_{201}{}^{c}+3(A_{101}{}^{c})^2/RT_c)$. The critical isotherm-isobar is determined by the pressure expansion (5.2) at $T=T_c$ and $p=p_c$:

$$\Delta V^3 = \frac{-6A_{101}{}^{c}}{A_{400}{}^{c}}x \tag{5.11}$$

The partial molar volume of the solute is found from:

$$\left(\frac{\partial V}{\partial x}\right)_{pT} = -\mathrm{sign}(A_{101}{}^{c})\left|\frac{2A_{101}{}^{c}}{9A_{400}{}^{c}}\right|^{1/3}\frac{1}{x^{2/3}} \tag{5.12}$$

Thus, for nonvolatile solutes the partial molar volume diverges to $-\infty$. The partial molar volume of the solvent is given by:

$$\overline{V}_1 = V_c + -\mathrm{sign}(A_{101}{}^{c})\left|\frac{2A_{101}{}^{c}}{9A_{400}{}^{c}}\right|^{1/3} x^{1/3} \tag{5.13}$$

Thus, on the critical isotherm-isobar the partial molar volume of the solvent approaches V_c, but not linearly in x. The partial molar enthalpies follow from the expansion [3]:

$$\left(\frac{\partial H}{\partial x}\right)_{pT} = A_{001} - TA_{011} + TA_{101}\frac{A_{110}}{A_{200}} = A''_{001} - TA''_{011} + TA_{101}V\alpha_p \qquad \alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{px} \quad (5.14)$$

The coefficient α_p is the thermal expansion coefficient at constant composition. It is clear that the partial molar enthalpy at infinite dilution diverges as the thermal expansion coefficient. Since the thermal expansion coefficient and the compressibility have similar critical behaviour, the partial molar enthalpies depend on the path of approach of the critical point in the same manner as the partial molar volumes. This is clear from the Clapeyron equation, which connects the partial molar volume and the partial molar enthalpy, with the finite slope of the vapour pressure curve as the proportionality factor. The derivative $(\partial V/\partial x)_{pT}$ can be read off from the initial slope of the critical line in *p*-*T*-space. Therefore, solutes that have a critical line that starts in the left and upper-half plane of the *p*-*T*-diagram will have positive divergences of their infinite-dilution partial molar volumes and enthalpies. Those that have critical lines that start in the right and lower half plane have negative divergences [132, 133]. Measurements of partial molar volumes and partial molar heat capacities of non-polar solutes and salts near infinite dilution in water have been done by Wood [134]. Other measurements of partial molar properties are given by the Oak Ridge group [135].

The partial molar heat capacity of the solute is a composition derivative of a property that already exhibits a strong divergence. Thus, it behaves more strongly anomalous than the partial molar volumes. The analysis of the path dependence of the partial molar heat capacity of the solute and the determination of the critical exponents on these paths have been done by Chang and Levelt Sengers [135A]. Results are given in Table 5.1.

5.5 Non-classical path-dependence of the partial properties

The critical exponent β characterizes the shape of the coexistence curve and the critical exponent δ characterizes the isotherm-isobar. Therefore, the derivative $(\partial V/\partial x)_{pT}$ diverges as $x^{1/\delta-1}=x^{-\gamma/(\beta\delta)}$. The divergences and limits of the partial molar enthalpies, volumes, and heat capacities for the classical and non-classical case are summarized in Table 5.1 [3]:

Table 5.1: Difference between classical and non-classical behaviour

Property	Classical			Non-classical		
Path	$\bar{V}_2$, $\bar{H}_2$	$\bar{C}_{p2}$	$\bar{V}_1$	$\bar{V}_2$, $\bar{H}_2$	$\bar{C}_{p2}$	$\bar{V}_1$
p_c, T_c	$x^{-2/3}$	$x^{-5/3}$	V_c	$x^{-(1-1/\delta)}$	$x^{-(2-1/\delta)}$	V_c
p_c, ρ_c	x^{-1}	x^{-2}	Not V_c	x^{-1}	$x^{-(3-\gamma)}$	Not V_c
T_c, ρ_c	x^{-1}	x^{-2}	Not V_c	x^{-1}	$x^{-(3-\gamma)}$	Not V_c
Critical line	x^{-1}	x^{-2}	Not V_c	x^{-1}	N.A.	Not V_c

5.6 Osmotic susceptibilities

The osmotic susceptibilities diverge strongly at the critical line. The way in which they reach their finite or zero limiting values at infinite dilution can be considered by the expansions of the chemical potentials (5.2), the definition of the osmotic susceptibilities (3.58) and the relation between volume and composition at constant *p* and *ΔT=0*. It follows:

$$\left(\frac{\partial\mu_2}{\partial x}\right)_{pT} = A''^{\,c}_{002} + RTx^{-1} - \left|A_{101}{}^{c}\right|\left|\frac{6A_{101}{}^{c}}{A_{400}{}^{c}}\right|^{1/3}\frac{x^{-2/3}}{3} + \ldots \qquad (5.17)$$

While in the limit of infinite dilution the term RTx^{-1} dominates, the osmotic susceptibility $(\partial x/\partial\mu_2)_{pT}$ behaves as x/RT and approaches zero. The osmotic susceptibility $(\partial x/\partial\mu_1)_{pT} = x/(1-x)\,(\partial x/\partial\mu_2)_{pT}$, behaves as $1/RT$ and remains finite [3].
The osmotic susceptibility in a dilute mixture is experiencing a serious dilemma. The competition between diluteness and criticality can be enlightened by the following relations that follow from (3.57):

$$\left(\frac{\partial x}{\partial\mu_2}\right)_{pT}^{-1} = (1-x)\left[A_{002} - \frac{A_{101}{}^{2}}{A_{200}}\right] = (1-x)\frac{\mathrm{Det}(A)}{A_{200}}$$

$$\left(\frac{\partial x}{\partial\mu_1}\right)_{pT}^{-1} = -x\left[A_{002} - A_{101}{}^{2}\right] = -x\frac{\mathrm{Det}(A)}{A_{200}} \qquad (5.18)$$

The term A_{002} contains RT/x that forces the osmotic susceptibility of the solute to zero at infinite dilution. For the solvent the divergence is cancelled by a factor *x*. Both osmotic susceptibilities diverge at the critical line, where *Det(A)=0*, for finite *x*. Away from the critical line, *Det(A)≠0*, and the osmotic susceptibilities behave as the compressibility of the mixture. As *x* approaches zero in this case, the osmotic susceptibility of the solute approaches zero while the osmotic susceptibility of the solvent becomes proportional to the compressibility of the pure solvent [3]. As a consequence, the way the mixture actually behaves depends on the path of approach to criticality. On any path that intersects the critical line at finite composition, the osmotic susceptibility must diverge, while the isothermal compressibility K_{Tx} remains finite. If the path of infinite dilution is reached before the system becomes critical, the osmotic susceptibility of the solute becomes zero, and K_{Tx} approaches K_T, the strongly diverging compressibility of the pure solvent [19]. This holds for the classical and the non-classical case. See also Table 3.7 for competition between diluteness and criticality.

Chapter 6: Crossover Theory

6.1 The need for a crossover model

The scaling laws are only valid in a limited temperature and density range, even when corrected for vapour-liquid asymmetry and lack of scaling. To be able to describe the whole thermodynamic surface one is forced to supplement the scaled fundamental equation in the critical region with a classical global Van der Waals-like equation outside the critical region. However, this causes discontinuities in the thermodynamic properties in the intermediate region. Therefore, it is necessary to develop a formulation that incorporates the scaling laws near the critical point and the thermodynamic surface far away from the critical point. A first attempt has been made by Chapela and Rowlinson [136]. They use a switch function that suppresses the analytic equation near the critical point and the scaled equation far away from the critical point. However, use of a switch function is theoretically unsatisfactory [137]. An alternative empirical approach has been made by Fox [138] who accomplished the crossover by an appropriate redefinition of the variables in the classical potential. However, his method does not correctly represent the crossover from the actual singular critical behaviour of C_V to the jump-like discontinuous behaviour in the mean-field theory [2, 139].

Until recently, the application of the principle of critical-point universality was restricted to the immediate asymptotic vicinity of the critical point. However, the principle of critical-point universality is valid in a wide region of temperatures and pressures where any critical enhancements of the compressibility are observed. As a consequence, it is possible to develop a general formulation of the equation of state for the entire *global critical region*. This general description can be developed by solving the crossover problem between the limits of the asymptotic critical region and the classical Van der Waals-like limit, far away from the critical point. Most of the theoretical approaches are based on the Landau-Ginzburg-Wilson theory of critical fluctuations.

In the RG-Theory, one takes into account the co-operative effect of fluctuations with all wavelengths down to a minimum cutoff wavelength of the order of the range of the molecular interaction [140, 141]. To obtain the critical behaviour, the effects due to the cutoff are neglected because the correlation length near the critical point is much longer than the range of molecular interaction. By linearization of the RG-equations one obtains the Wegner expansions (3.31, 3.33). However, to solve the crossover problem one has to solve the non-linear RG-equations. The non-linear equations must be solved to effectively sum the Wegner series expansion, including the cutoff effects, to ensure that the theory reduces to the proper molecular theory at distances far away from the critical point where the correlation length becomes of the same order as the range of molecular interactions [2]. A satisfactory crossover procedure should satisfy the following conditions [142]:

- The classical limit must imply critical parameters that differ from the actual critical parameters. Crossover theory must account for this phenomenon.
- The crossover equation should recover the asymptotic scaling laws near the critical point and an estimate of the Wegner correction-to-scaling terms.
- Some properties, such as C_V and the slope of the coexistence curve diameter, contain both singular and regular terms due to fluctuations near the critical

point, which merge and cancel far away from the critical point. The crossover equation must incorporate these non-scaling features.

Near the critical point, in a very small range, simple scaling laws with universal scaling functions and universal critical exponents can characterize the thermodynamic behaviour. An important question is; how far away from the critical point will the classical theory become valid? A rough estimate can be made with the Ginzburg criterion.

A solution of the asymptotic crossover problem is by itself not sufficient to describe the actual thermodynamic crossover behaviour observed in fluids, since the classical theory does not become valid until one reaches temperatures and densities so far away from the critical point that an asymptotic classical critical description will no longer be applicable. Chen proposed a non-asymptotic solution to this problem by including higher-order terms in the classical Landau expansion and by taking into account vapour-liquid asymmetry [143]. Kiselev made a phenomenological crossover model [144-146]. These solutions will be dealt with in this chapter.

6.2 Classical approach and the Ginzburg theory

How close to the critical point should one expect the asymptotic scaling laws to be applicable? How close can one approach the critical point neglecting the effects of critical fluctuations and continue to use classical theories for the thermodynamic properties? Answers to these questions can be formulated using the classical approach. The power law for the susceptibility along the critical isochore above T_c (Table 1.1) is modified by the leading term of he confluent singularities predicted by the RG-theory in the following way:

$$\bar{\chi} = \Gamma_0 |\Delta T^*|^{-\gamma} \rightarrow \bar{\chi} = \Gamma_0 |\Delta T^*|^{-\gamma} \left[1 + \Gamma_1 |\Delta T^*|^{\Delta} + ...\right] \qquad (6.1)$$

The exponent Δ of this Wegner expansion is about 0.5 and the critical amplitude Γ_1 is of order unity. Hence, for the correction term to be smaller than 1 %, ΔT^* must be smaller than 10^{-4}. Therefore, it is clear that the validity of the asymptotic scaling laws is restricted to an extremely small range of temperatures. A rough estimate of the range where fluctuations can be neglected is given by the Ginzburg criterion. To deduce this criterion a first order estimate of the fluctuations, based on the theory of Ornstein and Zernike, is made.

The Helmholtz free-energy density is given by equation (3.4). The variables in this classical approach are defined in equation (1.3). To account for critical fluctuations the order parameter $\phi(r)$, which is a function of position and whose average value in the volume V corresponds to the density difference $\Delta\rho^*$, is introduced:

$$< \phi(r) >= \frac{1}{V} \int \phi(r) dr = \Delta\rho^* \qquad (6.2)$$

The local Helmholtz free-energy density $a(\phi(r))$ and the local ordering field $h(\phi(r)) \equiv \delta a/\delta\phi(r)$ are related to the corresponding macroscopic quantities by:

$$< a(\phi(r)) >= \Delta A^* \qquad < h(\phi(r)) >= \Delta\mu^* \qquad (6.3)$$

If the fluctuations are neglected, the parameters equal their average values. The local Helmholtz free-energy density and the ordering field can be written in the form of a Landau expansion [147]:

$$a(\phi(r)) = \frac{1}{2} a_0 \Delta T^* \phi^2(r) + \frac{1}{4!} u_0 \phi^4(r) + ... \qquad h(\phi(r)) = a_0 \Delta T^* \phi(r) + \frac{1}{3!} u_0 \phi^3(r) + ... \qquad (6.4)$$

Above the critical temperature, ($\Delta T^*\geq 0$), $h=0$ implies $\phi=0$, which corresponds to the critical isochore. Below the critical temperature, ($\Delta T^*\leq 0$), $h=0$ has two nonzero solutions ϕ_{liq} and ϕ_{vap} that correspond to the vapour and liquid branches of the coexistence curve:

$$\phi_{\mathrm{liq,vap}} = \Delta\rho^*_{\mathrm{liq,vap}} = \pm\left(\frac{6a_0}{u_0}\right)^{1/2} \left|-\Delta T^*\right|^{1/2} \qquad (6.5)$$

The inverse compressibility at the critical isochore, ($\Delta T^*\geq 0$), will asymptotically vary as:

$$\chi^{*-1}(\rho_c, \Delta T^* \geq 0) = \left(\frac{\partial h}{\partial \phi}\right)_{\Delta T^*} = a_0 \Delta T^* \qquad (6.6)$$

The finite jump of the isochoric heat capacity at the critical isochore upon crossing the critical temperature is given by [2]:

$$\lim_{T\to T_c}\left[C_V^*(\rho_c, T\leq T_c) - C_V^*(\rho_c, T\geq T_c)\right] = \frac{3a_0^2}{u_0} \qquad (6.7)$$

For the Van der Waals equation of state, a typical mean-field equation, the coefficients a_0 and u_0 are respectively 6 and 9 [2]. The main characteristic of the mean-field equation is that the critical fluctuations have been neglected. If the fluctuations are not neglected, the order parameter becomes a function of the position r. In the classical theory this dependence is given by the square gradient $(\nabla\phi)^2$. Equation (6.4) for the local free Helmholtz free-energy density becomes:

$$a(\phi(r)) = \frac{1}{2}a_0\Delta T^*\phi^2(r) + \frac{1}{4!}u_0\phi^4(r) + \frac{1}{2}c_0(\nabla\phi)^2 \ldots.. \qquad (6.8)$$

The coefficient c_0 is system-dependent. The theory of Ornstein and Zernike yields for the correlation function of the order parameter between the position r_1 and r_2 [148]:

$$G(r) = <\phi(r_1)\phi(r_2)> - <\phi>^2 = \frac{v_0}{4\pi c_0'}\frac{\exp(-r/\xi)}{r} \qquad r = |r_2 - r_1| \qquad (6.9)$$

The parameter v_0 is the volume per molecule and $c_0'=c_0Z_c$. The correlation length in equation (6.9) is related to the susceptibility by:

$$\xi^2 = c_0\chi^* = c_0/a_0|\Delta T^*|^{-1} \qquad (6.10)$$

The correlation length along the critical isochore in the theory of Ornstein and Zernike diverges as [149]:

$$\xi(\rho_c, \Delta T^* \geq 0) = \overline{\xi}_0|\Delta T^*|^{-1/2} = \sqrt{c_0/a_0}|\Delta T^*|^{-1/2} \qquad (6.11)$$

The resulting fluctuation contribution to the susceptibility χ^* has been evaluated by Vaks *et al.* for magnetic systems [150] and for fluids by Anisimov *et al.* [151]. The asymptotic divergence of the fluctuation contribution to the heat capacity has been evaluated by Levanyuk [152]:

$$\begin{aligned}\chi^{*-1}(\rho_c, \Delta T^* \geq 0) &= a_0\Delta T^*\left[1 - \frac{u_0 v_0}{8\pi a_0^2 \overline{\xi}_0^3}|\Delta T^*|^{-1/2}\right] \\ \Delta C_V^*(\rho_c, \Delta T^* \geq 0) &= \frac{v_0}{16\pi\overline{\xi}_0^3}|\Delta T^*|^{-1/2}\end{aligned} \qquad (6.12)$$

A possible criterion for the range of validity of the classical theory is to require that the fluctuation contribution to the heat capacity be small compared to the classical jump of the heat capacity or that the fluctuation contribution to the compressibility be small [151]:

$$\Delta T^* >> \frac{u_0^{\,2}}{(48\pi)^2 a_0^{\,4}}\left(\frac{v_0}{\bar{\xi}_0^{\,3}}\right)^2 \qquad \Delta T^* >> \frac{u_0^{\,2}}{64\pi^2 a_0^{\,4}}\left(\frac{v_0}{\bar{\xi}_0^{\,3}}\right)^2 \tag{6.13}$$

All possible criteria depend on the parameters u_0, a_0, v_0 and $\bar{\xi}_0$ but differ in the value of the prefactor. From this equation it follows that the effects of fluctuations can be neglected when:

$$\Delta T^* >> Gi \qquad Gi = \frac{u_0^{\,2}}{64\pi^2 a_0^{\,4}}\left(\frac{v_0}{\bar{\xi}_0^{\,3}}\right)^2 \tag{6.14}$$

Here, the Ginzburg number is related to the susceptibility in the one-phase region, since the susceptibility is closely related to the correlation length (6.10) and the inverse compressibility serves as a measure of the distance from the critical point in the one-phase region [143, 153]. The Ginzburg number can be estimated by the Van der Waals parameters a_0 and u_0 and by the assumption that $v_0=4\pi\bar{\xi}_0^{\,3}/3$. These values result in $Gi\approx 0.01$. Thus, classical equations of state for fluids will be applicable as long as $\Delta T^*>>0.01$. However, ΔT^* should be much larger than Gi, since the fluctuation correction in (6.12) decreases only with the square root of the reduced temperature difference. It is clear that asymptotic scaling laws, wherever the range of these fluctuations is larger than the range of microscopic intermolecular interaction, can not describe the effects of critical fluctuations [149].

The Ginzburg criterion is only a qualitative estimate of the breakdown of the classical theory, while the fluctuations change the critical temperature and hence the variable ΔT^*. Far away from the critical point, retention of only the leading two terms in the expansion will not be enough for quantitative estimates. Furthermore, this Ginzburg criterion is restricted to the critical isochore [151].

It can be tried to take into account corrections to scaling in the form of a Wegner expansion. The Wegner expansions for the Helmholtz free-energy density and the corresponding heat capacity and vapour and liquid densities in the alternative reduced variables (1.4) read [149]:

$$\Delta\tilde{A}_s(\Delta\tilde{T},\Delta\tilde{\rho}) = \frac{A_0^{\,+}\left|\Delta\tilde{T}_s\right|^{2-\alpha}}{(2-\alpha)(1-\alpha)\alpha}\left[f_0(v) + \frac{(2-\alpha)(1-\alpha)}{(2-\alpha-\Delta)(1-\alpha-\Delta)}A_1^{\,+}\left|\Delta\tilde{T}_s\right|^{\Delta} g_0(v) + ...\right]$$

$$\tilde{C}_{Vs} = \frac{A_0^{\,+}}{\alpha}\left|\Delta\tilde{T}_s\right|^{-\alpha}\left[1 + A_1^{\,+}\left|\Delta\tilde{T}_s\right|^{\Delta}\right] \qquad \Delta\tilde{\rho}_{Liq,Vap} = \pm B_0\left|\Delta\tilde{T}_s\right|^{\beta}\left[1 + B_1^{\,+}\left|\Delta\tilde{T}_s\right|^{\Delta}\right] \tag{6.15}$$

These Wegner expansions are valid for systems that are symmetric in the order parameter. Thus, equation (6.15) is valid for a hypothetical symmetric fluid with variables $\Delta\tilde{T}_s$ and $\Delta\tilde{\rho}_s$. Equations of state that incorporate first order correction-to-scaling terms and corrections for asymmetry have been developed and applied to represent thermodynamic properties. However, the range of validity is still too small to make contact with the classical equations far away from the critical point. Extrapolation of these modified equations of state causes disagreement with experimental data. Therefore, a crossover equation that accounts for the crossover from singular behaviour at the critical point to the classical mean-field behaviour must be developed.

6.3 Asymptotic crossover in first order ε-expansion

This is a simple crossover solution from asymptotic singular critical behaviour to asymptotic classical critical behaviour. An explicit solution to first order in the perturbation parameter $\varepsilon=4-d$ is given by Belyakov and Kiselev [154]. It is restricted to the one-phase region in zero ordering field ($M=0$), which for fluids corresponds to the critical isochore. The effect of the long-range critical fluctuations on the thermodynamic properties can be evaluated by the RG-theory. The Landau-Ginzburg-Wilson hamiltonian is given by [151]:

$$H(\phi)=\frac{k_B T}{v_0}\int d^d x\left[\frac{1}{2}a_0\Delta T^*\phi^2(r)+\frac{1}{4!}u_0\phi^4(r)+\frac{1}{2}c_0\left(\nabla\phi^2(r)\right)^2\right] \qquad (6.16)$$

In implementing the renormalization due to the presence of long-range fluctuations, one must integrate over all fluctuations with wave numbers between a minimum value $\Lambda_1=\xi^{-1}$ and a maximum value Λ_0 corresponding to an inverse microscopic length scale. Near the critical point, $\Lambda_0 >> \Lambda_1=\xi^{-1}\rightarrow 0$ and if one integrates over all wavelengths from $\Lambda_1=0$ to $\Lambda_0=\infty$, one obtains the asymptotic scaling laws. To account for non-asymptotic effects, a nonzero lower limit, $\Lambda_1=\xi^{-1}$, and a non-infinite upper limit, Λ_0, must be taken into account. In the crossover model of Belyakov and Kiselev the upper limit is still taken to be infinite and, therefore, system-dependent cutoff effects are neglected. As a result the crossover expressions can be represented in a universal form. Belyakov and Kiselev define a rescaled susceptibility and a rescaled temperature difference:

$$\hat{\chi}=\chi^* a_0 \mathrm{Gi} \qquad \Delta\hat{T}=\frac{\Delta T^*}{\mathrm{Gi}} \qquad \mathrm{Gi}=\frac{u_0^2}{2(4\pi^2)^2 a_0^4}\left(\frac{v_0}{\bar{\xi}_0^3}\right)^2 \qquad (6.17)$$

The crossover expression along the critical isochore representing the rescaled susceptibility as a function of the rescaled temperature difference is given by:

$$\Delta\hat{T}=\left(1+3\hat{\chi}^{\varepsilon/2}\right)^{1/3}\left[\hat{\chi}^{-1}+(1+3\hat{\chi}^{\varepsilon/2})^{-2/\varepsilon}\right] \qquad (6.18)$$

The classical limit in rescaled and unrescaled variables reads:

$$\hat{\chi}^{-1}=(\Delta\hat{T}-1)\left[1-(\Delta\hat{T}-1)^{-\varepsilon/2}\right] \qquad \chi^{*-1}=a_0\Delta\bar{T}\left[1-\left(\frac{\Delta\bar{T}}{\mathrm{Gi}}\right)^{-\varepsilon/2}\right] \qquad \Delta\bar{T}=\Delta T^*-\mathrm{Gi} \qquad (6.19)$$

For $\varepsilon=1$, the mean-field result (6.2) is obtained but with a difference between actual and classical critical temperature $T_C'-T_C=T_C Gi$. On comparing equation (6.14) and (6.17) we see that the Ginzburg number obtained in first order ε-expansion equals the one in the Ornstein-Zernike theory except for a factor $2/\pi^2$. The asymptotic fluctuation regime corresponds to $\hat{\chi}>>1$. In this limit one recovers equation (6.1) from equation (6.18) with the exponents $\gamma=1+\varepsilon/6$ and $\Delta=\varepsilon/2$ and the amplitudes:

$$\Gamma_0=\frac{3^{1/3}}{a_0}\mathrm{Gi}^{\gamma-1}+O(\varepsilon) \qquad \Gamma_1=\frac{1}{9}\mathrm{Gi}^{-\Delta}+O(\varepsilon) \qquad (6.20)$$

Belyakov and Kiselev obtain the following relation for the crossover behaviour of the specific heat:

$$\Delta C_V^*=C_V^*-C_0^*=B_{cr}(1+3\hat{\chi}^{\varepsilon/2})^{1/3}-B_{cr} \qquad B_{cr}=\frac{a_0^2}{u_0}=\frac{1}{4\pi^2\sqrt{2}}\frac{v_0}{\bar{\xi}_0^3}\mathrm{Gi}^{-1/2} \qquad (6.21)$$

C_0^* is the background specific heat in the limit $\hat{\chi}\rightarrow 0$ and B_{cr} represents the fluctuation-induced modification of the background specific heat. The crossover equation for the specific heat can be rewritten in universal form using B_{cr}:

$$\Delta\hat{C}_V = \Delta C_V{}^* / B_{cr} = (1+3\hat{\chi}^{\varepsilon/2})^{1/3} - 1 \qquad (6.22)$$

The limit in the classical region,

$$\Delta C_V{}^* = C_V{}^* - C_0{}^* = B_{cr}\left(\frac{\Delta\overline{T}}{Gi}\right)^{-1/2} \qquad (6.23)$$

must be compared with equation (6.12). We see that equations (6.12) and (6.23) differ only by a factor $\pi\sqrt{2}/4$. In the fluctuation regime, $\hat{\chi} >> 1$, the expansion becomes:

$$\Delta C_V{}^* = C_V{}^* - C_0{}^* = \alpha^{-1} A_0{}^+ (\Delta T^*)^{-\alpha} (1 + A_1{}^+ (\Delta T^*)^{\Delta}) - B_{cr} \qquad (6.24)$$

The exponents and amplitudes are given by:

$$\alpha = \frac{\varepsilon}{6} \qquad \Delta = \frac{\varepsilon}{2} \qquad A_0{}^+ = 3^{1/3}\alpha Gi^{\alpha} B_{cr} + O(\varepsilon) \qquad A_1{}^+ = \frac{1}{9} Gi^{-\Delta} + O(\varepsilon) \qquad (6.25)$$

Bagnuls and Bervillier suggest that the amplitude combination $R_{cr}{}^+ \equiv A_0{}^+ (A_1{}^+)^{\alpha/\Delta} / \alpha B_{cr}$ should be universal [155]. In the model of Belyakov and Kiselev, $R_{cr}{}^+ = 0.693$. The value for *3*-dimensional Ising-like systems is 0.708 [156]. It is clear that the value of $R_{cr}{}^+$ is not universal. With the *0th*-order approximation (6.25) for $A_i{}^+$, the approximation (6.25) for α, and the principle of two-scale factor universality, the amplitude of the correlation length becomes:

$$\xi_0{}^3 = R_\xi{}^3 \frac{v_0}{3^{1/3}\alpha Gi^{\alpha} B_{cr}} \qquad \xi_0{}^d \frac{A_0{}^+}{v_0} = R_\xi{}^d \qquad (6.26)$$

R_ξ is a universal constant (R_ξ equals 0.27 for $d=3$ [151]). Substitution of B_{cr} (6.21) into (6.26) yields:

$$\frac{\xi_0}{\overline{\xi}_0} = \left(\frac{2^{5/2}\pi^2}{3^{1/3}\alpha}\right)^{1/3} R_\xi Gi^{\nu-1/2} \qquad (6.27)$$

The fluctuations renormalize the amplitude $\overline{\xi}_0$ of the classical power law (6.11) into a modified amplitude ξ_0 of the non-classical power law $\xi=\xi_0\tau^{-\nu}$. For the classical theory to be valid near the critical point, the Ginzburg number must be very small, which means that $\overline{\xi}_0$ must be larger than ξ_0.

Belyakov and Kiselev also introduced a phenomenological generalization of (6.18) and (6.22) that agrees better with the *3*-dimensional values of the Ising model than the results obtained in first order ε-expansion [157, 158]:

$$\Delta\hat{T} = (1+\chi_0\hat{\chi}^{\Delta/\gamma})^{(\gamma-1)/\Delta}\left[\hat{\chi}^{-1} + (1+\chi_0\hat{\chi}^{\Delta/\gamma})\right]^{-\gamma/\Delta} \qquad \Delta\hat{C}_V = (1+\chi_0\hat{\chi}^{\Delta/\gamma})^{\alpha/\Delta} - 1 \qquad (6.28)$$

The exponents α, γ, and Δ are the actual critical exponents for the *3*-dimensional Ising system. Characteristic values for this crossover model are $A_1{}^+/\Gamma_1=0.99$ and $R_{cr}{}^+=0.733$, to be compared with the theoretical values $A_1{}^+/\Gamma_1=0.95$ and $R_{cr}{}^+=0.708$ [156]. Sengers called this phenomenological model the asymptotic crossover model of Belyakov and Kiselev [151]. Disadvantages of this crossover model are that it only describes the crossover of the susceptibility and the specific heat in the one-phase region along the critical isochore; it does not yield the crossover behaviour of the complete thermodynamic surface. The crossover model does not yield the square-root correction of equation (6.12) to the classical limit implied by the Ornstein-Zernike theory [151].

Bagnuls and Bervillier obtained an alternative solution of the asymptotic crossover problem by field-theoretical techniques applicable to $d=3$ [156]. This solution also yields a universal relation between the fluctuation-induced-specific-heat background

B_{cr} and the amplitudes A_0^+ and A_1^+ at the cost of an infinite wave number Λ_0. Belyakov and Kiselev also investigated the effects of a finite cutoff wave number up to first order in ε. The 'universal' constant R_{cr}^+ in this model reads:

$$R_{cr}^{\ +} = R_0\left[1-\frac{3\sqrt{2Gi}}{\Lambda_0\xi_0}\right]^{\alpha/\Delta} \tag{6.29}$$

R_0 equals $3^{-1/3}=0.693$ and the universal value $R_{cr}^+=R_0$ is only obtained in the limit of infinite Λ_0. In general, there are non-universal contributions to the crossover behaviour that depend on the system-dependent cutoff wave number and the Ginzburg number [151]. That the amplitude ratio R_{cr}^+ is not universal was earlier pointed out by Nicoll and Albright [159].

6.4 Asymptotic crossover by renormalization-group matching

A crossover approach that is not restricted to systems in zero ordering field, based on the work of Nicoll, Albright and Chen, is given here [160, 161, 68, 162-164, 143, 149]. Equation (1.4) and (3.4) give the dimensionless variables and the Helmholtz free-energy density. In the mean-field theory, the order parameter $\phi(r)$ is replaced by its mean value $<\phi(r)>=\Delta\tilde{\rho}$. The classical Landau expansion for the Helmholtz free-energy density (6.4) is written in the following form [164, 143]:

$$\Delta\tilde{A}_{cl} = \frac{1}{2}tM^2 + \frac{u^*\bar{u}\Lambda}{4!}M^4 + \ldots\ldots \qquad t = c_t\Delta\tilde{T}_s \qquad M = c_\rho\Delta\tilde{\rho}_s \tag{6.30}$$

The subscript *s* refers again to systems symmetric in the order parameter *M*. The coefficient a_0 in equation (6.4) has been absorbed in c_t. $\bar{u}=u/u^*$ is the ratio of the actual coupling constant of the system over u^*. u^* is the so-called *fixed-point coupling constant for 3-dimensional Ising-like systems.* Its value is 0.472 [165]. Λ is a dimensionless cutoff wave number, which is related to the maximum cutoff wavenumber Λ_0 of the critical fluctuations. The role of the two system-dependent amplitudes of the Helmholtz free-energy density in equation (6.15) is in the crossover theory played by the scaling factors c_t and c_ρ, while the coefficient $\bar{u}\Lambda$ determines the strength of the corrections to scaling. The expansion of the isothermal compressibility is proportional to κ^2. The expansion of κ^2 becomes [149, 151]:

$$\tilde{\chi}_{cl}^{\ -1} \propto \kappa^2{}_{cl} = \left(\frac{\partial\Delta\tilde{A}_{cl}}{\partial M^2}\right)_t = t + \frac{1}{2}u^*\bar{u}\Lambda M^2 \propto \xi^{-2} \tag{6.31}$$

As seen from equation (6.10) and (6.31), the property κ^2 serves as measure of the distance from the critical point. Because of the long-range fluctuations, the Helmholtz free-energy density satisfies a RG-equation that shows how the Helmholtz free-energy density changes with a change in length scale. To obtain a complete crossover expression from the nonlinear renormalization equations one considers the solution for a special value of the length scale that is called the *match-point value* [160, 68, 166]. The non-classical, renormalized, Helmholtz free-energy density $\Delta\tilde{A}_{sr}$ (symmetric) is related to the classical Helmholtz free-energy density $\Delta\tilde{A}_{cl}$ by the following transformations and the addition of a kernel factor [149]:

$$t \rightarrow tTU^{-1/2} \qquad M \rightarrow MD^{1/2}U^{1/4} \qquad -\frac{1}{2}t^2K \tag{6.32}$$

Two approximations are made in this transformation. The transformations are obtained on the basis of a match-point value which is strictly correct only for *M=0*.

The additive kernel term, which includes fluctuation-induced contributions analytic in temperature, is truncated after t^2; terms of higher order have been neglected [149].

The classical expansion (6.30) is transformed by the renormalization-group matching procedure to:

$$\Delta\tilde{A}_{sr} = \frac{1}{2}tM^2TD + \frac{u^*\bar{u}\Lambda}{4!}M^4D^2U - \frac{1}{2}t^2K..... \tag{6.33}$$

And equation (6.31) is transformed into:

$$\kappa^2 = \left(\frac{\partial\Delta\tilde{A}_{sr}(tT, MD^{1/2})}{\partial(MD^{1/2})^2}\right)_t = tT + \frac{1}{2}u^*\bar{u}\Lambda M^2DU \tag{6.34}$$

The rescaling functions *T*, *U*, *D*, and *K* can be calculated from the RG-coefficients but it is simpler to represent the rescaling functions by closed-form approximates [167]. There are several closed-form approximates varying in complexity and accuracy. The approximates of crossover model II of Chen *et al.* [143, 167] and the crossover equation in terms of the parametric variable *Y* are given by:

$$\begin{gathered} T = Y^{(2\nu-1)/\Delta} \qquad D = Y^{(\gamma-2\nu)/\Delta} \qquad U = Y^{\nu/\Delta} \qquad K = \frac{\nu}{\alpha\bar{u}\Lambda}(Y^{-\alpha/\Delta} - 1) \\ 1-(1-\bar{u})Y = \bar{u}\frac{\Lambda}{\kappa}Y^{\nu/\Delta} \end{gathered} \tag{6.35}$$

The asymptotic critical limit and the classical limit are given by:

$$\lim_{\Lambda/\kappa\to\infty} Y = \left(\frac{\kappa}{\bar{u}\Lambda}\right)^{\Delta/\nu} \qquad \lim_{\Lambda/\kappa\to 1} Y = 1 \tag{6.36}$$

In the asymptotic critical limit the asymptotic behaviour of equation (6.15), including the correction-to-scaling contribution, is recovered and in the classical limit the classical Landau equation (6.30) is recovered [149, 151].

The physical features of the crossover behaviour can be showed more easily in other rescaled variables:

$$\hat{t} \equiv \hat{c}_t\Delta\tilde{T} = \frac{(1-\bar{u})^{1/\Delta}}{(\bar{u}\Lambda)^2}t \qquad \hat{M} \equiv \hat{c}_\rho(\Delta\tilde{\rho} - d_1\Delta\tilde{T}) = \frac{(1-\bar{u})^{\beta/\Delta}}{(\bar{u}\Lambda)^{1/2}}M \tag{6.37}$$

The crossover equation (6.33) for $\Delta\tilde{A}_r$ becomes:

$$\Delta\tilde{A}_{sr} = c_A\left\{\frac{1}{2}\hat{t}\hat{M}^2\hat{Y}^{\frac{(\gamma-1)}{\Delta}} + \frac{u^*}{4!}\hat{M}^4\hat{Y}^{\frac{(2\gamma-3\nu)}{\Delta}} - \frac{\nu}{2\alpha}\hat{t}^2\left(\hat{Y}^{\frac{-\alpha}{\Delta}} - 1\right) - \frac{\nu}{2\alpha}\hat{t}^2\left(1-(1-\bar{u})^{\frac{-\alpha}{\Delta}}\right)\right\} \tag{6.38}$$

The susceptibility and the specific heat can be derived from the renormalized Helmholtz free-energy density:

$$\tilde{\chi} = \hat{c}_\rho^{\,-2}\left(\frac{\partial^2\Delta\tilde{A}_{sr}}{\partial\hat{M}^2}\right)_{\hat{t}} \qquad \tilde{C}_V - \tilde{C}_0 = -\hat{c}_t^{\,2}\left(\frac{\partial^2\Delta\tilde{A}_{sr}}{\partial\hat{t}^2}\right)_{\hat{M}} \tag{6.39}$$

Asymptotically close to the critical temperature, relation (6.39) and the coefficients become:

$$\tilde{\chi} = \Gamma_0 \Delta\tilde{T}^{-\gamma}(1+\Gamma_1^{+}\Delta\tilde{T}^{\Delta}) \qquad \Delta\tilde{C}_V = \tilde{C}_V - \tilde{C}_0 = \alpha^{-1}A_0^{+}\Delta\tilde{T}^{-\alpha}(1+A_1^{+}\Delta\tilde{T}^{\Delta}) - B_{cr}$$

$$\Gamma_0 = \left(1+\frac{u^*\nu}{2}\right)^{-1} c_A^{-1}\hat{c}_\rho^{-2}\hat{c}_t^{-\gamma} \qquad \Gamma_1 = 2\left(\gamma-1+\frac{u^*\nu\Delta}{2+u^*\nu}\right)^{-1}\hat{c}_t^{\Delta}$$

$$A_0^{+} = \frac{\nu}{2}(2-\alpha)(1-\alpha)c_A\hat{c}_t^{2-\alpha} \qquad A_1^{+} = \frac{2\alpha(2-\alpha+\Delta)(1-\alpha+\Delta)}{(2-\alpha)(1-\alpha)}\hat{c}_t^{\Delta} \tag{6.40}$$

$$B_{cr} = \frac{\nu}{\alpha}c_A\hat{c}_t^{2}(1-\bar{u})^{-\alpha/\Delta} \qquad c_A = \frac{(\bar{u}\Lambda)^3}{(1-\bar{u})^{3\nu/\Delta}}$$

Now, the amplitude ratio R_{cr}^{+} becomes:

$$R_{cr}^{+} = R_0(1-\bar{u})^{\alpha/\Delta} \qquad R_0 = \frac{1}{2}(2-\alpha)(1-\alpha)\left(\frac{2\alpha(2-\alpha+\Delta)(1-\alpha+\Delta)}{(2-\alpha)(1-\alpha)}\right)^{\alpha/\Delta} \tag{6.41}$$

The value of R_0 is 0.704, to be compared with the value of 0.708 of Bagnuls and Bervillier [156]. The value of R_{cr}^{+} is not universal expect in the limit of infinite Λ_0. Sengers, Anisimov, and Tang refer to this model as the asymptotic crossover model of Chen *et al.* [151]. Results of this rescaled crossover model are that the leading correction to the classical limit varies again with the square root of the reduced temperature difference (6.12) and that the Ginzburg number is to be identified with [151]:

$$Gi = g_0\hat{c}_t^{-1} = g_0 c_t^{-1}\frac{(\bar{u}\Lambda)^2}{(1-\bar{u})^{1/\Delta}} \quad \text{with} \quad g_0 = \left(\frac{\gamma-1-\nu u^*/2}{\Delta}\right)^2 = 0.0314 \tag{6.42}$$

The ratio $\bar{\xi}_0/\xi_0$ has the same dependence on the Ginzburg number as (6.27) except for a different prefactor. This crossover solution contains four system-dependent constants, namely the crossover parameters $\bar{u}$ and Λ, and the critical amplitudes c_t and c_ρ. These constants have been determined for a number of fluids [143, 168, 153]. From equation (6.29) and (6.41) it is clear that $\bar{u}$ is to be compared with $3\sqrt{(2Gi)}/\Lambda_0\bar{\xi}_0 \approx 3\sqrt{(2Gi)}$, since $\Lambda_0\bar{\xi}_0$ is of the order of unity. For simple fluids $Gi \approx 0.02$, so that $3\sqrt{(2Gi)} \approx 0.6$, to be compared with $\bar{u} \approx 0.4$ for the same fluids (See Table 6.1). The amplitude of the two-scale-factor relation,

$$R_\xi = \xi_0\left(\frac{k_B T_c}{A_0^{+}p_c}\right)^{1/3} \tag{6.43}$$

is also given in table 6.1. According to the Ginzburg numbers in Table 6.1, it is concluded that the region of non-classical thermodynamic behaviour is very large.

Table 6.1: Ginzburg numbers of various fluids

Fluids	$\bar{u}$	Λ	c_t	c_ρ	Gi	ξ_0 (Å)
CO_2 [143]	0.3980	1.421	1.955	2.414	0.014	1.6
H_2O [143]	0.4973	1.414	2.371	2.084	0.025	1.3
C_2H_6 [143]	0.3691	1.122	1.556	2.500	0.009	1.9
R134a [168]	0.4497	2.316	2.716	2.274	0.040	1.9

According to the universal asymptotic crossover model of Belyakov and Kiselev, the ratio $\tilde{C}_V/B_{cr}$ for $M=0$ would be a universal function of the rescaled temperature $\Delta\tilde{T}/Gi$. It follows from (6.41) that this assumption is not true. However, an effective universal crossover function can be formulated by separating the fluctuation-induced background B_{cr} into two separate contributions:

$$B_{cr} = B_{cr}^{(0)} + B_{cr}^{(1)} \qquad \frac{A_0^+}{\alpha B_{cr}^{(0)}}(A_1^+)^{\alpha/\Delta} = R_0 \qquad \Delta\tilde{C}_V = \tilde{C}_V - \tilde{C}_0 + B_{cr}^{(1)} \quad (6.44)$$

Now, $\tilde{C}_V/B_{cr}^{(0)}$ will satisfy a universal crossover function. This procedure can be generalized to obtain an effective universal representation of the crossover behaviour of the Helmholtz free-energy density as a function of the rescaled temperature $\hat{t}$ and the rescaled order parameter $\hat{M}$. All system-dependent analytic terms are combined in the analytic background function $\tilde{A}_0(\tilde{T})$:

$$\Delta\hat{A}_r = \frac{1}{2}\hat{t}\hat{M}^2\hat{Y}^{\frac{(\gamma-1)}{\Delta}} + \frac{u^*}{4!}\hat{M}^4\hat{Y}^{\frac{(2\gamma-3\nu)}{\Delta}} - \frac{\nu}{\alpha}\hat{t}^2\left(\hat{Y}^{\frac{-\alpha}{\Delta}} - 1\right)$$
$$\hat{A}_0(\tilde{T}) = \tilde{A}_0(\tilde{T}) - c_A\frac{\nu}{2\alpha}\hat{t}^2\left(1-(1-\bar{u})^{\frac{-\alpha}{\Delta}}\right) \rightarrow \tilde{A}(\tilde{T},\tilde{\rho}) = c_A\Delta\hat{A}_r(\hat{t},\hat{M}) + \tilde{\rho}\tilde{\mu}_0(\tilde{T}) + \tilde{A}_0(\tilde{T}) \quad (6.45)$$

The associated rescaled susceptibility and singular part of the specific heat are defined by:

$$\hat{\chi} = \left(\frac{\partial^2\Delta\hat{A}_r}{\partial\hat{M}^2}\right)_{\hat{t}}^{-1} \qquad \Delta\hat{C}_V = -\left(\frac{\partial^2\Delta\hat{A}_r}{\partial\hat{t}^2}\right)_{\hat{M}} \quad (6.46)$$

The rescaled Helmholtz free-energy density contains no system-dependent parameters anymore and, hence, yields universal crossover behaviour as a function of $\hat{t}$ *and* $\hat{M}$. The parameter $\hat{c}_t$ (6.42) is inversely proportional to *Gi* and the parameter $\hat{t} = \hat{c}_t\Delta\tilde{T}$ is indeed proportional to $\Delta\tilde{T}/Gi$. Sengers calls equation (6.45) the *effective universal crossover solution* [151].

6.5 Non-asymptotic crossover behaviour

The crossover from asymptotic singular critical behaviour to asymptotic classical critical behaviour has been considered. However, we need the crossover from singular behaviour near the critical point to the actual non-asymptotic classical behaviour far away from the critical point. Chen introduced a solution to the non-asymptotic crossover problem by introducing a number of additional effects [143].

The correlation length, ξ, in the Landau-Ginzburg-Wilson theory refers to the correlation length associated with the critical fluctuations only. As a result, the classical limit is not reached when $\Lambda/\kappa \rightarrow 1$ (6.36) but when $\Lambda/\kappa \rightarrow 0$. This effect can be incorporated by replacing Λ/κ in equation (6.35) by $(1+\Lambda^2/\kappa^2)^{1/\omega_c}$ [160]. Instead of (6.35), Chen's crossover equation becomes [149]:

$$1-(1-\bar{u})Y = \bar{u}(1+\Lambda^2/\kappa^2)^{1/\omega_c}Y^{\nu/\Delta} \quad (6.47)$$

They exponent ω_c is a crossover exponent that equals 2 for the spherical model [160]. However, the exponent value should depend on the type of universality class. After this modification, the parameter Λ is the actual microscopic cutoff wavenumber Λ_0. The classical theory will not be valid unless one moves far away from the critical point where an asymptotic two-term classical expansion (6.30) will no longer be adequate. Chen extends the classical Landau expansion to a six-term classical expansion [143]:

$$\Delta\tilde{A}_{cl} = \frac{1}{2}tM^2 + \frac{u^*\bar{u}\Lambda}{4!}M^4 + \frac{1}{5!}a_{05}M^5 + \frac{1}{6!}a_{06}M^6 + \frac{1}{4!}a_{14}tM^4 + \frac{1}{2!2!}a_{22}t^2M^2 + ... \quad (6.48)$$

A term proportional to tM^3 does not appear in equation (6.48) because it can be eliminated by a transformation of variables [169]. The coefficients a_{ij} are system-dependent. Therefore, a disadvantage of this crossover model is that some experimental information is needed to obtain critical exponent values and critical amplitudes. The renormalization transformation from (6.30) to (6.33) can be generalized to include the higher-order terms in the Landau expansion. M^5 is to be replaced by [151]:

$$M^5 \rightarrow M^5D^{5/2}VU \qquad V = Y^{(2\Delta_a - \nu)/2\Delta} \quad (6.49)$$

The exponent Δ_a equals 1.323 and is an additional critical exponent associated with the leading term asymmetric in the order parameter [161, 63, 170, 171]. The renormalized Helmholtz free-energy density becomes [143]:

$$\begin{aligned}\Delta\tilde{A}_{sr} &= \frac{1}{2}tM^2TD + \frac{u^*\bar{u}\Lambda}{4!}M^4D^2U + \frac{1}{5!}a_{05}M^5D^{5/2}VU + \\ &\frac{1}{6!}a_{06}M^6D^3U^{3/2} + \frac{1}{4!}a_{14}tM^4TD^2U^{1/2} + \frac{1}{2!2!}a_{22}t^2M^2T^2DU^{-1/2} - \frac{1}{2}t^2K.....\end{aligned} \quad (6.50)$$

While the 3-dimensional Ising model and a magnetic system near the critical point are symmetric in the magnetization M, a fluid is not symmetric in the reduced density. Thus, equation (6.50) is valid for a hypothetical symmetric fluid with variables t_s and M_s. The term proportional to M^5 and the exponent Δ_a partially account for this lack of symmetry. The lack of symmetry in the order parameter leads to a mixing of the relevant scaling fields and can be accounted for by the following transformation [172, 161, 164, 143]:

$$\begin{aligned}&\Delta\tilde{A}(t,M) = \Delta\tilde{A}_{sr}(t_s,M_s) - c\left(\frac{\partial\Delta\tilde{A}_{sr}}{\partial M_s}\right)_{t_s}\left(\frac{\partial\Delta\tilde{A}_{sr}}{\partial t_s}\right)_{M_s} \\ &t = c_t\Delta\tilde{T} + c\left(\frac{\partial\Delta\tilde{A}_{sr}}{\partial M_s}\right)_{t_s} \qquad M = c_\rho(\Delta\tilde{\rho} - d_1\Delta\tilde{T}) + c\left(\frac{\partial\Delta\tilde{A}_{sr}}{\partial t_s}\right)_{M_s}\end{aligned} \quad (6.51)$$

The coefficients c and d_1 are system-dependent. The mixing term in equation (6.51) with the coefficient c yields an additional term proportional to $/\Delta T/^{1-\alpha}$ in the relation for the coexisting densities in equation (6.15), causing asymptotic singular behaviour of the coexistence curve diameter [173]. The term $d_1\Delta\tilde{T}$ yields the additional asymmetric term $\Delta T\phi^3$ in the Landau expansion (6.30). The total Helmholtz free-energy density is again given by:

$$\tilde{A} = \Delta\tilde{A} + \tilde{\rho}\tilde{\mu}_0(\tilde{T}) + \tilde{A}_0(\tilde{T}) \quad (6.52)$$

The analytic background functions are given by truncated Taylor expansions. The coefficients in the Taylor expansions are system-dependent. Except for the coefficients of the background of the chemical potential all the constants c_t, c_ρ, c, d_1, the crossover parameters $\bar{u}$ and Λ, the coefficients a_{ij} in the classical Landau expansion, and the constants of the Helmholtz free-energy background function can be determined from a fit to experimental p-ρ-T-data [143]. The coefficients of the background of the chemical potential (for $j \geq 2$) can be determined from a fit to caloric properties such as the velocity of sound or the specific heat [153].

This non-asymptotic crossover solution has been used to represent experimental thermodynamic-property data of a number of fluids in a large range of temperatures and densities around the critical point [143, 168, 153, 172, 174, 175]. All system-dependent coefficients for methane, ethane, CO_2, steam and R134a have been calculated. The range in which the crossover equation reproduces the experimental data to within experimental accuracy is given for CO_2 and R134a in [153].

A crucial test of any equation in the critical region of state is how well the equation represents properties that are related to second order derivatives of the equation of state such as the velocity of sound and the specific heat. The non-asymptotic crossover equation fits specific-heat (C_V) data of C_2H_6, velocity-of-sound data of CH_4 and R134a, and specific-heat (C_p) data of steam very well in a large range of temperatures and/or densities [153]. This range is almost the whole range where effects of critical fluctuations are significant.

A second non-asymptotic approach is given by Parola *et al.* [176-179]. They implement the RG procedure for a fluid of molecules that interact with a given interaction potential. Such a non-asymptotic solution has a number of limitations. It does not lead to explicit expressions for the equations of state and the theoretically correct exponent values are not recovered. Finally, it would seem difficult to extend the procedure to fluids of molecules whose interaction cannot be approximated by spherically symmetric potentials [149].

6.6 Phenomenological parametric crossover equation

To obtain an explicit representation of the asymptotic critical scaling-law behaviour of the thermodynamic properties one commonly uses parametric equations. See also Paragraph 3.3. Attempts to extend the range of the existing parametric equations have been made by extending them to include the leading correction-to-scaling terms and by revising the scaling fields to account for departures from vapour-liquid asymmetry. Balfour *et al.* introduced an extended and revised linear model [180]. Their model has been used to represent the thermodynamic properties of a number of fluids near the critical point [4]. Another extended and revised parametric equation has been used by Kiselev [181-183]. The practical advantage of a parametric crossover representation is that it simplifies the computation. The phenomenological parametric crossover function of Kiselev reads:

$$R(q) = 1 + \frac{q^2}{q_0 + q} \qquad q = gr \qquad \lim_{q\to 0} R(q) = 1 \qquad \lim_{q\to\infty} R(q) = q \tag{6.53}$$

The transformations for $\Delta\rho^*$ and ΔT^* are given by:

$$\Delta\rho^* - d_1\Delta T^* = kR^{-\beta+1/2}(q)r^{\beta}\theta \qquad \Delta T^* = r(1-b^2\theta^2) \tag{6.54}$$

The constant q_0 is universal and is taken to be 0.3 [145]. The relation between q and the parametric variable r is also given in equation (6.53). The coefficient g is a system-dependent constant that is inversely proportional to the Ginzburg number. Since q is proportional to r, the critical point corresponds to the limit $q \to 0$, while the classical limit corresponds to $q \to \infty$. For this phenomenological model, it follows that the amplitude ratio $A_1^+/\Gamma_1 = \alpha(\gamma+1)/\gamma(\gamma-1) \approx 0.83$, to be compared with the theoretical value $A_1^+/\Gamma_1 = 0.95 \pm 0.03$ [151]. In the classical limit, $q \to \infty$, the Helmholtz free-energy density has the form:

$$\Delta A_{cl}^* + \frac{1}{2}a_{20}\Delta T^{*2} = \frac{a_0}{2}\Delta T^* M^2 + \frac{u_0}{4!}M^4 + \frac{b_0}{3!}\Delta T^* M^3 + \frac{a_{21}}{2}\Delta T^{*2} M + \frac{a_{05}}{5!}M^5 \tag{6.55}$$

$$M = \Delta\rho^* - d_1\Delta T^*$$

The phenomenological parametric crossover model of Kiselev *et al.* does not recover terms in the Landau expansion beyond M^5. The confluent singularity with exponent Δ_a (6.49) is not incorporated in this model. Therefore, this model is actually an asymptotic crossover model with additional terms odd in M to account for vapour-liquid asymmetry [151].

6.7 Comparison between crossover solutions

The crossover solution of Belyakov and Kiselev up to first order of an expansion in $\varepsilon=4-d$, gerenalized to $\varepsilon=1$, yielded a universal asymptotic crossover solution (6.28) for the susceptibility and the specific heat for $M=0$. Another solution has been obtained by Bagnuls and Bervillier on the basis of a field-theoretical approach applicable to $d=3$ [156]. Both asymptotic crossover solutions depend on the two system-dependent parameters Λ and $Gi(\bar{u})$. In the phenomenological extension of the ε-expansion by Belyakov and Kiselev a universal representation is obtained by a simple rescaling of the variables. The solution of Bagnuls and Bervillier shows similar crossover behaviour. Unfortunately, both solutions correspond to the limit $\Lambda\rightarrow\infty$, in which system-dependent cutoff effects are neglected and which is an unphysical limit to deal with the crossover behaviour. However, an effective universal crossover behaviour can be obtained by a match-point procedure and a simple rescaling of the variables. Anisimov *et al.* compared the three crossover solutions by plotting the rescaled susceptibility and the rescaled specific heat as a function of the rescaled temperature [151]:

$$\chi^* a_0 \mathrm{Gi} = c_\chi \hat{\chi} = f\left(\frac{\Delta T^*}{\mathrm{Gi}}, M=0\right) \qquad \frac{\Delta C_V}{B_{cr}^{(0)}} = f\left(\frac{\Delta T^*}{\mathrm{Gi}}, M=0\right) \qquad (6.56)$$

The asymptotic crossover behaviour implies that the susceptibility asymptotically close to the critical temperature will diverge according to a power law with the critical exponent $\gamma=1.239$, while for large values of ΔT^* it will vary according to a power law with the classical critical exponent $\gamma=1$. Similarly, the specific heat crosses over from a power-law with critical exponent $\alpha=0.110$ for small values of ΔT^* to a non-diverging specific heat with $\alpha=0$ for large values of ΔT^*. One can define effective exponents γ_{eff} and α_{eff} as follows:

$$\gamma_{\mathrm{eff}} \equiv -\Delta T^* \left(\frac{d\ln\chi}{d\Delta T^*}\right)_{M=0} \qquad \alpha_{\mathrm{eff}} \equiv \Delta T^* \left(\frac{d\ln(\Delta C_V)}{d\Delta T^*}\right)_{M=0} \qquad (6.57)$$

Plots of these effective exponents versus $\Delta T^*/Gi$ show that all three asymptotic solutions show similar crossover behaviour for the susceptibility and the specific heat, notwithstanding the unphysical limit of the models of Bagnuls and Bervillier and of Belyakov and Kiselev [151]. In principle negligence of cutoff effects yields a good approximation [151].

The asymptotic (match-point procedure) and the non-asymptotic crossover solution can be compared by plotting the rescaled susceptibility and the rescaled specific heat as a function of the rescaled temperature for $\hat{M}=0$:

$$\hat{\chi} = f(\hat{t}, \hat{M}=0) \qquad \Delta\hat{C}_V = f(\hat{t}, \hat{M}=0) \qquad (6.58)$$

The system-dependent coefficients are taken for ethane. The actual (non-asymptotic) crossover behaviour deviates from the simple asymptotic universal crossover behaviour, however, the simple universal asymptotic crossover behaviour seems to be a good approximation [151].

The crossover behaviour of the effective exponents in the phenomenological crossover model deviates substantially from the crossover behaviour expected on the basis of theoretical crossover solutions. The classical exponent values $\alpha=0$ and $\gamma=1$ are not approached monotonically. The latter behaviour has been observed in ionic fluids and in polymer blends [184, 185]. This phenomenological model is able to represent actual thermodynamic-property data in a large temperature and density range [145]. Attempts to improve this phenomenological crossover model are in progress [151].

An asymptotic crossover solution representing crossover from asymptotic non-analytic critical behaviour to classical critical behaviour presupposes that the Ginzburg number is sufficiently small, so that there does exist a temperature range where asymptotic classical behaviour can be observed. This may be the case for certain micellar systems [186], for binary polymer blends [187, 188, 189], and for nonaqueous ionic liquids [190-193]. For fluids with short-range forces the range of fluctuation-induced non-classical behaviour is so large that asymptotic classical behaviour is never observed. This more general problem can be dealt with by the non-asymptotic crossover solution. The asymptotic crossover solution serves as a good approximation [151].

6.8 Corrected Van der Waals-like equations of state

A crossover equation for the Helmholtz free-energy density based on a transformed Landau expansion yields a good representation of the thermodynamic properties of supercritical fluids in a large range of temperatures and densities. However, the large number of system-dependent adjustable coefficients, namely the scaling-field constants c_t, c_ρ, c, d_1, the crossover parameters $\bar{u}$ and Λ, the coefficients a_{ij} in the classical Landau expansion and the coefficients in the background functions often force chemical engineers to use simple closed-form equations of state that are generalizations of the Van der Waals equation of state. Such closed-form equations of state can also be corrected for the effects of critical fluctuations by a transformation similar to the ones of equation (6.32) if one enters some modifications to account for the difference between the classical critical temperature without fluctuations and the actually observed critical temperature [172]. A resulting global equation of state should explicitly demonstrate how fluctuations change the classical behaviour and the classical equation of state. Such a transformation has been applied to the Carnahan-Starling-DeSantis (CSD) equation of state [194, 195]. The CSD equation of state in terms of reduced variables reads [195]:

$$\tilde{p}=\frac{1}{Z_0}\tilde{\rho}\left[\frac{64+16\tilde{b}\tilde{\rho}+4\tilde{b}^2\tilde{\rho}^2-\tilde{b}^3\tilde{\rho}^3}{(4-\tilde{b}\tilde{\rho})^3}-\frac{\tilde{a}\tilde{b}\tilde{\rho}}{1+\tilde{b}\tilde{\rho}}\right]\quad \tilde{b}=\frac{\tilde{b}_0}{(1-\Delta\tilde{T}_{cl})^2}\left(1+\tilde{b}_1\Delta\tilde{T}_{cl}+\tilde{b}_2\Delta\tilde{T}_{cl}{}^2\right)$$

$$\tilde{a}=\frac{\tilde{a}_0}{\tilde{b}}(1-\Delta\tilde{T}_{cl})\exp\left\{\frac{1}{(1-\Delta\tilde{T}_{cl})^2}\left(\tilde{a}_1\Delta\tilde{T}_{cl}+\tilde{a}_2\Delta\tilde{T}_{cl}{}^2\right)\right\}\qquad \tilde{\rho}=\frac{\rho}{\rho_0}\qquad \tilde{p}=\frac{pT_0}{p_0T}\qquad \Delta\tilde{T}_{cl}=-\frac{T_0}{T} \tag{6.58}$$

Z_0 is the critical compressibility factor. p_0, ρ_0 and T_0 are the real (actual) critical parameters. The variable $\Delta\tilde{T}_{cl}$ is defined as $(T-T_c^{cl})/T$, where T_c^{cl} is the classical critical temperature. The parameters with indices 0, 1 and 2 also depend on the *classical* critical temperature:

$$\tilde{a}_0 = \frac{a_0\rho_c}{RT_c^{cl}}\exp(a_1T_c^{cl} + a_2T_c^{cl^2}) \qquad \tilde{a}_1 = a_1T_c^{cl} + 2a_2T_c^{cl^2}$$

$$\tilde{a}_2 = -a_1T_c^{cl} - a_2T_c^{cl^2} \qquad \tilde{b}_0 = \rho_c(b_0 + b_1T_c^{cl} + b_2T_c^{cl^2}) \tag{6.59}$$

$$\tilde{b}_1 = \frac{2b_0 + b_1T_c^{cl}}{b_0 + b_1T_c^{cl} + b_2T_c^{cl^2}} \qquad \tilde{b}_2 = \frac{b_0}{b_0 + b_1T_c^{cl} + b_2T_c^{cl^2}}$$

The reduced Helmholtz free-energy density can be calculated by integration of the CSD equation. The renormalized singular part of the Helmholtz free-energy density is calculated via the procedure of Chen *et al.* [143]. This renormalization theory consists of the following transformations [172, 174]:

$$\Delta\tilde{T} = \frac{T - T_c}{T} \qquad \Delta\tilde{T}_{sh} = \frac{T_c - T_c^{cl}}{T_c} \qquad \Delta\tilde{\rho} = \frac{\rho - \rho_c^{cl}}{\rho_c^{cl}} \qquad \Delta\tilde{\rho}_r = \Delta\tilde{\rho}Y^{\nu(1-2\eta)/4\Delta}$$

$$\Delta\tilde{T}_r = \Delta\tilde{T}Y^{(3\nu/2-1)/\Delta} + (1-\Delta\tilde{T})\Delta\tilde{T}_{sh}G \qquad \Delta\tilde{A} = \Delta\tilde{A}_{cl}(\Delta\tilde{\rho} = \Delta\tilde{\rho}_r, \Delta\tilde{T} = \Delta\tilde{T}_r) - \frac{1}{2}\Delta\tilde{T}^2K \tag{6.60}$$

The crossover function and the function G are given below:

$$1-(1-\bar{u})Y = \bar{u}\left[1 + X^{\omega_c}\exp(-c_1/X)\right]^{1/\omega_c}Y^{\nu/\Delta} \qquad X = \frac{\Lambda}{\kappa} \qquad G = \left[\frac{\lambda}{1-(1-\lambda)Y}\right]Y^{2\nu/\Delta} \tag{6.61}$$

Van Pelt *et al.* applied their crossover equation of state to experimental data of certain thermodynamic properties of R134a. They treated $\tilde{u}$ and Λ as system-dependent adjustable constants. The constant λ is taken to be 0.02. The classical coexistence curve and the crossover coexistence curve are plotted into one graphic. It is seen that the crossover equation describes the experimental data much better. The critical temperature is suppressed from its classical value by more than 10 K. The renormalized CSD equation yields a dramatic improvement in the description of the isobaric heat capacity [195].

Kostrowicka Wyczalkowska *et al.* developed a global crossover equation of state for a Van-der-Waals fluid [196]. They show how the classical critical point shifts to its actual position. The 'classical' critical-point parameters according to the Van der Waals equation of state are given by:

$$T_c^{cl} = \frac{8a}{27bR} \qquad \rho_c^{cl} = \frac{1}{3b} \qquad p_c^{cl} = \frac{a}{27b^2} \tag{6.62}$$

In terms of the reduced variables the Van der Waals equation reads:

$$\tilde{p} = \frac{8(\Delta\tilde{\rho}+1)}{2-\Delta\tilde{\rho}} + 3(\Delta\tilde{T}-1)(\Delta\tilde{\rho}+1) \tag{6.63}$$

The analytic background terms of the Helmholtz free-energy density are not given by truncated Taylor expansions but by other terms that result in specific properties of the Van der Waals equation of state in the classical limit. The singular part of the Helmholtz free-energy density is given by:

$$\Delta\tilde{A} = \frac{8}{3}(\Delta\tilde{\rho}+1)\log\left|\frac{\Delta\tilde{\rho}+1}{1-\Delta\tilde{\rho}/2}\right| - 4\Delta\tilde{\rho} + 3(\Delta\tilde{T}-1)\Delta\tilde{\rho}^2 \tag{6.64}$$

Near the critical point the Helmholtz free-energy density can be expanded into a Landau expansion in rescaled variables (6.37 without asymmetry term d_1):

$$\Delta\tilde{A} = \frac{1}{2}tM^2 + \frac{a_{04}}{4!}M^4 + \frac{a_{05}}{5!}M^5 + \frac{a_{06}}{6!}M^6 + \frac{a_{14}}{4!}tM^4 + \frac{a_{22}}{2!2!}t^2M^2 + \ldots..$$
$$c_t c_\rho = 6 \qquad a_{04} = \frac{9}{c_\rho{}^4} \qquad a_{05} = -\frac{9}{c_\rho{}^5} \qquad a_{06} = \frac{81}{c_\rho{}^6} \qquad a_{14} = a_{22} = 0 \tag{6.65}$$

The influence of the fluctuations changes the expansion (6.65):

$$\Delta\tilde{A} = a_0\Delta\tilde{T}(r)\Delta\tilde{\rho}^2(r) + u_0\Delta\tilde{\rho}^4(r) + \frac{c_0}{2}(\nabla(\Delta\tilde{\rho}(r))^2 + \ldots.. =$$
$$\frac{1}{2}t(r)M^2(r) + \frac{a_{04}}{4!}M^4(r) + \frac{1}{2}\left(\tilde{\nabla}M(r)\right)^2 + \ldots.. \tag{6.66}$$

After renormalization, the Helmholtz free-energy density of the Van der Waals fluid reads:

$$\Delta\tilde{A}_r = \frac{8}{3}(Rd+1)\log\left|\frac{\Delta Rd+1}{1-Rd/2}\right| - 4Rd + 3(tTU^{-1/2} - 1)R^2d^2 +$$
$$\frac{3}{40}R^5d^5 - \frac{3}{40}U^{-1/4}VR^5d^5 - \frac{1}{2}c_t{}^2t^2K \tag{6.67}$$

The rescaling functions and the crossover function have been defined in equation (6.35) and (6.49). The definition of t is $1\text{-}T_c/T$, where T_c is the actual critical temperature. The definition of d is $1\text{-}\rho_c/\rho$, where ρ_c is the actual critical density. The rescaling function R is a combination of other rescaling functions:

$$R = D^{1/2}U^{1/4} \tag{6.68}$$

One of the important consequences of the Van der Waals equation of state and the other mean-field equations is that the actual critical parameters T_c, ρ_c, and p_c differ from the classical critical parameters T_c^{cl}, ρ_c^{cl}, and p_c^{cl}. The critical-temperature shift is given by:

$$\frac{T_c - T_c{}^{cl}}{T_c{}^{cl}} = -c_t{}^{-1}f(\bar{u})\frac{u^*\bar{u}\Lambda^2}{2} \qquad f(\bar{u}) = \frac{1}{u^*\left[(1-\bar{u})\omega + \bar{u}\right]}\left(2 - \frac{1}{\nu} - \eta\right) \tag{6.69}$$

This result is in good agreement with the value in first-order perturbation predicted by the renormalization-group theory [197]. The shift in the critical density is given by:

$$\frac{\rho_c - \rho_c{}^{cl}}{\rho_c{}^{cl}} = \frac{c_t}{54} \tag{6.70}$$

The shift in the critical pressure can be estimated by assuming that the actual critical point is located on the classical vapour-pressure curve [197].

In the analysis of the crossover behaviour, the parameters Λ and c_t can not be calculated. Kostrowicka Wyczalkowska *et al.* take the dimensionless Λ to be unity, *i.e.* the cutoff corresponds to the average distance between molecules at the critical density. In most calculations they choose $c_t=1$, *i.e.* the range of the intermolecular interactions equals the average one. If the classical coexistence curve and the coexistence curve of the crossover Van der Waals equation of state are plotted we see that the critical fluctuations suppress the critical temperature from its mean-field value and that they flatten the top of the coexistence curve. Far away from the critical point the classical Van der Waals equation of state is recovered. The rescaled classical inverse susceptibility diverges with an exponent $\gamma=1$ at the classical critical temperature. After the transformation the inverse susceptibility diverges with the non-classical exponent $\gamma=1.24$ at the shifted critical temperature. It is also seen that the critical fluctuations change the classical jump of the isochoric heat capacity at the classical critical temperature to singular divergent behaviour at the shifted critical temperature. A striking phenomenon is that the crossover from Ising to mean-field values of γ_{eff} for small values of c_t is gradual and monotonic. For large values of c_t the crossover becomes sharp and nonmonotonic. The latter behaviour has been observed in ionic fluids and in polymer blends [184, 185].

Chapter 7: Critical scaling laws and a Excess Gibbs model

Some commonly used Excess Gibbs energy models that are used to describe liquid-liquid equilibria in fluids are the regular solution model, the Wilson model, the Non-Random Two-Liquid (NRTL) model, and UNIQUAC [198]. These models are typical mean-field models, which fail to account for the effects of long-range concentration fluctuations in the vicinity of the consolute critical point. In an attempt to describe both the critical region and the region far away from the critical point, various modifications of classical equations have been proposed. De Pablo and Prausnitz obtained a good representation of liquid-liquid equilibria by using a phenomenological correction to classical equations [199]. They accounted for non-classical behaviour by implementing a transformation proposed by Fox [200]. However, the transformation of Fox fails to reproduce the correct universal amplitude ratios asymptotically close to the critical point [167].
Based on the Landau-Ginzburg-Wilson theory of fluctuations, Edison *et al.* developed a crossover procedure to incorporate the effects of critical fluctutations into a classical Excess Gibbs energy model. The crossover procedure has been applied to the NRTL Excess Gibbs energy model. This procedure is given here.

The molar Gibbs free energy for a binary liquid mixture is given by:

$$dG = -SdT + Vdp + \mu_2 dx_2 + \mu_1 dx_1 \qquad (7.1)$$

G, *S*, and *V* are molar properties. At constant pressure, equation (7.1) reads:

$$dG = -SdT + \mu_{21} dx_2 \qquad \mu_{21} = \mu_2 - \mu_1 \qquad (7.2)$$

Near the consolute point of a binary liquid mixture, the difference in the concentration of either component in the two coexisting phases is the order parameter. This concentration difference at constant pressure asymptotically behaves as [201]:

$$x_i' - x_i = 2B|\Delta T^*|^{\beta} \qquad (7.3)$$

The reduced molar Gibbs free energy of mixing is given by:

$$\frac{\Delta G}{RT} = x_1 \ln(x_1) + x_2 \ln(x_2) + \frac{G^E}{RT} \qquad (7.4)$$

The reduced Gibbs-Excess energy at constant *p*, defined by the NRTL equation, is given by [Renon 1968]:

$$\frac{G^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right] \qquad \tau_{21} = \frac{u_{21} - u_{11}}{RT} \qquad \tau_{12} = \frac{u_{12} - u_{22}}{RT} \qquad (7.5)$$

$$G_{21} = \exp(-\alpha_{12} \tau_{21}) \qquad G_{12} = \exp(-\alpha_{12} \tau_{12})$$

The energy parameter u_{ij} is a temperature-dependent interaction parameter. The parameter α_{12} is related to the non-randomness of the molecular distribution. Thus, the NRTL equation has 3 parameters τ_{12}, τ_{21}, and α_{12}. However, α_{12} is generally fixed at a value between 0.2 and 0.470 [203].
The NRTL parameters can be rewritten in reduced variables. The reduced variables and the NRTL parameters are given in equation (7.6):

$$\Delta\tilde{T} = \frac{T - T_c}{T} \qquad \Delta\tilde{x} = \frac{x - x_c}{x_c} \qquad \tilde{G} = \frac{G}{RT} \qquad \tilde{\mu}_{21} = \frac{\mu_{21}}{RT} \tag{7.6}$$

$$\tau_{21} = \tilde{a}(1 - \tilde{b}\Delta\tilde{T}) \qquad \tau_{12} = \tilde{c}(1 - \tilde{d}\Delta\tilde{T})$$

The number of parameters can be reduced by two by applying the conditions of inciepient immiscibility $(\partial^2\Delta G/\partial x^2)|_{xc}=(\partial^3\Delta G/\partial x^3)|_{xc}=0$. The parameters $\tilde{a}$ and $\tilde{c}$ equal 1.3474 and 0.94366 [202].

The classical Gibbs energy of mixing is separated into a regular and a singular part:

$$\Delta\tilde{G}_{cl}(\tilde{T},\tilde{x}) = \Delta\tilde{G}_{reg}(\tilde{T},\tilde{x}) + \Delta\tilde{G}_{sing}(\tilde{T},\tilde{x}) \tag{7.7}$$

The singular part is given by the terms of second and higher order in the Taylor series expansion:

$$\begin{aligned}
\Delta\tilde{G}_{sing} &= x\ln\left(\frac{x}{1-x}\right) + \ln\left(\frac{1-x}{1-x_c}\right) - x\ln\left(\frac{x_c}{1-x_c}\right) + \\
& x(1-x)\left[\frac{\tau_{21}G_{21}}{x+(1-x)G_{21}} + \frac{\tau_{12}G_{12}}{xG_{12}+(1-x)}\right] - \\
& (x_c^{\,2} + x - 2xx_c)\left[\frac{\tau_{21}G_{21}}{x_c+(1-x_c)G_{21}} + \frac{\tau_{12}G_{12}}{x_cG_{12}+(1-x_c)}\right] - \\
& (x - x_c)x_c(1-x_c)\left[\frac{\tau_{21}G_{21}(1-G_{21})}{\{x_c+(1-x_c)G_{21}\}^2} + \frac{\tau_{12}G_{12}(G_{12}-1)}{\{x_cG_{12}+(1-x_c)\}^2}\right]
\end{aligned} \tag{7.8}$$

$$\begin{aligned}
\Delta\tilde{G}_{reg} &= x\ln\left(\frac{x_c}{1-x_c}\right) + \ln(1-x_c) + \\
& (x_c^{\,2} + x - 2xx_c)\left[\frac{\tau_{21}G_{21}}{x_c+(1-x_c)G_{21}} + \frac{\tau_{12}G_{12}}{x_cG_{12}+(1-x_c)}\right] + \\
& (x - x_c)x_c(1-x_c)\left[\frac{\tau_{21}G_{21}(1-G_{21})}{\{x_c+(1-x_c)G_{21}\}^2} + \frac{\tau_{12}G_{12}(G_{12}-1)}{\{x_cG_{12}+(1-x_c)\}^2}\right]
\end{aligned}$$

Edison *et al.* use the transformation developed by Chen *et al.* to take into account the effects of critical fluctuations [203]:

$$\Delta\tilde{G}_r = \Delta\tilde{G}_{sing}(\Delta\tilde{T}_r, \Delta\tilde{x}_r) - \frac{1}{2}\Delta\tilde{T}^2K \qquad \Delta\tilde{T}_r = \Delta\tilde{T}TU^{-1/2} \qquad \Delta\tilde{x}_r = \Delta\tilde{x}D^{1/2}U^{1/4} \tag{7.8}$$

The rescaling functions *T*, *D*, *U*, *K*, and the crossover function are defined in equation (6.35). Edison *et al.* applied the renormalized NRTL equation to the near-critical region of the binary liquid *n*-heptane+acetic anhydride and the near-critical region of the binary liquid nitroethane+cyclohexane. They plotted the experimental data, the classical equation, and the renormalized equation into one figure. The improvement of the renormalized equation with respect to the classical equation is appreciable.

The renormalized NRTL equation can also be used to represent caloric properties like the molar isobaric heat capacity. To calculate these properties, a caloric background contribution must be added to the regular part of the Gibbs free energy of mixing. The classical NRTL equation predict a jump in C_{px} at the critical point. The renormalized equation shows a weak divergence in accordance with $C_{px}=A|\Delta T^{*}|^{-\alpha}$ for the binary liquid nitroethane+cyclohexane near the consolute critical point [203].

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Tables

Table 1.2: Taylor expansions for the three-point contact

Pressure	$p^* - p_{00} = \frac{1}{6} p_{30} (\Delta\rho^*)^3 + ...$	Critical isotherm $(\Delta T^*=0)$
Chemical potential	$\mu^* - \mu_{00} = \frac{1}{6} p_{30} (\Delta\rho^*)^3 + ...$	Critical isotherm $(\Delta T^*=0)$
Compressibility	$K_T{}^{*-1} = \left(\frac{\partial p^*}{\partial \rho^*}\right)_T = p_{11}\Delta T^* + \frac{1}{2} p_{12} (\Delta T^*)^2 + ...$	Critical ioschore $(\Delta\rho^*=0, \Delta T^*>0)$
Heat capacity $(C_V{}^*)$	$\frac{C_V{}^*}{T^*} = -\left(\frac{\partial^2 A^*}{\partial T^{*2}}\right)_\rho = -(A_{02} + A_{03}\Delta T^* + ...)$	Critical isochore $(\Delta\rho^*=0, \Delta T^*>0)$

Table 1.3: Comparison of gas and liquid-side coefficients

Term	Result	With use of
$\lvert\Delta T^*\rvert^{3/2}$	$B_{1L}{}^2 + B_{1L}B_{1G} + B_{1G}{}^2 = \frac{6p_{11}}{p_{30}}$	
$\lvert\Delta T^*\rvert^2$	$(B_{1L}{}^2 - B_{1G}{}^2)\left(B_{1L}{}^2 + B_{1G}{}^2 - \frac{4p_{11}}{p_{30}}\right) = 0$	$p_{40}-\mu_{40}=3p_{30}$ $p_{21}-\mu_{21}=p_{11}$
$\lvert\Delta T^*\rvert^{5/2}$	$B_2 = \frac{p_{21}}{p_{30}} - \frac{3p_{11}p_{40}}{5p_{30}{}^2} + \frac{4p_{11}}{5p_{30}} = \frac{\mu_{21}}{\mu_{30}} - \frac{3\mu_{11}\mu_{40}}{5\mu_{30}{}^2}$	$B_{1L}=-B_{1G}=B$ $B_{2L}=B_{2G}$ $\mu_{30}=p_{30}$, $\mu_{11}=p_{11}$

Table 1.4

Property	Relation	Results
Compressibility along coexistence curve, one-phase region	$\left(\frac{\partial \mu^*}{\partial \rho^*}\right)_T = (\mu_{11} - \frac{1}{2}\mu_{30}B^2)\lvert\Delta T^*\rvert + .. = 2p_{11}\lvert\Delta T^*\rvert + ..$	$\gamma'=1$ $\Gamma'=1/(2p_{11})$ $\gamma'=\gamma$
Specific heat along coexistence curve, one-phase region	$\frac{C_{VCoex}{}^*}{T^*} = -\left(A_{02} \pm A_{12}B\lvert\Delta T^*\rvert^{1/2} + \left(\frac{1}{2}A_{22}B^2 - A_{03}\right)\lvert\Delta T^*)\rvert + ..\right)$	$\alpha'=0$
Pressure in the two-phase region	$p_{II}{}^* = p_{00} + p_{01}\Delta T^* +$ $\frac{1}{2}\left(p_{02} + \frac{p_{11}}{p_{30}{}^2}\left\{\frac{3}{5}p_{11}p_{40} - 2p_{21}p_{30} + \frac{16}{5}p_{11}p_{30}\right\}\right)(\Delta T^*)^2 + ...$	

Table 1.4

Chemical potential in the two-phase region	$\mu_{ll}^* = \mu_{00} + \mu_{01}\Delta T^* + \frac{1}{2}\left(\mu_{02} + \frac{\mu_{11}}{\mu_{30}^2}\left\{\frac{3}{5}\mu_{11}\mu_{40} - 2\mu_{21}\mu_{30}\right\}\right)(\Delta T^*)^2 + \ldots$	

Table 3.1: Generalized homogeneous functions

Property	Rusults from	Function
Chemical potential	$\Delta\mu^* = \left(\frac{\partial A_{sing}^*}{\partial \Delta\rho^*}\right)_T$	$\Delta\mu^*(\lambda^{a_\rho/(1-a_\rho)}\Delta\rho^*, \lambda^{a_T/(1-a_\rho)}\Delta T^*) = \lambda\Delta\mu^*(\Delta T^*, \Delta\rho^*)$
Compress-ibility	$\chi_T^{-1} \equiv (\rho^{*2} K_T^*)^{-1} = \left(\frac{\partial \Delta\mu^*}{\partial \Delta\rho^*}\right)_T$	$\chi^*{}_T^{-1}(\lambda^{a_\rho/(1-2a_\rho)}\Delta\rho^*, \lambda^{a_T/(1-2a_\rho)}\Delta T^*) = \lambda\chi^*{}_T^{-1}(\Delta T^*, \Delta\rho^*)$
Anomalous entropy	$S_{sing}^* = -\left(\frac{\partial A_{sing}^*}{\partial \Delta T^*}\right)_\rho$	$S_{sing}^*(\lambda^{a_\rho/(1-a_T)}\Delta\rho^*, \lambda^{a_T/(1-a_\rho)}\Delta T^*) = \lambda S_{sing}^*(\Delta T^*, \Delta\rho^*)$
Anomalous heat capacity	$\frac{C_{Vsing}^*}{T^*} = -\left(\frac{\partial^2 A_{sing}^*}{\partial \Delta T^{*2}}\right)_\rho$	$\frac{C_{Vsing}^*}{T^*}(\lambda^{a_\rho/(1-2a_T)}\Delta\rho^*, \lambda^{a_T/(1-2a_\rho)}\Delta T^*) = \frac{C_{Vsing}}{T^*}^*(\Delta T^*, \Delta\rho^*)$

Table 3.2: Scaled expressions

Property along a path	Scaled functions	Exponent relation
Chemical potential along critical isotherm: $\Delta T^*=0$	$\Delta\mu^*(0,\Delta\rho^*) = \mathrm{sign}(\Delta\rho^*)\Delta\mu^*(0,1)\,\lvert\Delta\rho^*\rvert^{\frac{1-a_\rho}{a_\rho}}$	$\delta=(1-a_\rho)/a_\rho$
Compressibility along critical isochore: $\Delta\rho^*=0$, $\Delta T^*\geq 0$	$\chi_T{}^{*-1}(\Delta T^*,0) = \chi_T{}^{*-1}(1,0)\,\lvert\Delta T^*\rvert^{\frac{1-2a_\rho}{a_T}}$	$\gamma=(1-2a_\rho)/a_T$
Singular heat capacity along critical isochore: $\Delta\rho^*=0$, $\Delta T^*\geq 0$	$\frac{C_{Vsing}^*}{T^*}(\Delta T^*,0) = \frac{C_{Vsing}^*}{T^*}(1,0)\,\lvert\Delta T^*\rvert^{\frac{1-2a_T}{a_T}}$	$\alpha=(2a_T-1)/a_T$
Chemical potential along coexistence curve: $\Delta\mu^*=0$, $\Delta T^*\leq 0$, $\Delta\rho^*\neq 0$	$\Delta\mu^*(-1, \lvert\Delta T^*\rvert^{-\frac{a_\rho}{a_T}}\Delta\rho^*) = 0$	$\beta=a_\rho/a_T$ (a)
Compressibility along coexistence curve: $\Delta\mu^*=0$, $\Delta T^*\leq 0$, $\Delta\rho^*\neq 0$	$\chi_T^{-1}(\Delta T^*, \Delta\rho_{coex}^*) = \chi^{-1}(-1,B)\,\lvert\Delta T^*\rvert^{\frac{1-2a_\rho}{a_T}}$	$\gamma'=\gamma=$ $(1-2a_\rho)/a_T$ (a)

Table 3.2: Scaled expressions

Singular heat capacity along coexistence curve: $\Delta\mu^*=0$, $\Delta T^*\leq 0$, $\Delta\rho^*\neq 0$	$\frac{C_{V_{sing}}{}^*}{T^*}(\Delta T^*, \Delta\rho_{Coex}{}^*) = \frac{C_{V_{sing}}{}^*}{T^*}(-1,B)\,\lvert\Delta T^*\rvert^{\frac{1-2a_T}{a_T}}$	$\alpha'=\alpha=$ $(2a_T-1)/a_T$ (a)
Singular Helmholtz free-energy density, two-phase region: $\Delta\mu^*=0$	$A_{sing}{}^* = A_{sing}{}^*(\Delta T^*, \Delta\rho_{Coex}{}^*) = A_{sing}{}^*(-1,B)\lvert\Delta T^*\rvert^{\frac{1}{a_T}}$	(b)
Singular heat capacity, two-phase region: $\Delta\mu^*=0$	$\left(\frac{C_{V_{sing}}{}^*}{T^*}\right) = A_{sing}{}^*(-1,B)\frac{1}{a_T}\left(\frac{1}{a_T}-1\right)\lvert\Delta T^*\rvert^{\frac{1-2a_T}{a_T}}$	$\alpha''=\alpha'=\alpha=$ $(2a_T-1)/a_T$

1. The result of the scaling law of the chemical potential along the coexistence curve is: $\lvert\Delta T^*\rvert^{-Cp/CT}\Delta\rho^*=\pm B$, which results in the known power law $\Delta\rho^*=\pm B\ \lvert\Delta T^*\rvert^{-\beta}$.
2. $\Delta\mu^*=0$ in the two phase region. According to the definition of $\Delta\mu^*$, the singular part of the Helmholtz free-energy density is independent of the density and equal to the value along the coexistence curve at the same temperature.

Table 3.3: Scaled expressions for thermodynamic functions

Property	Scaled power laws
Chemical potential, one-phase region	$\mu^* = \mu^*(\rho_c, T^*) + \Delta\rho^*\,\lvert\Delta\rho^*\rvert^{\delta-1}\,Dh\left(\frac{x}{x_0}\right)$
Chemical potential, two-phase region	$\Delta\mu^* = 0$
Helmholtz free-energy density, one-phase region	$A^* = A_0{}^*(T^*) + \rho^*\mu^*(\rho_c, T^*) + \lvert\Delta\rho^*\rvert^{\delta+1}Da\left(\frac{x}{x_0}\right)$
Helmholtz free-energy density, two-phase region	$A^* = A_0{}^*(T^*) + \rho^*\mu^*(\rho_c, T^*) + \lvert\Delta T^*\rvert^{2-\alpha}x_0{}^{\alpha-2}Da(-1)$
Compressibility	$(\rho^{*2}K_T{}^*)^{-1} = \lvert\Delta\rho^*\rvert^{\delta-1}D\left\{\delta h\left(\frac{x}{x_0}\right) - \frac{x}{\beta x_0}h'\left(\frac{x}{x_0}\right)\right\}$
Pressure, one-phase region	$p^* = -A_0{}^*(T^*) + D\left(\Delta\rho^*\lvert\Delta\rho^*\rvert^{\delta-1}h\left(\frac{x}{x_0}\right) + \lvert\Delta\rho^*\rvert^{\delta+1}\left\{h\left(\frac{x}{x_0}\right) - a\left(\frac{x}{x_0}\right)\right\}\right)$
Pressure, two-phase region	$p^* = -A_0{}^*(T^*) - \lvert\Delta T^*\rvert^{2-\alpha}x_0{}^{\alpha-2}Da(-1)$
Entropy, one-phase region	$-S^* = \frac{dA_0{}^*(T^*)}{dT^*} + \rho^*\frac{d\mu^*(\rho_c, T^*)}{dT^*} + \lvert\Delta\rho^*\rvert^{\frac{1-\alpha}{\beta}}x_0{}^{-1}Da'\left(\frac{x}{x_0}\right)$
Entropy, two-phase region	$-S^* = \frac{dA_0{}^*(T^*)}{dT^*} + \rho^*\frac{d\mu^*(\rho_c, T^*)}{dT^*} - (2-\alpha)\lvert\Delta T^*\rvert^{1-\alpha}x_0{}^{\alpha-2}Da(-1)$
Heat capacity, one-phase region	$-\frac{C_V{}^*}{T^*} = \frac{d^2A_0{}^*(T^*)}{dT^{*2}} + \rho^*\frac{d^2\mu^*(\rho_c, T^*)}{dT^{*2}} + \lvert\Delta\rho^*\rvert^{-\frac{\alpha}{\beta}}x_0{}^{-2}Da''\left(\frac{x}{x_0}\right)$

Table 3.3: Scaled expressions for thermodynamic functions

Heat capacity, two-phase region	$-\frac{C_V^*}{T^*}=\frac{d^2A_0^*(T^*)}{dT^{*2}}+\rho^*\frac{d^2\mu^*(\rho_c,T^*)}{dT^{*2}}+(2-\alpha)(1-\alpha)\lvert\Delta T^*\rvert^{-\alpha}x_0^{\alpha-2}Da(-1)$

Table 3.4: Amplitudes, linear model c=0, cubic model c≠0

$B=k(b^2-1)^{-\beta}=x_0^{-\beta}$	$D=ab^{\delta-3}(b^2-1)/k^{\delta}=E_1(1+E_2)^{(\gamma-1)/2\beta}$
$\Gamma=k/a=x_0^{\gamma}/E_1E_2^{(\gamma-1)/2\beta}$	$\Gamma'=(b^2-1)^{\gamma-1}\{1-b^2(1-2\beta)\}k/2a=\beta x_0^{\gamma}/E_1$
$A^+=-(2-\alpha)(1-\alpha)\alpha f_0$	$A_{II}^-=-(2-\alpha)(1-\alpha)\alpha(f_0+f_2+f_4)/(b^2-1)^{2-\alpha}$
$A_I^-=-\alpha\beta(b^2-1)^{\alpha}\{1-b^2(1-2\beta)\}^{-3}[\{(1-\alpha)[1-b^2(1-2\beta)]-2\beta b^2(1-2\beta)\}\cdot$ $\{(\delta+1)f_0+(\delta-1)f_2+(\delta-3)f_4\}-2\beta\{1-b^2(1-2\beta)\}\{(\delta-1)f_2+2(\delta-3)f_4\}]$ $f_0=-ak\{\delta-3-b^2\alpha(\delta-1)\}/\{2b^4(1-\alpha)\alpha(\delta+1)\}$ $f_2=ak\{\beta(\delta-3)-b^2\alpha(1-2\beta)\}/\{2b^2(1-\alpha)\alpha\}$ $f_4=-ak(1-2\beta)/2\alpha$ $a_1=(1-\alpha)\{1-b^2\theta^2(1-2\beta)\}-2\beta b^2\theta^2(1-2\beta)$ $a_2=(\delta+1)f_0+(\delta-1)f_2\theta^2+(\delta-3)f_4\theta^4$ $a_3=2\beta\theta^2\{1-b^2\theta^2(1-2\beta)\}\{(\delta-1)f_2+2(\delta-3)f_4\theta^2\}$	

Table 3.5: Thermodynamic parametric functions

Chemical potential, one-phase region	$\Delta\mu^*=\mu^*(T^*)-\mu^*(\rho_c^*,T^*)=r^{\beta\delta}a\theta(1-\theta^2)$
Chemical potential, two-phase region	$\Delta\mu^*=0$
Helmholtz free-energy density, one-phase region	$A^*=A_0^*(T^*)+\rho^*\mu^*(\rho_c,T^*)+r^{2-\alpha}(f_0+f_2\theta^2+f_4\theta^4)$
Helmholtz free-energy density, two-phase region	$A^*=A_0^*(T^*)+\rho^*\mu^*(\rho_c,T^*)+r^{2-\alpha}(f_0+f_2+f_4)$
Compressibility	$\chi_T^*=(\rho^{*2}K_T^*)^{-1}=r^{-\gamma}\frac{k}{a}\left(\frac{1-\theta^2(b^2-2\beta b^2-3c)-(3-2\beta)b^2c\theta^4}{1-\theta^2(b^2-2\beta\delta b^2-3c)+(3-2\beta\delta)b^2\theta^4}\right)$
Pressure, one phase region	$p^*=-A_0^*(T^*)+r^{\beta\delta}a\theta(1-\theta^2)+r^{2-\alpha}ak\{\theta^2(1-\theta^2)$ $-f_0-f_2\theta^2-f_4\theta^4\}$
Pressure, two-phase region	$p^*=-A_0^*(T^*)-r^{2-\alpha}\left\{f_0+f_2+f_4\right\}$
Entropy, one-phase region	$-S^*=\frac{dA_0^*(T^*)}{dT^*}+\rho^*\frac{d\mu^*(\rho_c^*,T^*)}{dT^*}+r^{1-\alpha}\frac{\beta a_2}{1-b^2\theta^2(1-2\beta)}$

Table 3.5: Thermodynamic parametric functions

Entropy, two-phase region	$-S^* = \frac{dA_0^*(T^*)}{dT^*} + \rho^* \frac{d\mu^*(\rho_c^*, T^*)}{dT^*} + r^{1-\alpha} \frac{(2-\alpha)(f_0 + f_2 + f_4)}{1-b^2}$
Heat capacity, one-phase region	$-\frac{C_V^*}{T^*} = \frac{d^2A_0^*(T^*)}{dT^{*2}} + \rho^* \frac{d^2\mu^*(\rho_c^*, T^*)}{dT^{*2}} + r^{-\alpha} \frac{\beta(a_1a_2 - a_3)}{\{1-b^2\theta^2(1-2\beta)\}^3}$
Heat capacity, two-phase region	$-\frac{C_V^*}{T^*} = \frac{d^2A_0^*(T^*)}{dT^{*2}} + \rho^* \frac{d^2\mu^*(T^*)}{dT^{*2}} + r^{-\alpha} \frac{(2-\alpha)(1-\alpha)(f_0 + f_2 + f_4)}{(1-b^2)^2}$