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The role of temperature in nucleation processes

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Heat and mass transfers are coupled processes, also in nucleation. In principle, a nucleating cluster would have a different temperature compared to the surrounding supersaturated old phase because of the heat release involved with attaching molecules to the cluster. In turn a difference in temperature across the cluster surface is a driving force for the mass transfer to and from the cluster. This coupling of forces in nonisothermal nucleation is described using mesoscopic nonequilibrium thermodynamics, emphasizing measurable heat effects. An expression was obtained for the nonisothermal nucleation rate in a one-component system, in the case where a temperature difference exists between a cluster distribution and the condensed phase. The temperature is chosen as a function of the cluster size only, while the temperature of the condensed phase is held constant by a bath. The generally accepted expression for isothermal stationary nucleation is contained as a limiting case of the nonisothermal stationary nucleation rate. The equations for heat and mass transport were solved for stationary nucleation with the given cluster distribution and with the temperature controlled at the boundaries. A factor was defined for these conditions, determined by the heat conductivity of the surrounding phase and the phase transition enthalpy, to predict the deviation between isothermal and nonisothermal nucleation. For the stationary state described, the factor appears to give small deviations, even for primary nucleation of droplets in vapor, making the nonisothermal rate smaller than the isothermal one. The set of equations may lead to larger and different thermal effects under different boundary conditions, however. © *2011 American Institute of Physics*. [doi:10.1063/1.3544689]

I. INTRODUCTION

Nucleation is the start of a phase transformation.[1] Nuclei of the new phase form from a supersaturated old phase. In metallurgy, the evolution of microstructure during casting strongly depends on the grain nucleation behavior.[2] For pharmaceuticals, different nucleation conditions can lead to different and often unwanted solid states (polymorphism).[3] In the earth's atmosphere, clouds form by heterogeneous nucleation of water droplets on tiny dust and aerosol particles.[4] The stability of these clouds toward dissolution is a well-known natural problem. Nucleation is also associated with technical issues, for instance, in the production of magnesium metal.[5]

Nucleation is a highly nonlinear process with respect to the chemical driving force or the difference in chemical potential between the phases. It takes place at the nanoscale where molecules randomly attach to and detach from new phase clusters. Classical nucleation theory is still the state-of-the-art theory to describe nucleation processes.[6] However, in many cases nucleation rates from experiments and simulations are orders of magnitude different from the predicted values.[7] This has spurred an interest in theoretical developments, taking other variables than the cluster size into account[8–13] but still no comprehensive predictive theory exists for nucleation. It is our aim to contribute to this development, paying special attention to the role of the coupling between heat and mass transfers.

When clusters form from an old phase, a temperature difference between cluster and old phase is expected to develop due to the accompanying enthalpy change. Such a difference would result in a heat flux. The first theory that so took the nucleus temperature and energy flux into account was given in the now classical paper of Feder *et al*.[12] These authors derived a contribution to the nucleation rate from the rate of energy transfer to the cluster, using a mesoscopic approach. Typically, the nonisothermal nucleation rate would be about 20% of the isothermal nucleation rate using this theory. This finding has been confirmed also in a stochastic simulation model[13] for nucleation on a lattice. A recent review was given by Rybin.[14] As variables, all these authors and others[15] used the energy flux rather than the measurable heat flux. The use of the energy flux, however, does not give a direct link to the measuring situation.

The temperature difference across the cluster boundary may be significant. It was observed in molecular dynamics simulations of nucleating clusters in a supersaturated old phase that the cluster temperature was different from that of the surrounding old phase and was distributed in a non-Gaussian manner.[16] Subcritically sized clusters were colder and postcritically sized clusters were warmer than the old phase.[10] Holyst and Litniewski[17] likewise demonstrated, using computer simulations with Lennard-Jones clusters, that a large temperature discontinuity existed at the interface, as large as nearly 30% of the liquid temperature.

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Also, under transient conditions thermal effects may be large.[18]

Clearly, there is a need for a theory that includes the thermal driving force as an explicit force in nonisothermal nucleation, in order to be able to model nucleation under various boundary conditions. Our aim is, therefore, to develop a description of nucleation,[8,9] which has the temperature difference between the new phase clusters and the bulk old phase as an explicit and additional driving force. Nonequilibrium thermodynamics[19,20] is the theory to describe processes where more forces are acting. We, therefore, choose to describe nonisothermal stationary nucleation with the aid of nonequilibrium thermodynamics, building on the mesoscopic procedure first presented by de Groot and Mazur[19] and further developed for nucleation by Reguera and co-workers.[8,9] Another feature of our approach is that we shall use a heat flux that can be measured, facilitating the comparison with experimental results. In mesoscopic nonequilibrium thermodynamics one introduces internal variables, i.e., variables, which are not originally included in the Gibbs equation. Examples are molecular properties such as the velocity, orientation, and dipole moment. We shall use the cluster size as internal coordinate as was done before.[9] The concentration of clusters and their temperatures are the internal variables. The resulting new description, made to emphasize measurable heat effects, may be fruitful in describing temperature effects in nucleation in experiments or simulations.

The system with the growing clusters obeys certain overall boundary conditions for conservation of mass and energy, which are stated first in Sec. II A. The corresponding versions of these conservation equations for the mesoscopic level are given next in Sec. II B. From these equations and the Gibbs equation, we next derive the expression for the (mesoscopic) entropy production for cluster growth in Sec. II C. This expression determines the rate equations (Sec. III A). The coefficients of the rate equations are identified in Sec. III B, while the driving force due to supersaturation is detailed in Sec. III C. The general rate expressions can next be given and compared to the classical nucleation theory, in Sec. III D. Before concluding we show by an example in Sec. III E the extent of the deviation from the classical nucleation theory that can be expected.

II. BALANCE EQUATIONS

By nucleation, we mean the formation of clusters of a new phase in a supersaturated old phase due to attachment and detachment to and from these clusters of molecules or atoms. The old phase thus contains clusters of the new phase of size $n = 1, 2, \ldots$ It is common in the theory of nucleation to distinguish new phase clusters with size 1 and separate old phase molecules.[6] A collection of concentrations $c(n,t)$ (number per unit of volume) of new phase clusters of size n at time t exists next to the old phase. The nucleation process can then be considered as a diffusion process along the internal coordinate n of the cluster concentration $c(n,t)$ with a diffusion flux $J(n,t)$. The system, we consider in particular, is a collection of clusters of varying size n growing at stationary state in a bath of old phase molecules at constant temperature. The stationary state is maintained by exchange of heat and mass through the container walls, as described below. We shall consider growth as having a positive flux, $J(n,t)$. Figure 1 shows the mass and energy flows in the system in case of nonisothermal nucleation. The clusters of various sizes and temperatures can exchange heat and mass with the old phase. A net attachment of molecules to clusters causes a positive diffusion flux along the internal coordinate n.

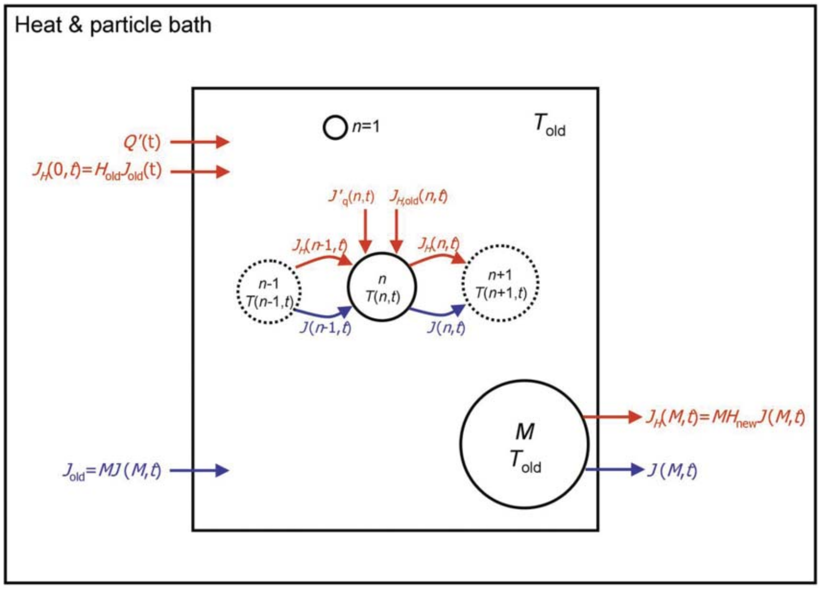

FIG. 1. In a supersaturated old phase, new phase clusters of various sizes grow and decay in size because of attachment and detachment of old phase molecules. In case of nonisothermal nucleation, along with this process, an enthalpy flux $J_H(n)$ occurs, changing the cluster temperature $T(n)$. Nucleation is a diffusion process over the internal coordinate of the cluster size n. Clusters have various temperatures and thus can exchange heat with the old phase, causing a heat flux $J_q'(n)$. The old phase is kept at a temperature T_{old} by adding a net heat flux $Q'(t)$ to the system. Overall an enthalpy flux is leaving the system with the removal of clusters of size M. These clusters are replaced with a flux J_{old} of M molecules in the old phase at the temperature T_{old}.

The old phase is connected to a heat bath which keeps the old phase at temperature $T_{\rm old}$ due to a net measurable heat flux Q' from the old phase to the heat bath. When an old phase molecule attaches to a cluster it carries along an enthalpy $H_{\rm old}(T_{\rm old})$, which is the enthalpy of the old phase molecules in units of energy. The enthalpy difference of molecules in the old and the new phases causes temperature differences between the bulk old phase and the clusters of the new phase. We assume that the internal thermal conductivity of a new phase cluster is sufficiently large so that the clusters can be considered to be isothermal with a temperature $T(n,t)$. The temperature differences between clusters and the old phase cause a measurable heat flux $J'_q(n,t)$, which is positive from the old phase to the clusters. We assume that all clusters of size n are at temperature $T(n,t)$. Due to the statistical nature of the detachments and attachments, a temperature distribution for clusters of size n may exist in reality.

The old phase is also connected to a reservoir of old phase molecules. It is assumed that macroscopically large clusters with size $n \geq M$ have had a life time long enough to thermally equilibrate with the old phase so that they reach $T(M,t) = T_{\rm old}$ at the boundary of the system, where they are leaving the system. Such macroscopically sized clusters with size $n = M$ are removed from the system and replaced by M old phase molecules from the reservoir in order to maintain the supersaturation of the old phase at a constant level. There is thus a cluster flux $J(M,t)$ leaving the system and a flux $J_{\rm old}(t)$ of old phase molecules entering the system. These fluxes are accompanied with an enthalpy flux $J_H(M,t) = H(M,t)J(M,t)$ leaving the system carried by the clusters, and an enthalpy flux $J_H(0,t) = H_{\rm old}J_{\rm old}(t)$ carried by the old phase molecules entering the system. $H(n,t)$ is the enthalpy of the clusters with size n in units of energy.

A. Overall mass and energy balances

A total of $J(M,t)$ clusters of size $n = M$ and temperature $T_{\rm old}$ are removed from the system per unit of time and volume. A total of $J_{\rm old}(t)$ old phase molecules enter the system per unit time and volume. The accumulation of molecules in the system is thus described as

$$\frac{\partial c_{\rm system}(t)}{\partial t} = J_{\rm old}(t) - MJ(M,t)\,, \tag{1}$$

where $c_{\rm system}$ is the total concentration counted as monomers in the system per unit of volume.

The addition of $J_{\rm old}(t)$ old phase molecules of temperature $T_{\rm old}$ to the system into the old phase, causes an enthalpy flux $J_H(0,t) = H_{\rm old}J_{\rm old}(t)$. Furthermore there is a net measurable heat flux Q' added to the old phase via the wall in order to retain its temperature $T_{\rm old}$. The cluster flux $J(M)$ out of the system is accompanied by an enthalpy flux $J_H(M,t) = H(M,t)J(M,t) = MH_{\rm new}(T_{\rm old})J(M)$. We used that for large clusters where the enthalpy per monomer becomes equal to $H_{\rm new}(T_{\rm old})$ in the last identity. The accumulation of energy in the system is thus

$$\frac{\partial u_{\rm system}(t)}{\partial t} = J_{\rm old}(t)\,H_{\rm old} - M\,J(M,t)\,H_{\rm new} + Q'(t)\,. \tag{2}$$

In stationary nonisothermal nucleation, there is no mass and energy accumulation in the system. This means that the total concentration $c_{\rm system}$, the total energy $u_{\rm system}$, cluster concentration $c(n)$, cluster temperature $T(n)$ and mass, enthalpy, and heat fluxes in and out the system $J_{\rm old}$, $J(n)$, $J_H(n)$, Q' are all independent of the time. This gives the overall mass balance for stationary nucleation,

$$J_{\rm old} = MJ(M)\,. \tag{3}$$

In stationary state, one obtains for the net measurable heat flux Q',

$$Q' = M\left[H_{\rm new}(T_{\rm old}) - H_{\rm old}(T_{\rm old})\right]J = MJ\Delta H. \tag{4}$$

The net measurable heat flux into the system is equal to the enthalpy of the phase transformation at temperature $T_{\rm old}$. The intermediate size clusters will still have a temperature different from $T_{\rm old}$.

B. Mesoscopic mass and energy balance

A close-up of the energy and mass balances in Fig. 1 is given in Fig. 2. This figure shows the fluxes concerned with clusters of size n. The flux $J(n,t)$ along the cluster size coordinate is the nucleation rate. When a size n cluster grows to size $n+1$ and takes up a molecule from the old phase, there is a positive contribution to $J(n,t)$. When a size $n+1$ cluster shrinks to size n by detaching a molecule to the old phase, there is a negative contribution to $J(n,t)$. The cluster concentration $c(n,t)$ increases because of a positive flux $J(n-1,t)$ of clusters of size $n-1$ to clusters of size n. Similarly the clus-

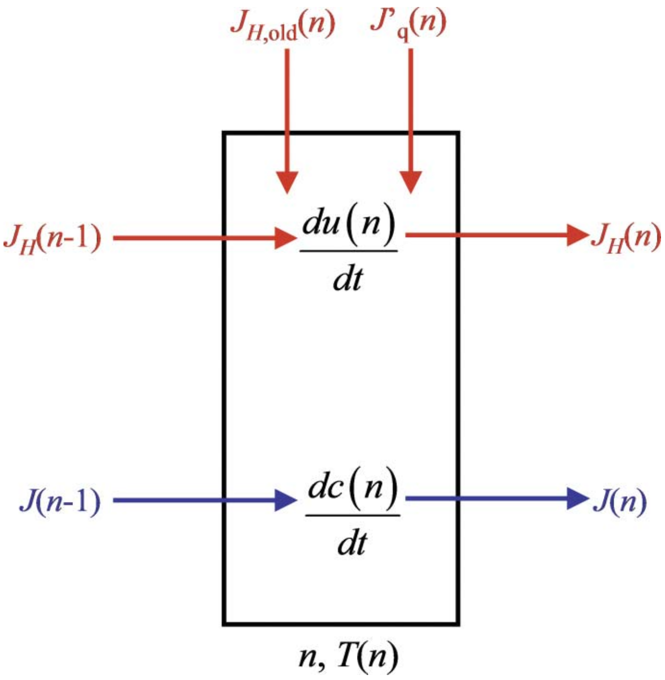

FIG. 2. A close up of the enthalpy and mass balances in Fig. 1, showing the heat and mass fluxes entering and leaving clusters of size n. The heat fluxes $J'_q(n,t)$ and $J_{H,\rm old}(n,t)$ are directed into the clusters and not along the n-coordinate.

ter concentration $c(n,t)$ decreases because of a positive flux $J(n,t)$ of clusters of size n to clusters of size $n + 1$. The rate of change of the cluster concentration can, therefore, be written as

$$\frac{\partial c(n,t)}{\partial t} = -J(n,t) + J(n-1,t) \equiv -\frac{\partial J(n,t)}{\partial n}. \tag{5}$$

In the analysis, we will often treat n as a continuous coordinate, which varies between 0 and M. A summation over cluster size n can then equivalently be replaced by an integral from 0 to M. It is in this manner, that the growth rate can be pictured as a diffusion process along the n-coordinate. For convenience, from this point we will no longer indicate the time dependence of variables in places where it is not strictly necessary.

Figure 2 shows also that the internal energy $u(n,t)$ of clusters of size n changes by a number of contributions. There is an incoming enthalpy flux $J_H(n-1,t) = J(n-1,t)H(n-1,t)$ and an outgoing enthalpy flux $J_H(n,t) = J(n,t)H(n,t)$ caused by clusters moving along the n-coordinate. There is also an incoming enthalpy flux $J_{H,\mathrm{old}}(n)$ due to old phase molecules that attach to the clusters of size $n - 1$ to give a cluster size of n. This accompanying flux is $J_{H,\mathrm{old}}(n,t) = J(n-1,t)H_{\mathrm{old}}$, which we conveniently approximate by $J_{H,\mathrm{old}}(n,t) = J(n,t)H_{\mathrm{old}}$. The old phase also transfers heat to the clusters of size n due to the temperature difference between clusters and old phase. This causes a flux $J'_q(n,t)$ into the clusters of size n. The internal energy change for the clusters of size n becomes

$$\begin{aligned}\frac{\partial u(n,t)}{\partial t} &= J(n-1,t)\,H(n-1,t) - J(n,t)\,H(n,t)\\ &\quad + J(n,t)\,H_{\mathrm{old}} + J'_q(n,t).\end{aligned} \tag{6}$$

This can be written as

$$\begin{aligned}\frac{\partial u(n,t)}{\partial t} &= J'_q(n,t) - H(n,t)\frac{\partial J(n,t)}{\partial n}\\ &\quad - J(n,t)\frac{\partial\left[H(n,t) - nH_{\mathrm{old}}\right]}{\partial n}.\end{aligned} \tag{7}$$

For a stationary state, $J(n) = J$, and the total energy content $u(n)$ is independent of the time. Equation (7) then gives a relation between the heat flux $J'_{\mathrm{q}}(n)$ into the cluster and the nucleation rate J at stationary state,

$$J'_q(n) = J\frac{\partial\left[H(n) - nH_{\mathrm{old}}\right]}{\partial n}. \tag{8}$$

This will be used later to obtain an equation for nonisothermal stationary nucleation. The measurable heat exchanged by cluster and old phase depends on the change in cluster energy with cluster size. Summing $J'_{\mathrm{q}}(n)$ over all cluster sizes from $n = 1$ to M we obtain the measurable heat Q' that must be transferred from the bath to the old phase to keep T_{old} constant in a stationary state,

$$Q' = \sum_{n=1}^{M} J'_q(n). \tag{9}$$

With the aid of Eq. (6) for stationary state, an expression for the measurable heat Q' is obtained,

$$Q' = JH(0) + JH(M) - MJH_{\mathrm{old}} = MJ\Delta H, \tag{10}$$

where $H(0) = 0$ (a nonexisting cluster of size $n = 0$ has zero enthalpy) and $H(M) = MH_{\mathrm{new}}(T_{\mathrm{old}})$ (a cluster of size M has a temperature T_{old} and is sufficiently large so that the surface does not contribute to the enthalpy). This is identical to the result of the overall balance in Eq. (4). In most cases (with large clusters), the enthalpy of the new phase is smaller than that of the old phase, making $Q' < 0$. Net heat is moved from the old phase to the bath to keep T_{old} constant.

C. The entropy production

As a first step in deriving an equation for the nonisothermal stationary nucleation rate, we will find an expression for the entropy production of the clusters in order to identify the driving forces in the system. The entropy differential of all clusters of size n is given by the Gibbs relation,[19]

$$\frac{\partial s(n,t)}{\partial t} = \frac{1}{T(n,t)}\frac{\partial u(n,t)}{\partial t} - \frac{\mu(n,t)}{T(n,t)}\frac{\partial c(n,t)}{\partial t}, \tag{11}$$

where $\mu(n,t)$ is the chemical potential of the n-sized clusters. Filling in Eqs. (5) and (7) gives

$$\begin{aligned}\frac{\partial s(n,t)}{\partial t} &= \frac{1}{T(n,t)}J'_q(n,t) - \frac{H(n,t)}{T(n,t)}\frac{\partial J(n,t)}{\partial n}\\ &\quad - \frac{J(n,t)}{T(n,t)}\frac{\partial\left[H(n,t) - nH_{\mathrm{old}}\right]}{\partial n}\\ &\quad + \frac{\mu(n,t)}{T(n,t)}\frac{\partial J(n,t)}{\partial n}.\end{aligned} \tag{12}$$

We show in Appendix that this equation leads to the following expression for the entropy production $\sigma(n,t)$ in J/(s m^3 K),

$$\sigma(n,t) = J'_q(n,t)\,X_T(n,t) - J(n,t)\frac{\partial X_n(n,t)}{\partial n}, \tag{13}$$

where the thermodynamic force X_T is defined as

$$X_T(n,t) = \frac{1}{T(n,t)} - \frac{1}{T_{\mathrm{old}}}. \tag{14}$$

And the term X_n as

$$X_n(n,t) = \frac{\mu(n,t;T_{\mathrm{old}}) - n\mu_{\mathrm{old}}}{T_{\mathrm{old}}}, \tag{15}$$

where $\mu(n,t;T_{\mathrm{old}}) \equiv \mu(n,t) + s(n,t)\left[T(n,t) - T_{\mathrm{old}}\right]$ is the chemical potential of the nth cluster evaluated at the temperature of the old phase. The entropy production $\sigma(n,t)$ identifies the thermodynamic driving forces $-\partial X_n/\partial n$ and X_T acting on the conjugate fluxes $J(n,t)$ and $J'_q(n,t)$.

The entropy production in the case of isothermal nucleation, when $T(n) = T_{\mathrm{old}}$, is

$$\sigma_{\mathrm{iso}}(n,t) = -J(n,t)\frac{\partial X_n(n,t)}{\partial n}. \tag{16}$$

The local entropy production cannot be negative, so $\sigma(n,t) \geq 0$, similar to the entropy production of the whole system.

III. A MESOSCOPIC DESCRIPTION OF NONISOTHERMAL NUCLEATION

A. The linear relation between the nucleation rate and its driving forces

Now that the driving forces and fluxes are identified, we can use the basic assumption of nonequilibrium thermodynamics, which states that a flux is linearly related to all existing driving forces through the Onsager coefficients.[19] The resulting flux–force relations are

$$J(n,t) = -L_{nn}(n,t)\frac{\partial X_n(n,t)}{\partial n} + L_{nT}(n,t)X_T(n,t), \tag{17}$$

$$J_q'(n,t) = -L_{Tn}(n,t)\frac{\partial X_n(n,t)}{\partial n} + L_{TT}(n,t)X_T(n,t), \tag{18}$$

where $L_{nT} = L_{Tn}$ (The Onsager reciprocity relation). The Onsager coefficients do not depend on the forces or the fluxes. In this sense, the flux–force relations are linear. However, they may depend on, e.g., temperature and cluster concentration so that the resulting description can be far from linear.

It follows from $\sigma(n,t) \geq 0$ that the following relation applies,[19]

$$L_{nn}L_{TT} - L_{nT}L_{Tn} \geq 0. \tag{19}$$

The Onsager coefficients L_{nn} and L_{TT} on the Onsager matrix diagonal are positive, while the coupling coefficients can be positive or negative. The units for the Onsager coefficient L_{TT}, $L_{nn,}$ and L_{nT} are, respectively, JK/m^{3}s, K/Jm^{3}s, and K/m^{3}s.

Equation (18) gives the following relation between the forces:

$$X_T(n,t) = \frac{J_q'(n,t)}{L_{TT}(n,t)} + \frac{L_{Tn}(n,t)}{L_{TT}(n,t)}\frac{\partial X_n(n,t)}{\partial n}. \tag{20}$$

Using this relation, we can eliminate the driving force X_T from Eq. (17),

$$J(n,t) = -\left(L_{nn} - \frac{L_{nT}^2}{L_{TT}}\right)\frac{\partial X_n(n,t)}{\partial n} + \frac{L_{nT}}{L_{TT}}J_q'(n,t). \tag{21}$$

For ease of notation, we will further suppress the explicit dependence of the Onsager coefficients on n and t. From Eq. (19), it follows that the first term in the brackets in Eq. (21) must be larger than 0.

The isothermal case is obtained by setting X_T equal to zero in Eq. (17), which gives

$$J_{\text{iso}}(n,t) = -L_{nn}\frac{\partial X_n(n,t)}{\partial n}. \tag{22}$$

By comparing Eqs. (21) and (22), we see that temperature effects the cluster flux $J(n,t)$ and thus nucleation in two ways. The linear coefficient between the force $-\partial X_n/\partial n$ and the flux $J(n,t)$ reduces in size for nonisothermal nucleation. Additionally, there is a coupling L_{nT}/L_{TT} between the cluster flux $J(n,t)$ and the measurable heat flux $J'_q(n,t)$ which either increases or decreases the nucleation rate depending on the sign of the Onsager coefficient L_{nT}.

B. Relating the Onsager coefficients to measurable properties

In order to find an estimate for L_{nn}, we define the diffusion coefficient $D(n,t)$ in n-space,

$$D(n,t) \equiv \frac{kL_{nn}(n,t)}{c(n,t)}, \tag{23}$$

where k is the Boltzmann constant. The diffusion coefficient $D(n,t)$ has the dimensionality s^{-1} and will be identified later with the attachment frequency of old phase molecules to a cluster of size n.

The coefficient L_{Tn} is best identified via its ratio to L_{nn}. We define the measurable heat of transfer $q^*(n,t)$, as is normal in macroscopic systems,[20] as the ratio of measurable heat flux (in the old phase) from the old phase into the clusters and the cluster flux $J(n,t)$ at zero temperature difference,

$$q^*(n,t) \equiv \left[\frac{J_q'(n,t)}{J(n,t)}\right]_{\Delta T=0} = \frac{L_{Tn}(n,t)}{L_{nn}(n,t)}. \tag{24}$$

Similar to the old phase molecule flux, the heat flux into the cluster is defined as positive (Fig. 2). It is known that the measurable heat of transfer $q^*(n,t)$ is negative for a condensing vapor at a planar liquid interface.[9] This makes it likely that $q^*(n,t)$ is negative for large clusters when curvature effects are negligible. For clusters below the critical size, we expect the measurable heat of transfer to be positive, since energy is needed to form the surface.

As relation between the Onsager coefficient L_{TT} and the thermal conductivity λ, we propose

$$\lambda(n,t) \equiv L_{TT}(n,t)\frac{d(n,t)}{A(n)c(n,t)T_{\text{old}}^2} = L_{TT}(n,t)\frac{d(n,t)}{a(n,t)T_{\text{old}}^2}, \tag{25}$$

where $A(n)$ is the surface area of a cluster of size n and $a(n,t) = A(n)c(n,t)$ is the total surface area of all clusters of size n per unit of volume. The thickness d of the interfacial layer in which the heat transfer takes place could be estimated by the mean interparticle distance in a supersaturated vapor. A decrease of the interface thermal conductivity with the increasing cluster radius was found by Lervik *et al.*[21] That is, the smaller the cluster becomes, the better is heat conducted across its surface.

The above three equations make it possible to rewrite Eqs. (17) and (18),

$$J(n,t) = -\frac{c(n,t)D}{k}\left(\frac{\partial X_n(n,t)}{\partial n} - q^*X_T(n,t)\right), \tag{26}$$

$$J_q'(n,t) = -\frac{c(n,t)Dq^*}{k}\frac{\partial X_n(n,t)}{\partial n} + \frac{Ac(n,t)T_{\text{old}}^2\lambda}{d}X_T(n,t). \tag{27}$$

Equation (21) can similarly be rewritten into

$$J(n,t) = -\frac{c(n,t)\,D}{k}(1-p)\frac{\partial X_n(n,t)}{\partial n} + \frac{p}{q^*}J'_q(n,t), \tag{28}$$

where the dimensionless *nonisothermal nucleation number* $p(n,t)$ is defined as a product of two dimensionless numbers,

$$p = \frac{q^{*2}Dd}{\lambda A k T_{\mathrm{old}}^2} = \frac{q^*}{kT_{\mathrm{old}}}\cdot\frac{q^*Dd}{\lambda A T_{\mathrm{old}}}. \tag{29}$$

The first dimensionless number q^*/kT is related to the enthalpy release per attachment of a molecule to the cluster and thus to the quantity of excess enthalpy of the cluster that can be exchanged with the old phase. If attachments generate large excesses the value of the nonisothermal nucleation number would be large. The second dimensionless number is related to the resistance to heat transfer from the cluster. If the resistance is high, for instance, due to a low heat conductivity, then the nonisothermal nucleation number would be large.

Equations (26)–(28) give a thermodynamic basis for description of nonisothermal nucleation, since they are derived from the entropy production for nucleation. The equations obey Onsager symmetry, and we see that the coupling coefficient is essential. The growth in Eq. (26) is thus directly proportional to the thermal driving force via the heat of transfer, which is a large quantity for interfaces.[20] We see that the sign of the flux can change, if the thermal forces change sign. From Eq. (27), we see that a large heat flux across the boundary, promoted by changes in the surroundings, can lead to large temperature differences, and initiate changes in the chemical driving force through the heat of transfer. Earlier descriptions of nonisothermal nucleation did not take these cross effects into account.

The restriction on the Onsager coefficients in Eq. (19) gives the restriction $0 \le p \le 1$ for the nonisothermal nucleation number p. The isothermal case is obtained by setting X_T equal to zero in Eq. (26), which gives

$$J_{\mathrm{iso}}(n,t) = -\frac{c(n,t)\,D}{k}\frac{\partial X_n(n,t)}{\partial n}. \tag{30}$$

By comparing Eqs. (28) and (30) the effect of accounting for temperature differences between clusters and old phase is twofold. First, the linear dependency of the nucleation rate $J(n,t)$ on the driving force $-\partial X_n/\partial n$ is decreased by the factor $(1-p)$. This factor would decrease the nonisothermal cluster flux $J(n,t)$ compared to the isothermal cluster flux $J_{\mathrm{iso}}(n,t)$. Second, the nonisothermal cluster flux $J(n,t)$ is decreased, or possibly increased if $J'_q(n,t) < 0$, compared to the isothermal cluster flux J_{iso} by an amount linear in the measurable heat flux $J'_{\mathrm{q}}(n,t)$.

Equation (18) can be rewritten to

$$J'_q(n,t) = q^*J(n,t) + \frac{aT_{\mathrm{old}}^2\lambda}{d}(1-p)\,X_T(n,t), \tag{31}$$

which, when the measurable heat of transfer q^* for n-sized clusters is known, should lead to the cluster temperature $T(n,t)$.

C. The chemical driving force and classical nucleation theory

In order to arrive at results, which can be compared to experiments, it is necessary to integrate over the internal variable n. We focus first on the chemical driving force $-\partial X_n/\partial n$. The chemical potential $\mu(n,t)$ at temperature T_{old} of a cluster of size n for an ideal system, where clusters do not interact, is given by[6,19]

$$\mu(n,t) = n\mu_{\mathrm{new}} + \gamma(n)A(n) + kT_{\mathrm{old}}\ln\frac{c(n,t)}{c_0}. \tag{32}$$

The cluster chemical potential $\mu(n,t)$ contains the chemical potential μ_{new} of molecules in the bulk new phase at temperature T_{old}. These clusters have a surface area $A(n)$ that contributes to the chemical potential $\mu(n,t)$ through the surface tension $\gamma(n)$ of the interface between the new phase cluster and the old phase. In the classical nucleation theory, the surface tension is assumed to be equal to that of an infinitely large, flat interface. We will assume that it only depends on n and not on the time. The logarithmic term is an entropic contribution originating from considering the system as a mixture of differently sized clusters. The concentration c_0 of nucleation sites accounts for all positions in the volume where a cluster can appear.

The term X_n from Eq. (15) can thus be written as

$$\begin{aligned} X_n(n,t) &= k\ln\frac{c(n,t)}{c_0} + \frac{-n\Delta\mu + \gamma(n)A(n)}{T_{\mathrm{old}}} \\ &= k\ln\frac{c(n,t)}{c_0} + \frac{\phi(n)}{T_{\mathrm{old}}}. \end{aligned} \tag{33}$$

The chemical potential difference between old and new phases is defined as $\Delta\mu = (\mu_{\mathrm{old}} - \mu_{\mathrm{new}})$ where we note that, follow the convention used in nucleation research,[6] this difference does not refer to the same states as in ΔH [Eq. (4)]. In this equation, we can recognize the work $\phi(n)$ to create a cluster of size n and temperature T_{old} in a supersaturated old phase,

$$\phi(n) = -n\Delta\mu + \gamma(n)A(n) = n\Delta\mu + \alpha v^{2/3}n^{2/3}\gamma(n). \tag{34}$$

The cluster surface area $A(n) = \alpha v^{2/3}n^{2/3}$ is a function of the shape factor α, the new phase molecular volume v, and the cluster size n. For a small cluster size n, the work $\phi(n)$ is positive and increases due to the contribution of the specific surface energy. For larger n, the first contribution dominates and the work becomes negative. In between, there is a cluster n^*, the nucleus, with the maximum work ϕ^*, the nucleation work, for its formation. The nucleus size n^* and nucleation work $\phi^* = \phi(n^*)$ can be obtained by taking the derivative of Eq. (34) toward the cluster size n and equal this to zero. This gives for nucleus size n^*,

$$n^* = \frac{8\alpha^3v^2\gamma^3}{27\Delta\mu^3}. \tag{35}$$

And for the nucleation work ϕ^*,

$$\phi^* = \frac{4\alpha^3v^2\gamma^3}{27\Delta\mu^2}. \tag{36}$$

The nucleus size n^* and the nucleation work ϕ^* do not differ from those defined in the classical nucleation theory for isothermal stationary nucleation.[6]

At equilibrium between the supersaturated old phase and a cluster concentration $c_{\mathrm{eq}}(n)$, there is no overall exchange of mass and internal energy between the old phase and the clusters and the fluxes $J(n,t)$ and $J'_q(n,t)$ will be zero. In this case there is no drive in the system to create larger or smaller clusters. In equilibrium $X_n = X_{n,\mathrm{eq}} = 0$, independent of the cluster size. Together with Eq. (33), this gives

$$k \ln \frac{c_{\mathrm{eq}}(n)}{c_0} + \frac{\phi(n)}{T_{\mathrm{old}}} = 0. \tag{37}$$

It follows that the equilibrium cluster concentration $c_{\mathrm{eq}}(n)$ at the temperature T_{old} is given by

$$c_{\mathrm{eq}}(n) = c_0 \exp\left(-\frac{\phi(n)}{kT_{\mathrm{old}}}\right), \tag{38}$$

which is identical to the expression that describes equilibrium in the classical nucleation theory.[6] Combining Eqs. (33) and (37), it follows that

$$X_n(n,t) = k \ln \frac{c(n,t)}{c_{\mathrm{eq}}(n)}. \tag{39}$$

The chemical driving force $-\partial X_n/\partial n$ for nonisothermal nucleation can, therefore, be rewritten as

$$\begin{aligned} -\frac{\partial X_n(n,t)}{\partial n} &= -\frac{\partial}{\partial n} k \ln \frac{c(n,t)}{c_{\mathrm{eq}}(n)} \\ &= -\frac{k}{c(n,t)} c_{\mathrm{eq}}(n) \frac{\partial}{\partial n} \frac{c(n,t)}{c_{\mathrm{eq}}(n)}, \end{aligned} \tag{40}$$

which is the same as found in the isothermal case.

D. The general expression

Equation (40) for the driving force can be combined with Eq. (28) to give the following expression for nonisothermal nucleation:

$$J(n,t) = -D(1-p)\, c_{\mathrm{eq}}(n) \frac{\partial}{\partial n} \frac{c(n,t)}{c_{\mathrm{eq}}(n)} + \frac{p}{q^*} J'_q(n,t). \tag{41}$$

For isothermal nucleation, we find

$$J_{\mathrm{iso}}(n,t) = -D c_{\mathrm{eq}}(n) \frac{\partial}{\partial n} \frac{c(n,t)}{c_{\mathrm{eq}}(n)}. \tag{42}$$

The general equation for nonisothermal nucleation becomes with the help of Eq. (5),

$$\begin{aligned} \frac{\partial c(n,t)}{\partial t} &= -\frac{\partial J(n,t)}{\partial n} \\ &= -\frac{\partial}{\partial n}\left[-D(1-p)\, c_{\mathrm{eq}}(n) \frac{\partial}{\partial n} \frac{c(n,t)}{c_{\mathrm{eq}}(n)}\right] \\ &\quad - \frac{\partial}{\partial n}\left[\frac{p}{q^*} J'_q(n,t)\right]. \end{aligned} \tag{43}$$

In principle, this is a general equation valid not only for nucleation processes but for any process involved with clusters moving along the size coordinate in which the surface tension plays a key role, for instance, in droplet evaporation.

To the general description belongs the expression for the heat flux given earlier, for instance, as written in the form of Eq. (31). The set of equations can be solved for transient and other conditions, if sufficient information is available. They apply for the premise used in the derivation that the cluster temperature is a unique function of its size. In order to obtain equations, which can be compared with experimental results, one has to integrate over n.

We proceed to do so in a simple manner, introducing further restrictions, namely that the system is stationary and that there is no accumulation of mass or energy in any part of the system.

E. The stationary nonisothermal nucleation rate in a boundary-controlled system

Now Eq. (41) can be integrated to relate to quantities of interest. By assuming that the transport coefficients, D, p, and q^*, do not depend much on n, we obtain

$$\begin{aligned} MJ &= \int_0^M J(n)\,\mathrm{d}n \\ &= -D(1-p) \int_0^M c_{\mathrm{eq}}(n) \frac{\partial}{\partial n} \frac{c(n)}{c_{\mathrm{eq}}(n)} \mathrm{d}n \\ &\quad + \frac{p}{q^*} \int_0^M J'_q(n)\,\mathrm{d}n, \end{aligned} \tag{44}$$

where we used that $J(n) = J$ for stationary states, and the rate can be determined at the boundary. From the classical nucleation theory, we know that the most important part of the first integral on the right-hand side is around n^*. We can safely assume that D is not a strong function of the cluster size n in this area and use the value in n^*. To evaluate the last term, we use the relation between the nucleation rate J and the heat $J'_q(n)$ transferred by the n-sized clusters through the total measurable heat Q' that the system exchanges with the heat bath, given in Eqs. (9) and (10),

$$\int_0^M J'_q(n)\,\mathrm{d}n = Q' = M \Delta H J. \tag{45}$$

Only the integral over the heat fluxes can be determined at the boundary. Using this in Eq. (44), we obtain an expression for the integral of $J(n)$, using constant transport coefficients,

$$J = -\frac{D}{M} \frac{1-p}{1-p\dfrac{\Delta H}{q^*}} \int_{n=0}^M c_{\mathrm{eq}}(n) \frac{\partial}{\partial n} \frac{c(n)}{c_{\mathrm{eq}}(n)} \mathrm{d}n. \tag{46}$$

Integrating isothermal nucleation, Eq. (42), similarly results in

$$J_{\mathrm{iso}} = -\frac{D}{M} \int_{n=0}^M c_{\mathrm{eq}}(n) \frac{\partial}{\partial n} \frac{c(n)}{c_{\mathrm{eq}}(n)} \mathrm{d}n. \tag{47}$$

Both equations show that, in agreement with others,[9] the generally accepted expression for isothermal stationary nucleation from classical nucleation theory is contained as a limiting case. For details of the integration, see Ref. 6. The isothermal rate is an exponential function of the supersaturation. To obtain the general expression for the nucleation rate, the term with the thermal driving force in Eq. (26) must be integrated, or alternatively Eq. (28).

We need not carry out the integration here, as we can compare nonisothermal nucleation, Eq. (46), and isothermal nucleation, Eq. (47) directly. We can then define a correction factor τ on the isothermal stationary nucleation rate to obtain the nonisothermal stationary nucleation rate for this case,

$$\tau = \frac{J}{J_{\text{iso}}} = \frac{1-p}{1-p\dfrac{\Delta H}{q^*}}. \tag{48}$$

Consider first the growth process. We know that $\Delta H = H_{\text{new}} - H_{\text{old}} < 0$, while $0 < p < 1$. When $n < n^*$ we may speculate that $q^* < 0$, while $n > n^*$ has $q^* > 0$, in agreement with the temperature variation observed by Wedekind *et al.*[10] for clusters smaller and larger than the critical size. The heat of transfer is in any case comparable in size to $|\Delta H|$.[20] A negative value for q^* implies that the denominator can become small, while the numerator is finite. The nonisothermal nucleation rate can then be much larger than the isothermal nucleation rate. Conversely, when $q^* > 0$, the factor τ becomes small. Nothing is known about the heat of transfer at a curved interface, so the above is a speculation. It implies, however, that the formation of a critical-sized cluster may be rate limited by heat transfer to the cluster.

Some numerical examples are now of interest.

The factor τ is the ratio of the stationary nonisothermal nucleation rate and isothermal nucleation rate for the present model, relating the observed rate J to the maximum rate J_{iso}. In Eq. (48), a relation between the dimensionless nonisothermal nucleation number p and τ is given. The heat of transfer q^* for the nucleus can be written as a fraction of the enthalpy change between new and old phases,[20]

$$q^* = -\varepsilon|\Delta H|, \tag{49}$$

where the fraction $0 \le \varepsilon \le 1$ and ΔH is the condensation enthalpy. A value of 0.2, for instance, means that 20% of the condensation enthalpy is involved in heating up the cluster.

This is used to construct Fig. 3 where the factor τ is plotted as a function of the dimensionless nonisothermal nucleation number p. Since nothing is known about the fraction ε we used the values $\varepsilon = 0.2$, 0.5, and 0.8. It can be seen that the factor τ decreases with increasing p. The higher the fraction ε the higher the response on p because it becomes more difficult for the same cluster size to get rid of the higher amount of latent heat at higher fractions of ε. Since the correction factor $0 \le \tau \le 1$ the nonisothermal nucleation rate is always smaller than the isothermal one.

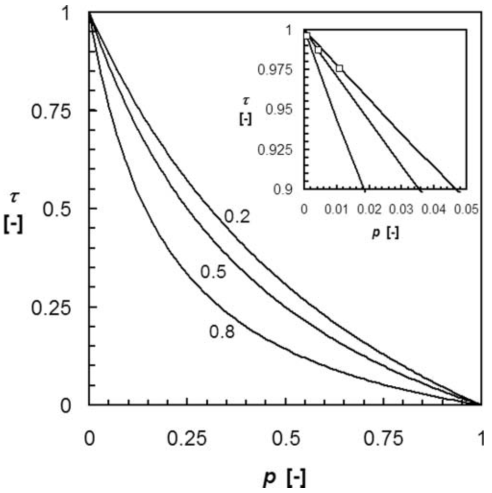

FIG. 3. The factor τ for the isothermal nucleation rate as a function of the dimensionless nonisothermal nucleation number p for the values $\varepsilon = 0.2$, 0.5, and 0.8. The inset shows the temperature effect in a typical condensation of argon.

The nonisothermal nucleation dimensionless number p defined in Eq. (29) was determined for the primary nucleation of liquid droplets during the condensation of water and argon vapor. To maximize temperature effects, we chose the case of homogeneous nucleation from a single component vapor. Single component nucleation in liquids, solids, or even mixtures of gases would facilitate a faster thermal equilibration because of an increased number of (foreign) molecule collisions without an attachment as a result. Further, in case of heterogeneous nucleation, the heterogeneous particles onto which the nucleation takes place can act as a heat sink, and thus a faster thermal equilibration. For the model systems, condensation of pure vapors probably leads to relatively large cluster temperatures because of the low heat conductivity λ of the gas phase and the high condensation enthalpy ΔH. The condensation enthalpy determines the heat of transfer q^*, which is included in the dimensionless number p. All physical properties are derived from literature data and are shown in Table I.[22]

The factor p is further a function of among others the diffusion coefficient $D(n)$ along the n-coordinate. This diffusion coefficient D can be estimated by the attachment frequency of vapor molecules to a nucleus in equilibrium. The attachment frequency D is often taken as the product of the Hertz-Knudsen impingement rate I, the surface area $A(n)$ of the nucleus and a sticking coefficient.[6] If the sticking coefficient is set to 1 (all impingements result in attachment), the attachment frequency per unit of cluster surface area becomes

$$\frac{D\,(n)}{A\,(n)} = \frac{P}{(2\pi m_0 k T_{\text{old}})^{1/2}}. \tag{50}$$

Here P is the saturation pressure of the pure vapor and m_0 is the mass of a molecule. At high supersaturation, the

TABLE I. Properties of water and argon relevant for condensation.

	Symbol [units]	Water	Argon
Old phase temperature	T_{old} [K]	293	100
Equilibrium vapour pressure (Ref. 22)	P_e [kPa]	323.8	2.34
Heat of condensation (Ref. 22)	ΔH [kJ/mol]	−44.2	−6.01
New phase density (Ref. 22)	ρ [g/dm^3]	998	1314
Old phase heat conductivity (Ref. 22)	λ [mW/mK]	18.2	6.689

pressure is leading to high specific attachment frequencies, or $D(n)$.

The boundary layer thickness d through which heat is transferred is estimated on the basis of the liquid density ρ of water or argon: $d = \rho^{-1/3}$, where the density is expressed in m^{-3}. Typically thermal conductivity is much lower in vapors than in condensed phases. From this, we would expect relatively large p-values for nucleation in old phases with small thermal conductivity, such as vapors.

Calculating the dimensionless p-values for the two systems for $\varepsilon = 0.5$ shows that, under the given conditions in Table I, $p = 4.3 \times 10^{-3}$ and 1.6×10^{-3} for, respectively, argon and water. However, even for these systems with relatively large temperature effects compared to other systems, the factor p does not exceed 0.01. This means that the nonisothermal correction factor for the isothermal nucleation rate is probably small and does not exceed 2%. The points in the inset of Fig. 3 show p and τ for $\varepsilon = 0.2$, 0.5, and 0.8 in case of the argon system. All in all, it can be concluded that for our nonisothermal model the nonisothermal effect is small with the present choice of variables. The relatively large cluster surface area of the clusters quickly evens out any large temperature differences existing between new phase clusters and old phase bulk, even when the heat transfer rate is small.

IV. DISCUSSION AND CONCLUSIONS

We have derived a thermodynamic description of nonisothermal nucleation using mesoscopic nonequilibrium thermodynamics, emphasizing measurable heat effects. Doing this, we have extended earlier descriptions[8,9,12] of this phenomenon. The general set of equations (26)–(28) show that there is a significant coupling of heat and mass transfer across the cluster surface. This may be expected to play a significant role in the modeling of transient phenomena, and also in cases where the system is exposed to external heat sinks or sources altering the boundary temperatures. The full set of equations can be used to analyze temperature effects observed in molecular simulations or in experiments of this nature. In order to determine whether the heat of transfer is a weak or strong function of n, molecular simulation experiments similar to the ones done before[10] may be helpful. For instance, once the distribution of nuclei temperature is known, Eq. (31) can be used to find the (average) heat of transfer, using Eq. (9) for the interaction with the boundaries.

The set of equations were solved here for a restricted stationary case, with the temperature being constant at the boundaries of the system. We then find that the nucleation rate has the same form as in the isothermal case and deviates from this rate by a certain factor. The factor is a function of the heat of transfer associated with the process, the resistance to heat transfer, and the attachment frequency, as combined in a dimensionless number for nonisothermal nucleation. The largest temperature effects on growth or dissolution of clusters are to be expected when the enthalpy change of the phase transition is large, while the thermal conductivity in the supersaturated old phase is small. The case study shows that the temperature effect is minor for nucleation of liquid water and argon droplets from their vapor. The set of equations may lead to larger and different thermal effects under different boundary conditions, however.

Some simplifications and assumptions were made in the derivations and need to be discussed. There was no accumulation of energy allowed in the system, and the temperatures at the boundaries were held constant, i.e., Eq. (4) and its mesoscopic equivalent (45) apply. When the latent heat is not removed, one has to resort to the general set of transport equations (26)–(27). We further assumed that clusters of a certain size n all have equal temperature $T(n)$. Some justification for this assumption can be found in the work of Wedekind *et al.*,[10] but other investigators[18] report deviations from this. Whether the assumption is good or not, depends on the conditions that the system is exposed to. From a statistical nature of nucleation, one may expect that a distribution of temperatures of n-sized clusters would develop under several circumstances. A degeneration of n-sized cluster temperature might then lead to nucleation routes through the size–temperature–space that result in increased nucleation rates (decreased nucleation work). Nucleation statistics could be captured within the theory of nonequilibrium thermodynamics by adding randomness to the description of cluster temperature. In the present development, we have shown that the thermal driving force plays a direct role, also for mass transport. This altogether points to a future direction of research.

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NOMENCLATURE

$a(n,t)$	Total surface area of all clusters per unit of volume with size n at time t [m^{-1}]
$A(n)$	Surface area per cluster [m^2]
$c(n,t)$	Cluster concentration [m^{-3}]
d	Boundary layer thickness [m]
$D(n)$	Diffusion coefficient, attachment/detachment frequency [s^{-1}]
$H(n,t)$	Cluster enthalpy [J]
H_{old}	Enthalpy of the old phase [J]
ΔH	Condensation enthalpy [J/particle]
J_{iso}	Isothermal cluster flux (Isothermal nucleation rate) [$\mathrm{m}^{-3}\ \mathrm{s}^{-1}$]
$J'_q(n)$	Measurable heatflux along the n coordinate [$\mathrm{J/m}^3$ s]
J_H	Enthalpy flux due to mass flux [$\mathrm{J/m}^3$ s]
$J_s(n,t)$	Entropy flux along the n-coordinate [J/K m^3 s]
$J_{n,s}(n,t)$	Entropy flux out of the cluster to the old phase [J/K m^3 s]
$J(n)$	Particle flux along the n-coordinate (nucleation rate) [$\mathrm{m}^{-3}\ \mathrm{s}^{-1}$]
k	Boltzmann constant [J/K]
L_{nn}	Onsager coefficient relating driving force ($-\partial X_{\mathrm{n}}/\partial n$) and particle flux J [K/J m^3 s]
L_{nT}	Onsager coefficient relating driving force X_T and particle flux J [$\mathrm{K/m}^3$ s]

L_{nT}	Onsager coefficient relating driving force $(-\partial X_n/\partial n)$ and heat flux $(\partial u/\partial t - J\partial H_n/\partial n)$ [K/m^3 s]
L_{TT}	Onsager coefficient relating driving force X_T and heat flux $(\partial u/\partial t - J\partial H_n/\partial n)$ [J K/m^3 s]
M	Maximum number of particles in cluster [–]
n	Cluster size [–]
n^*	Nucleus size [–]
p	Dimensionless number for nonisothermal nucleation [–]
P	Saturation pressure [Pa]
q^*	Measurable heat of transfer [J]
Q'	Heat taken from bath to the surroundings [J]
$S(n,t)$	Total entropy for all clusters of size n [J/K m^3]
t	Time [s]
T_{old}	Old phase temperature [K]
$T(n)$	Temperature of the clusters of size n [K]
$u(n,t)$	Internal energy per unit of volume of all clusters of size n [J/m^3]
$X_T(n,t)$	Inverse temperature difference between cluster and old phase [K^{-1}]
$X_n(n,t)$	Chemical potential difference between cluster and old phase at old phase temperature [J/K]
γ	Specific surface energy of a cluster [J/m^2]
λ	Interface thermal conductivity of the cluster [J/K m s]
φ	Activation energy potential [J]
μ_{old}	Old phase chemical potential in units of energy per particle [J]
$\mu(n)$	Chemical potential of n-sized cluster [J]
$\mu_{\text{eq}}(n)$	Chemical potential at equilibrium between cluster and old phase [J]
$\sigma(n,t)$	Entropy production [J/K m^3 s]
τ	Factor to describe ratio of nucleation rates at non-isothermal and isothermal conditions [–]

APPENDIX: THE ENTROPY PRODUCTION

Adding and subtracting the reference old phase quantities in Eq. (12) gives

$$\frac{\partial s_n}{\partial t} = J_q'(n)\,X_T - H_n X_T \frac{\partial J_n}{\partial n} + \frac{\mu_n}{T_n}\frac{\partial J_n}{\partial n} + \frac{J_q'(n)}{T_{\text{old}}} - \frac{H_n}{T_{\text{old}}}\frac{\partial J_n}{\partial n} - \frac{J_n}{T_n}\frac{\partial H_n - nH_{\text{old}}}{\partial n}, \tag{A1}$$

where X_T is defined by Eq. (14). We can rewrite the term,

$$\frac{\mu_n}{T_n} = \frac{\mu_n(T_{\text{old}})}{T_{\text{old}}} + \left(\frac{\partial \mu_n/T}{\partial 1/T}\right)_{T_{\text{old}}}$$

$$X_T = \frac{\mu_n(T_{\text{old}})}{T_{\text{old}}} + H_n(T_{\text{old}})\,X_T. \tag{A2}$$

With this we can rewrite the entropy equation to

$$\frac{\partial s_n}{\partial t} = X_T J_q'(n) + \frac{\mu_n(T_{\text{old}})}{T_{\text{old}}}\frac{\partial J_n}{\partial n} + \frac{J_q'(n)}{T_{\text{old}}} - \frac{H_n}{T_{\text{old}}}\frac{\partial J_n}{\partial n} - \frac{J_n}{T_n}\frac{\partial H_n - nH_{\text{old}}}{\partial n}. \tag{A3}$$

Adding and subtracting the reference old phase quantities,

$$\frac{\partial s_n}{\partial t} = X_T J_q'(n) + X_n \frac{\partial J_n}{\partial n} + \frac{J_q'(n)}{T_{\text{old}}} - \frac{H_n - n\mu_{\text{old}}}{T_{\text{old}}}\frac{\partial J_n}{\partial n} - \frac{J_n}{T_n}\frac{\partial H_n - nH_{\text{old}}}{\partial n}, \tag{A4}$$

where X_n is defined by Eq. (15). We can apply the rule for the derivative of a product on the part containing X_n,

$$\frac{\partial s_n}{\partial t} = J_q'(n)\,X_T - J_n \frac{\partial X_n}{\partial n} + \frac{J_q'(n)}{T_{\text{old}}} - \frac{H_n - n\mu_{\text{old}}}{T_{\text{old}}}\frac{\partial J_n}{\partial n} - \frac{J_n}{T_n}\frac{\partial H_n - nH_{\text{old}}}{\partial n} + \frac{\partial}{\partial n}J_n X_n. \tag{A5}$$

In this expression we can distinguish three contributions to the entropy differential: an entropy production $\sigma(n,t)$, an entropy flux $J_s(n,t)$ into the clusters from the old phase, and an entropy flux $J_{s,n}(n,t)$ along the n-coordinate,

$$\frac{\partial s_n}{\partial t} = \sigma + J_s - \frac{\partial}{\partial n}J_{s,n}. \tag{A6}$$

In our case the entropy flux in J/(s m^3 K) into the clusters from the old phase is

$$J_s = \frac{J_q'(n)}{T_{\text{old}}} - \frac{H_n - n\mu_{\text{old}}}{T_{\text{old}}}\frac{\partial J_n}{\partial n} - \frac{J_n}{T_n}\frac{\partial H_n - nH_{\text{old}}}{\partial n}. \tag{A7}$$

The entropy flux in J/(s m^3 K) along the n-coordinate is

$$J_{s,n} = -J_n X_n. \tag{A8}$$

The entropy production term $\sigma(n,t)$ in J/(s m^3 K) is given by

$$\sigma = J_q'(n)\,X_T - J_n \frac{\partial X_n}{\partial n}. \tag{A9}$$

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