Structuring Effects in Binary Nucleation: Molecular Dynamics Simulations and Coarse-Grained Nucleation Theory

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Abstract. Binary clusters formed by vapor-liquid nucleation are frequently nonhomogeneous objects in which components are not well mixed. The structure of a cluster plays an important role in nucleation and cluster growth. We demonstrate structuring effects by studying high-pressure nucleation and cluster growth in the n-nonane/methane mixture by means of molecular dynamics simulation. It is found that methane is squeezed out from the cluster core which is rich with n-nonane molecules. At typical simulation conditions - pressure 60 bar, temperature 240 K, nucleation rate \( J \approx 10^{26} \text{cm}^{-3} \text{s}^{-1} \) - the mole fraction of methane in the critical cluster reaches 80%, being much higher than its equilibrium bulk liquid fraction at the same pressure and temperature. These observations are supported by the recently formulated coarse-grained theory of binary nucleation.

Keywords: binary nucleation, adsorption, molecular dynamics, coarse-graining

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INTRODUCTION

Nonuniform structure of nuclei formed in the process of binary nucleation in a variety of mixtures play an important role in nucleation and cluster growth. Up to date the main theoretical tool describing binary nucleation is the binary classical nucleation theory (BCNT) [1] which considers a cluster to be an object with a rigid boundary and uniform intensive bulk liquid properties inside it. Meantime, it has been known for quite a while that predictions of BCNT can differ by many orders of magnitude from the experimental data and even lead to unphysical results violating the nucleation theorem (see e.g. [2] and references therein). One of the explanations of this discrepancy is the inability of BCNT to take into account adsorption effects resulting in a nonuniform cluster structure. Wilemski [3] proposed the revised BCNT based on the combination of capillarity approximation with the Gibbs concept of dividing surface. For a binary (and more generally, a multi-component) system the Gibbs construction is not just a useful tool (as in the single-component case) but a necessity, since it is impossible to choose a dividing surface for a mixture in such a way that adsorption of all species on it vanish. Taking into account adsorption
within the phenomenological approach does not resolve another deficiency of the capillarity approximation: the latter assumes that the surface energy of a cluster of any size can be described in terms of the plain layer surface tension. Obviously, for small clusters this concept loses its meaning.

In the present study we analyze structuring and size effects in binary nucleation using molecular dynamics simulation and theoretical considerations based on the recently formulated coarse-grained theory of binary nucleation [2, 4]. The system under study is the mixture of n-nonane and methane at high pressures.

**SIMULATION**

To simulate the binary mixture of n-nonane/methane we employ an interaction potential based on the Transferable Potentials for Phase Equilibrium - United Atom model developed by Steppmann et al. [5], in which the n-nonane molecule has 9 Lennard-Jones sites each representing a \( \text{CH}_2 \) or \( \text{CH}_3 \) group. It has a fixed bond length, harmonic angle bending potentials and dihedral torsion potentials. Simulations are performed using the *Moscito* [6] software package. To induce supersaturation we employ the earlier developed approach based on the expansion of the system utilizing the Joule-Thompson effect [7]. Expansion is simulated via a stepwise enlargement of the simulation box with short equilibration runs in between. The box is expanded by approximately 0.1 nm in all three dimensions until the desired density and pressure are reached (usually around 100 expansion steps are sufficient).

The n-nonane/methane mixture is characterized by a very low vapor molar fraction of n-nonane, \( \sim 10^{-4} \), so that the methane vapor fraction is \( \approx 1 \) while its fraction in the liquid phase at the given pressure \( p \) and temperature \( T \) varies between 0.05 and 0.45 - see Fig. 1. Calculations were performed with approximately 10^5 methane and 343 n-nonane molecules. The expansion starts at a supercritical density \( \rho(\text{CH}_4) = 25.9 \text{ mol/dm}^3 \), 300 K and supercritical pressure of 15-20 MPa. To detect clusters we use the Stillinger distance criterion combined with a life-time criterion [7]: two molecules belong to the cluster if their distance is less than \( 1.5 \sigma \) (where \( \sigma \) is the size of the n-nonane molecule) over the period of 2.5 ps. This is a residence time of a molecule in the Stillinger sphere and is larger than the time between collisions of two molecules. Nucleation rates are determined using the *Yasuioka-Matsimoto method* (for a detailed discussion see Ref. [2], Ch. 8) are found to be: \( J \sim 10^{26} - 10^{30} \text{cm}^{-3} \text{s}^{-1} \).

The question is: how the clusters, and especially the critical cluster, are structured. So far we are aware of only one experimental data on the structure of water/butanol nano-droplets [9]. These droplets exhibit a core-shell structure with the less volatile component (water) in the core and the more volatile one (butanol) on the surface. In this sense our simulation results are consistent with the experimental findings, though for a different system [10]. Figure 2(a) shows a typical snapshot of a cluster. Its core consists of n-nonane (green) surrounded by methane molecules (blue) located mainly on the outer shell. The cluster shown in Fig. 2(a) is beyond the critical size, but the critical clusters look similar. The reason for this core-shell structure is likely the minimization of the surface energy. This has a straightforward impact on the modeling of binary nucleation since the surface tension of the binary cluster is lower than that of the homogenous binary mixture in the bulk phase due to cluster structuring. Effectively, a lower surface energy leads to a higher
nucleation rate. Hence, nucleation theories using the bulk surface tension are expected to predict too low nucleation rates at least because of cluster structuring. In the phase diagram Fig. 1 we indicate the methane fraction in the critical cluster (green circle), for the nucleation conditions: \( p = 60 \text{ bar}, \ T = 240 \text{ K}, \ J \approx 10^{26}\text{cm}^{-3}\text{s}^{-1} \) which appears to be \( \approx 0.8 \) whereas the corresponding equilibrium molar fraction at these \( p \) and \( T \) is much lower: \( x_{\text{eq}}(p = 60\text{bar}, T = 248.15\text{K}) \approx 0.36 \).

**THEORY**

For theoretical study of the effects of adsorption we consider an arbitrary cluster of \( a \) (n-nonane) and \( b \) (methane) molecules with the bulk content \( (n_{a}^{0}, n_{b}^{0}) \) molecules. The bulk composition is characterized by the molar fraction of the more volatile component \( (b) \): \( x_{b}^{0} \). Within the general formalism of Gibbs dividing surface we present the total number of molecules of each component as \( n_{i} = n_{i}^{0} + n_{i}^{\text{exc}}, \ i = a, b \). The excess numbers \( n_{i}^{\text{exc}} \) are found by choosing the equimolar surface for the mixture, known also as the K-surface [11], which is defined through: \( \Sigma_{i=a,b} n_{i}^{\text{exc}} v_{i}^{0} = 0 \), where \( v_{i}^{0} \) is the partial molecular volume of component \( i \) in the liquid phase. Its combination with the Gibbs adsorption equation yields the excess numbers \( n_{i}^{\text{exc}} \). The Gibbs free energy of cluster formation \( g = \Delta G/k_{B}T \) (\( k_{B} \) is the Boltzmann constant) is a function of total numbers \( n_{a} \), as well as the bulk composition \( x_{b}^{0} [2, 4] \):

\[
g(n_{a}, n_{b}; x_{b}^{0}) = - \sum_{i=a,b} n_{i} \ln S_{i} - \sum_{i} n_{i} \ln \left[ \frac{y_{i}^{\text{eq}} P}{P_{\text{vap}}^{\text{eq}}(x_{b}^{0}, T)} \right] + \theta_{\text{micro}}[n_{\mu}^{0} - 1] \tag{1}
\]

Here the first term is the nonequilibrium part of \( g \) containing the supersaturations \( S_{i} \) of components. The equilibrium part \( g_{\text{eq}} \) consists of the bulk and surface contributions. The bulk contribution (second term in (1)) reflects the difference in the bulk composition between the given cluster and the bulk liquid at \( p \) and \( T \); \( P_{\text{vap}}^{\text{eq}}(x_{b}^{0}, T) \) is the total pressure above the bulk binary solution with the composition \( x_{b}^{0} \); \( y_{i}^{\text{eq}}(x_{b}^{0}, T) \) is the corresponding vapor fraction. The surface contribution (last term in (1)) is obtained using coarse-graining of the configuration integral of the binary \( (n_{a}, n_{b}) \)-cluster. It is based on tracing out the degrees of freedom of the more volatile component \( (b) \).
FIGURE 2: Cluster structure. (a) Snapshot of a big cluster in MD simulations. The core consists mainly of n-nonane (green) while methane is located mainly on the outer shell. (b) Methane fraction in the critical cluster at $p = 60$ bar, $T = 240$ K at various nucleation rates predicted by CGNT [4] (open circles). Also shown is the result of MD simulations (closed circle). Arrow points at equilibrium methane liquid fraction: $x_{\text{CH}_4, \text{eq}} \approx 0.36$

As a result one is left with the configuration integral of the single-component cluster of pseudo-$\alpha$ molecules with the interaction energy implicitly depending on the fraction of $\beta$-molecules in the original binary cluster. This $n_\beta$-cluster is treated by means of the mean-field kinetic nucleation theory [2]: $\theta_{\text{micro}, \alpha}(\chi^\alpha_{\beta})$ is the free energy per surface particle, $n^\alpha_{\beta}(n_\alpha, x_{\text{CH}_4})$ is the number of surface particles in the $n_\beta$-cluster. Critical cluster corresponds to the saddle point of $g$ in the space of total numbers $n_\alpha, n_\beta$ (for details see Ref. [2]). Predictions of this model, termed Coarse-Grained Nucleation Theory (CGNT), for the methane fraction in the critical cluster, $x_{\text{CH}_4}^{\text{crit}}$, at $p = 60$ bar, $T = 240$ K and various nucleation rates are shown in Fig. 2(b). At high rates $J \sim 10^{24}$ cm$^{-3}$s$^{-1}$ $x_{\text{CH}_4}^{\text{crit}}$ is consistent with the values found in our MD simulations.

REFERENCES
