Heterogeneous nucleation of molecular and dipolar fluids

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Abstract

We present a summary of the main properties of an interaction site model for heterogeneous nucleation of molecular and dipolar fluids on charged hard spheres. Density functional theory is used to calculate the work of formation of critical nuclei formed on small spherical particles. Nucleation rates depend on the size and charge of the central seed. Sign preferences lead to rates of nucleation that differ by several orders of magnitude.

1. Introduction

The formation of a new phase on the surface of a foreign particle or an ion is a problem of great interest in atmospheric science. The large concentration of aerosol particles in the atmosphere favors heterogeneous nucleation, and ion-induced nucleation occurs frequently in the stratosphere. Condensation on charged particles is particularly interesting because nucleation rates depend on the sign of the charge [1–3].

The classical theory of heterogeneous nucleation was originally developed by Volmer [4] and Turnbull [5]. Fletcher [6] extended these results to nucleation on aerosol particles, and Volmer [4] addressed the problem of ion nucleation within the capillarity approximation. Neither the detailed behavior of nucleation from the vapor on small particles nor the dependence of nucleation rates on ion polarity are explained by the classical approach.

In the past few years, density functional theory has been used to develop a nonclassical approach to nucleation [7,8]. The theory assumes that any nucleating entity can be considered as an inhomogeneous fluid, and the work of formation is then obtained from

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the structure of a free energy functional. The predicted dependence of the nucleation rates on supersaturation and temperature agrees qualitatively with experimental results for several systems.

We have also applied the density functional formalism to nucleation in Stockmayer (Lennard-Jones plus point dipole) fluids [9], and here we introduce a new model based on the interaction site formalism [10] to investigate heterogeneous nucleation of molecular and dipolar fluids on small neutral and charged hard spheres. The outline of the paper is as follows. In Section 2 we introduce the theory and the basic model, summarizing its bulk and interfacial properties in Section 3. A more detailed description of these properties will be published elsewhere [11]. Our results for heterogeneous nucleation on small seed particles are described in Section 4, followed by conclusions in Section 5.

2. Density functional formalism

We consider a one-component system of interacting diatomic molecules composed of two tangent or overlapping spheres with diameters \( \sigma_{11} \) and \( \sigma_{22} \), and centers located at a fixed bond length \( L \). The free energy of the fluid in a weighted density approximation can be written as [10,12,13]

\[
\beta_v F[\rho_\alpha(r)] = \sum_\alpha \int d\mathbf{r} \rho_\alpha(\mathbf{r}) \ln f_\alpha(\mathbf{r}) - \int \int d\mathbf{r} d\mathbf{r}' s(|\mathbf{r} - \mathbf{r}'|) f_1(\mathbf{r}) f_2(\mathbf{r}') \\
+ \int d\mathbf{r} \nabla \cdot \left( \tilde{\mathbf{v}}(\mathbf{r}) \right) \rho_\alpha(\mathbf{r}) + \frac{1}{2} \beta_v \sum_{\alpha,\beta} \int \int d\mathbf{r} d\mathbf{r}' \phi_\alpha^\beta(\mathbf{r} - \mathbf{r}') \rho_\alpha(\mathbf{r}) \rho_\beta(\mathbf{r}') \\
+ \beta_v \sum_\alpha \int d\mathbf{r} V_{\alpha\alpha}(\mathbf{r}) \rho_\alpha(\mathbf{r}) \quad (\alpha, \beta = 1, 2)
\]  

(1)

with \( \beta_v = 1/kT \), where \( k \) is Boltzmann's constant and \( T \) is the absolute temperature. Here, \( \rho_\alpha(\mathbf{r}) \) represents the local mean density which is taken to be

\[
\rho_\alpha(\mathbf{r}) = \frac{1}{v_{\alpha\alpha}} \sum_\alpha v_\alpha \rho_\alpha(\mathbf{r}).
\]  

(2)

where \( v_{\alpha\alpha} = \sum_\alpha v_\alpha \) is the molecular volume, and \( v_\alpha \) is the volume associated with site \( \alpha \).

The several factors on the right-hand side of Eq. (1) account for different contributions to the free energy of the system: ideal free energy, entropic decrease from the presence of intramolecular correlations \( s(r) \) [10], short-range repulsive interactions [14], long-range site–site interactions \( \phi_\alpha^\beta(r) \), and external potential \( V_{\alpha\alpha}(r) \) effects, respectively.

The equilibrium properties of the non-uniform fluid can be obtained by minimizing Eq. (1) with respect to \( \rho_\alpha(\mathbf{r}) \) and the "fictitious" site activities \( f_\alpha(\mathbf{r}) \) at constant temperature \( T \) and volume \( V \), with the restriction

\[
N_\alpha = \int d\mathbf{r} \rho_\alpha(\mathbf{r}) = N_\beta \quad (\alpha = 1, 2)
\]  

(3)
for the total number of atoms. The minimization leads to the Euler–Lagrange equations

\[ f_\alpha(r) = e^{\beta \lambda_\mu(r) - V_\alpha(r) - V_n(r)} \]

(4)

with

\[ \beta \lambda_\alpha(r) = \left( \frac{\lambda_\alpha}{\lambda_m} \right) \left( \psi(\tilde{n}(r)) \right) + \lambda_\alpha \int dr' \frac{\partial \psi(\tilde{n}(r))}{\partial \rho_\alpha(r')} \rho_\alpha(r') w_\alpha(|r - r'|) \]

\[ + \beta \sum_\beta \int dr' \phi_{\alpha\beta}(r - r'| \rho_\beta(r')) \]

(5)

and

\[ \rho_\alpha(r) = f_\alpha(r) \int dr' s(|r - r'|) f_\beta(r') \]

(6)

that can be solved given adequate boundary conditions.

In the limit of uniform densities \( \rho_1 = \rho_2 = \rho_m \) (\( \eta_m = \nu m \rho_m \)) the grand potential of the system \( \Omega = F - \mu N \) can be expressed as

\[ \frac{\Omega}{V} \rho_m = kT \rho_m [\ln \rho_m - 1 + \psi(\eta_m)] - \frac{1}{2} \alpha \rho_m^2 - \mu \rho_m = -P \]

(7)

with

\[ \alpha = -\sum_{\alpha\beta} \int dr \phi_{\alpha\beta}(r) \]

(8)

and \( \mu \) the chemical potential.

The atoms in our model fluid interact via a Lennard-Jones potential with the additional coulombic interaction of embedded point charges. The perturbative part of the interaction potential is then given by

\[ \phi_{\alpha\beta}(r) = \begin{cases} \phi_{\alpha\beta}^L(r), & r \leq \sigma_{\alpha\beta}, \\ \phi_{\alpha\beta}^L(r) + \phi_{\alpha\beta}^\epsilon(r), & r > \sigma_{\alpha\beta}, \end{cases} \]

where \( \phi_{\alpha\beta}^L(r) \) denotes the Lennard-Jones potential

\[ \phi_{\alpha\beta}^L(r) = 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right] \]

(\( \alpha, \beta = 1, 2 \))

(9)

and \( \phi_{\alpha\beta}^\epsilon(r) \) is the coulombic potential for two point charges \( q_\alpha \) and \( q_\beta \) in vacuum,

\[ \phi_{\alpha\beta}^\epsilon(r) = \frac{q_\alpha q_\beta}{r}. \]

(10)

The cross Lennard-Jones parameters \( \epsilon_{\alpha\beta} \) and \( \sigma_{\alpha\beta} \) satisfy the combination rules

\[ \sigma_{\alpha\beta} = \frac{1}{2} (\sigma_{\alpha\alpha} - \sigma_{\beta\beta}), \]

\[ \epsilon_{\alpha\beta} = (\epsilon_{\alpha\alpha} \epsilon_{\beta\beta})^{1/2}, \]

(11)

and the charges on different atoms of the same molecule are chosen to simulate an effective dipole moment \( (q_1 = -q_2) \).
Finally, the Helmholtz excess free energy per particle of the reference hard-body system $\Psi(\eta)$ is estimated from the well known Carnahan-Starling expression for a hard-sphere fluid [15]

$$\Psi(\eta) = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2}. \tag{12}$$

3. Bulk and interfacial behavior

The model fluid described by the thermodynamic potential $\Omega[\rho_m]$ in Eq. (7) undergoes a liquid–vapor phase separation for $\alpha > 0$ and temperatures lower than the critical value $T_c$. The structure of the phase diagram depends on the values of the dimensionless parameters $\varepsilon_{22}/\varepsilon_{11}$, $\sigma_{22}/\sigma_{11}$, and $L/\sigma_{11}$. The effect of the bare electrostatic interactions between dipolar molecules cancels out in the uniform fluid and bulk features are independent of the values of the dimensionless site charges $q_m/(\varepsilon_{11}\sigma_{11})^{1/2}$.

For any pair of coexisting densities $\rho_m^l$ and $\rho_m^v$, the associated equilibrium profiles ($\rho_m(r) = \rho_m(z)$) and surface tension can be obtained by solving Eqs. (4) and (6). The equilibrium profiles are the result of an energy vs entropy competition. In general, less attractive energy is lost when the atomic sites with the weaker “effective” interaction $\alpha$ are located at the surface. The energetic cost of a different configuration can be compensated, however, by reducing the entropic loss caused by packing in the liquid for systems with $\sigma_{22}/\sigma_{11} < 1$.

Charging the atomic sites to generate a dipole moment reduces the molecular orientation at the interface. The resulting surface tension is higher than the surface tension of the corresponding nonpolar case, but the effect is almost negligible within the range of site charges where stable solutions can be found: $|q/(\varepsilon_{11}\sigma_{11})^{1/2}| < 1$.

4. Heterogeneous nucleation

The planar interface becomes unstable away from coexistence, but between the binodal and the spinodal critical nuclei appear as saddle point solutions to the grand potential in an open system [7,8]. The same solutions become minima of the associated Helmholtz free energy when the system is enclosed in a spherical container of volume $V$, with the total number of atoms fixed ($N_1 = N_2 = N_m$) [16]. The properties of the external metastable vapor ($\rho, P, \mu$) are then obtained by demanding no density discontinuity at the bounding surface.

In this work we consider the condensation of metastable vapors on nucleating centers of molecular size. The nucleating agent is represented by a hard sphere of radius $R_c$ fixed at the center of the droplet. The interaction between this seed particle and the atomic sites of the surrounding molecules is treated as a spherically symmetric external potential $V_{ext}^n(r)$. This quantity is assumed to be composed of a hard-core repulsive part, plus the electrostatic interaction
Fig. 1. The density profile of a simple Lennard-Jones system \((L/\sigma_{11} = 0)\) in contact with a central hard sphere of radius \(R_c/\sigma_{11} = 1.0\) is compared here with the corresponding total density profile \((\rho_1(r) + \rho_2(r))\) of a symmetric dumb-bell \((\epsilon_{11}/\epsilon_{22} = 1.0, \sigma_{22}/\sigma_{11} = 1.0, L/\sigma_{11} = 1.0)\).

\[
V_{eff}(r) = \frac{Q_c q_n}{r},
\]

when a point charge \(Q_c\) is placed at the center of the seed. The site distribution functions \(\rho_n(r)\) are obtained by assuming homogeneous coating of the central particle by the fluid. The barrier height to heterogeneous nucleation \(\Delta\Omega^*\) is given by the work of formation of a critical nucleus from a vapor-solvated seed particle.

Let us first consider the case of heterogeneous nucleation on a neutral center. This allows us to analyze the effect of pure repulsive hard-core interactions. These are essentially responsible for the non-monotonic structure of the site density profiles \(\rho_n(r)\) in Fig. 1. The total density profiles of critical nuclei at the same supersaturation for a symmetric dumb-bell \((\epsilon_{22}/\epsilon_{11} = 1, \sigma_{22}/\sigma_{11} = 1)\) and a simple Lennard-Jones fluid \((L/\sigma_{11} = 0)\) are included here. The presence of intramolecular correlations in the former case enhances both the adsorption of particles at the surface of the central sphere and the molecular ordering around the seed. For a given reduced temperature \(T_r\) and supersaturation \(S\) the number of particles in the critical nucleus increases with \(L/\sigma_{11}\), but the barrier to nucleation on a particle of radius \(R_c/\sigma_{11}\) decreases when the bond length increases. Excluded volume effects in the liquid and the higher surface adsorption
at the surface of the seed reduce the work of formation of the critical droplet as we move toward the case of molecules composed of tangent spheres. For a simple Lennard-Jones fluid (united-atom limit) the entropic loss caused by packing and the energetic cost of a larger interfacial area dominate the heterogeneous nucleation on hard spheres; the work of formation on a spherical particle is always greater than the work of formation without a seed, and increases monotonically with $R_c$. Thus, nucleation proceeds homogeneously in all cases.

This behavior changes, however, as the bond length $L_i/\sigma_{11}$ is increased. Molecular adsorption at the surface of the central particle in systems with $L_i/\sigma_{11} > 0$ plays a relevant role in the heterogeneous nucleation of the fluid. As Samborski et al. found in their study of simple Lennard-Jones fluids in contact with spherical cavities [17], we find that for molecular systems the density at contact $\rho_n(R_c)$ exhibits a broad maximum as a function of the seed size not far from $R_c/\sigma_{11} \approx 1$. This behavior can be detected by following the density profiles for a symmetric dumb-bell in Fig. 2. Homogeneous coating by the fluid for nucleation on particles of size close to $R_c/\sigma_{11} \approx 1$ thus appears to be a reasonable assumption.

The peak in surface adsorption at the central particle strongly affects the rates of heterogeneous nucleation of molecular systems. Fig. 3 depicts the nucleation rate $J_{DFT}$
Fig. 3. Rate of nucleation as a function of the radius of the nucleating agent $R_c/\sigma_{11}$ for a polar dumb-bell ($\epsilon_{22}/\epsilon_{11} = 0.8$, $\sigma_{22}/\sigma_{11} = 1.0$, $L/\sigma_{11} = 1.0$, $q_1/(\epsilon_{11}\sigma_{11})^{1/2} = 0.8$) at $T_c = 0.5$. The central particle has no charge ($Q_c = 0$).

as a function of the radius $R_c/\sigma_{11}$ for a polar asymmetric dumb-bell ($\epsilon_{22}/\epsilon_{11} < 1$) at constant supersaturation. In the absence of a central charge ($Q_c = 0$), quantitatively similar results are obtained for equivalent polar and nonpolar molecular systems. The rate of nucleation is evaluated following the prescription [18]

$$J_{DFT} = J_0 e^{-\Delta\mu^*/kT},$$

(14)

with

$$J_0 = \frac{\rho_v^2}{\rho_{lm}^1} \left( \frac{2\gamma}{\pi m} \right)^{1/2},$$

(15)

where $m$ is the molecular mass. The density of the metastable vapor is $\rho_v$, while $\rho_{lm}^1$ is the coexistence liquid density at temperature $T$. The properties of nitrogen are used to generate results in common physical units. Given that our main interest is to analyze the impact of the work of formation of critical nuclei on the rates of nucleation, we assume that the density of nucleating agents is equal to the density of the metastable vapor $\rho_v$ in our calculations.
The nucleation rate of molecular dumb-bells on hard-spheres is a non-monotonic function of the size of the seed. For small radii \( R_c \) the barrier to nucleation increases slightly over the homogeneous limit \( (R_\infty = 0) \) until the adsorption at the surface of the central sphere favors heterogeneous nucleation. The adsorption peak can cause an increase of several orders of magnitude in the rates. In the case of molecular dumb-bells, the adsorption at the surface of small particles optimizes the energetic contributions from attractions between molecules. This effect overcomes the entropic loss caused by packing and the energetic cost of a larger interfacial area. As a consequence, the work of formation of the droplet decreases and reaches a minimum when the density at contact \( \rho_\infty(R_c) \) is close to its maximum. As the seed particle gets larger, adsorption decreases (see Fig. 2), the molecules at the surface are farther apart, and entropic effects take over. The barrier to heterogeneous nucleation starts growing because of the high cost of the internal surface and the larger vapor-exposed interface; homogeneous nucleation occurs faster than heterogeneous nucleation when the central particle exceeds a critical size. For the range of model parameters that we explored in this study, the peak effect increases the rates by a factor of \( 10^5 \text{--} 10^7 \), and its influence decreases slowly with supersaturation. This non-monotonic behavior strongly depends on the molecular length \( L/\sigma_{11} \) and disappears upon fusing the atomic spheres.

When a central charge \( Q_c \) is embedded in the seed particle, sign preferences for the heterogeneous nucleation of polar molecules \( (|q_0| > 0) \) are found when the site-site interactions are asymmetric \( (\varepsilon_{22}/\varepsilon_{11} < 1, \sigma_{22}/\sigma_{11} < 1) \). In the symmetric case nucleation is equally enhanced by opposite charges on small particles. We consider the following results indicative of the expected nucleation behavior of dipolar fluids about ions. Caution should be applied to any conclusion based on these results, however, as long as we are limited to central charges \( Q_c/(\varepsilon_{11}\sigma_{11})^{1/2} \) that correspond to small fractions of the electronic charge.

Figs. 4a and 4b show the site density profiles \( \rho_\infty(r) \) for the critical nuclei of a polar asymmetric dumb-bell \( (\varepsilon_{22}/\varepsilon_{11} < 1) \) on negative and positive charges, respectively. In the absence of a central charge, Lennard-Jones interactions force the molecular dipoles at the surface to point toward the center of the droplet \( (q_2 < 0) \). Nucleation on a negative charge favors this configuration (Fig. 4a), while it tends to be reversed by the positive charge (Fig. 4b). This competition is reflected in the rates of heterogeneous nucleation in Fig. 5, which show a clear preference for nucleation on the negative charge for all values of \( Q_c \). In fact, the higher nucleation rate over homogeneous nucleation associated with the positive charge is mainly due to the effect of the central hard core. The sign preference on charge-induced nucleation can be enhanced by increasing the central charge \( Q_c \), the molecular dipole moment (determined by \( q_0 \) and \( L \)), and the anisotropy of the interactions. The effect decreases as the supersaturation and the size of the central charge are increased. This latter effect is expected not only because of surface desorption but also because of the increase of the charge–dipole separation. As in the case of a “neutral” seed, increasing the radius \( R_c \) beyond a certain point starts favoring homogeneous nucleation but the critical size is also sign dependent.
5. Conclusions

Heterogeneous nucleation from the vapor on particles of atomic size appears to be highly sensitive to the nature of the condensed fluid and the size of the seed. Both factors can cooperate to induce unexpectedly high surface adsorption that reduces the barrier to nucleation.

For dipolar fluids, preferred molecular orientations at the liquid–vapor interface are the source of the sign preference for nucleation on small charged spheres. Recent work by Kusaka et al. [19] associates this preference with different strengths of the monopole–dipole interaction in ion-induced nucleation of anisotropic molecules. Both models predict the same qualitative effects on changing the charge or the radius of the central particle, however.

There are contradictory experimental results on the influence that the chemical makeup of the ions has on the process of nucleation [3,20]. The interaction site model predicts nucleation rates that depend strongly on the size and charge of the central seed. Additional work is needed to evaluate to what extent these results apply to real systems.
Fig. 4 — continued.

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References

Fig. 5. Rate of nucleation as a function of the central charge $Q_c/(e_{11}\sigma_{11})^{1/2}$ ($R_c/\sigma_{11} = 1.0$) at fixed supersaturation $S = 2.914$ for a polar dumb-bell with $\epsilon_{11}/\epsilon_{22} = 0.8$, $\sigma_{22}/\sigma_{11} = 1.0$, $L/\sigma_{11} = 1.0$, $q_1/(e_{11}\sigma_{11})^{1/2} = 0.8$. $J_n$ indicates the calculated rate for homogeneous nucleation at the given conditions.