Formation of droplets on nonvolatile soluble particles

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Density functional theory is used to analyze the stability and structural properties of droplets formed by the condensation of a volatile solvent on a soluble fluid particle composed of a fixed number of molecules of a second species with extremely low volatility. Interaction parameters between the species are chosen to ensure that the soluble particle is completely wetted by the solvent. We study the properties of miscible and partially miscible mixtures. Droplets with a partially soluble core may exhibit a solubility transition at a vapor pressure above the vapor pressure of the bulk saturated solution. This transition resembles deliquescence in water soluble salts, but exhibits distinctive features. The soluble particle dissolves spontaneously at a well defined value of the supersaturation and the relative change in the droplet’s size at the transition is greater for the smaller particles. Comparisons of our results with the predictions of Köhler theory of activation show that the capillarity approximation overestimates the vapor pressure of the droplets, particularly in small systems. © 2003 American Institute of Physics. [DOI: 10.1063/1.1613937]

I. INTRODUCTION

The properties of important physical systems depend on the structure and stability of droplets that contain trapped species that are partially soluble in the surrounding phase. Such is the case of emulsions and microemulsions, and atmospheric clouds. In this latter case, soluble and insoluble particles can act as condensation nuclei for water and other atmospheric gases and the resulting droplets have thermodynamic properties that vary with the relative humidity of the atmosphere.

A variety of theoretical approaches derived from the capillarity approximation have been used to study and analyze the properties of droplets that contain a soluble core of a nonvolatile species. Such studies have been central to the understanding of processes such as the deliquescence of water soluble salts, and the heterogeneous nucleation of atmospheric clouds. However, these types of macroscopic approaches are limited by their crude representation of the bulk and interfacial properties of small systems.

In the last several years, density functional theory has been used to introduce atomic level effects in models of molecular aggregates such as those formed during the nucleation of stable phases in simple and complex fluids. In particular, the theory has been successfully applied to the study of homogeneous nucleation in multicomponent systems, and heterogeneous nucleation of simple fluids on planar surfaces and insoluble particles. The density functional approach has also become a useful tool in identifying the range of applicability of theories based on the capillarity approximation.

In this paper, we apply density functional theory to study

II. DENSITY FUNCTIONAL THEORY

Let us consider a simple model for a binary mixture in which intermolecular interactions between molecules in the system are approximated using hard-sphere perturbation
theory. The Helmholtz free energy of the mixture can then be expressed as the sum of a local hard-sphere term and a long-range attraction term:\textsuperscript{16,17}

\[
F[\rho_1(r), \rho_2(r)] = \int d\mathbf{r} f_h[\rho_1(r), \rho_2(r)] + \frac{1}{2} \sum_{ij} \int d\mathbf{r} d\mathbf{r}' \phi_{ij}(|\mathbf{r} - \mathbf{r}'|) \rho_i(r) \rho_j(r')
\]

\[(i, j = 1, 2),
\]

where \(F[\rho_1(r), \rho_2(r)]\) is a functional of \(\rho_1(r)\) and \(\rho_2(r)\), the local number densities of species \(i\). The local Helmholtz free energy density \(f_h[\rho_1(r), \rho_2(r)]\) is taken to be that of the binary Carnahan-Starling form of Mansoori et al.,\textsuperscript{23} which is a function of the local densities \(\rho_i(r)\) and the packing fraction

\[
\eta(r) = \frac{\pi}{6} \sigma_{ii}^3 \rho_i(r) \quad (i = 1, 2),
\]

for spherical particles of diameter \(\sigma_{ii}\). The long-range interaction between particles in the system is characterized by the simple attractive potential

\[
\phi_{ij}^a(r) = \begin{cases} 
0 & \text{if } r \leq \sigma_{ij} \\
-4 \epsilon_{ij} (\sigma/r)^6 & \text{if } r > \sigma_{ij},
\end{cases}
\]

where \(\sigma_{ij}\) and \(\epsilon_{ij}\) represent energy and length interaction parameters. For simplicity we assume that all particles have the same size (\(\sigma_{11} = \sigma_{22} = \sigma_{12} = \sigma\)) in our calculations. The values of the energy parameters \(\epsilon_{ij}\) are chosen to mimic the properties of the mixtures of interest.

The equilibrium properties of the mixture can be obtained by minimizing the grand potential

\[
\Omega[\rho_1(r), \rho_2(r)] = F[\rho_1(r), \rho_2(r)] - \sum_i \mu_i \int d\mathbf{r} \rho_i(r)
\]

at constant temperature \(T\), volume \(V\), and chemical potentials \(\mu_i\), under appropriate boundary conditions.\textsuperscript{24} The minimization leads to Euler-Lagrange relations of the form

\[
\mu_i = \mu_i^b[\rho_1(r), \rho_2(r)] + \sum_{j=1}^{2} \int d\mathbf{r} \phi_{ij}^b(|\mathbf{r} - \mathbf{r}'|) \rho_j(r')
\]

\[(i = 1, 2),
\]

where \(\mu_i^b[\rho_1(r), \rho_2(r)]\) is the local chemical potential of the \(i\)th component in the reference hard-sphere fluid. This system of coupled equations can be solved by standard iteration procedures.

The bulk properties of a homogeneous mixture are derived by working in the limit of uniform densities \(\rho_1\) and \(\rho_2\), where

\[
\mu_i = \mu_i^b[\rho_1, \rho_2] - \sum_{j=1}^{2} \alpha_{ij} \rho_j - 2 \sum_{i=1}^{2} \mu_i \rho_i = -P,
\]

and

\[
\mu_i = \mu_i^b[\rho_1, \rho_2] - \sum_{j=1}^{2} \alpha_{ij} \rho_j - \sum_{i=1}^{2} \mu_i \rho_i = -P,
\]

with

\[
\alpha_{ij} = -\frac{1}{3} \int d\mathbf{r} \phi_{ij}^b(r) = \frac{4\pi}{3} \epsilon_{ij} \sigma^3 (i, j = 1, 2).
\]

For any pair of coexisting phases \(\alpha\) and \(\beta\) we have

\[
\mu_i^\alpha[\rho_1^\alpha, \rho_2^\alpha, T] = \mu_i^\beta[\rho_1^\beta, \rho_2^\beta, T],
\]

\[
P^\alpha[\rho_1^\alpha, \rho_2^\alpha, T] = P^\beta[\rho_1^\beta, \rho_2^\beta, T].
\]

The structure of the corresponding phase diagram depends on the value of two reduced energy parameters, defined in this work as \(\epsilon_{22}^* = \epsilon_{22}/\epsilon_{11} \) and \(\Lambda^* = \Lambda/\epsilon_{11} = (\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/\epsilon_{11}\). The first parameter, \(\epsilon_{22}^*\), is a measure of the relative volatility of the two components while \(\Lambda^*\) is a measure of the energy of mixing of molecules of different species.

The equilibrium profiles for every pair of coexisting phases at pressure \(P = -\Omega_b/V\) and temperature \(T\) are determined by the Euler-Lagrange relations in Eq. (4). These profiles can be used to evaluate the surface tension, \(\gamma\), of the corresponding interface

\[
\gamma A = \Omega[\rho_1(r), \rho_2(r)] - \Omega_b,
\]

where \(A\) is the interfacial area. On the other hand, the properties of spherical droplets can be obtained by working in a closed system of volume \(V\) with perfect nonwetting-nondrying walls.\textsuperscript{25} The solution profiles \(\rho_i(r)\) and \(\rho_2(r)\) correspond then to a minimum of the Helmholtz free energy in Eq. (1) for a system with a fixed number of particles

\[
N_i = \int d\mathbf{r} \rho_i(r) \quad (i = 1, 2).
\]

Under these thermodynamic conditions, the Euler-Lagrange relations, Eq. (4), take the form

\[
\mu_i^b[\rho_1(r), \rho_2(r)]
\]

\[
= kT \ln(N_i) - \frac{1}{2} \int d\mathbf{r} \phi_{ij}^b(|\mathbf{r} - \mathbf{r}'|) \rho_j(r')
\]

\[
- kT \int d\mathbf{r} \rho_i(r)
\]

\[
\times e^{-[\mu_i^b[\rho_1(r), \rho_2(r)] + \sum_{j=1}^{2} \int d\mathbf{r} \phi_{ij}^b(|\mathbf{r} - \mathbf{r}'|) \rho_j(r')] / kT},
\]

where \(k\) is Boltzmann’s constant. The solutions for this set of coupled equations for given \(N_i\) correspond to the density profiles of a stable droplet with an excess number of particles,

\[
n_i = \int d\mathbf{r} (\rho_i(r) - \rho_i^b) \quad (i = 1, 2),
\]

and the work of formation

\[
\Delta \Omega^b = \Omega[\rho_1(r), \rho_2(r)] - \Omega_b[\rho_1^a, \rho_2^a],
\]

where \(\rho_i^b\) is the density of component \(i\) in the surrounding vapor.
III. RESULTS AND DISCUSSION

In the present work, we study the properties of spherical droplets formed by the condensation of a volatile component on the surface of a soluble particle composed of a fixed number of atoms of a second species with a very low volatility. The relative volatility of the two components is determined by the value of $\varepsilon_{22}^*/\varepsilon_{11}^*$ in our model. We use the value $\varepsilon_{22}^*=2.0$ in all our calculations, which leads to a saturation vapor pressure for pure component 2 (solute) that is $10^5$ times smaller than the saturation vapor pressure for pure component 1 (solvent) at the same temperature. All of our results correspond to the same reduced temperature $T^*=kT/\varepsilon_{11}=0.8$ and are illustrative of the behavior of the system at temperatures far below the liquid-vapor critical point of the pure components (in particular, $kT/\varepsilon_{11}=1.5093$ for the solvent). Under these conditions, the solubility of the nonvolatile component in the condensing fluid is essentially determined by the value of the mixing energy parameter $\Lambda^*$.

We have studied the structural and thermodynamic properties of condensed droplets on soluble and partially soluble particles of a fixed size $n_2\approx N_2$, as a function of the vapor supersaturation, defined as:

$$S=P_v^o/P_1^o,$$

where $P_v^o$ is the partial pressure of the solvent in the surrounding vapor (for which all practical purposes is equal to the total vapor pressure), and $P_1^o$ is the saturation vapor pressure of the pure solvent at the same temperature. This conventional definition of the supersaturation leads to a value of $S=1$ for the thermodynamic conditions at which the pure solvent coexists with its vapor. The behavior of the surrounding vapor is almost ideal and the value of $S$ is very close to the solvent’s thermodynamic activity in the vapor, $a_1^o=\exp(\mu_1^o/\mu_1)$, where $\mu_1^o$ is the chemical potential of the pure saturated vapor.

Given our selection of interaction parameters, the surface tension for the solute, $\gamma_{12}^{s}=5.90$ (with $\gamma^s=\gamma_0^s/\varepsilon_{11}$), is much higher than the surface tension for the solvent, $\gamma_{11}^{s}=1.34$, at the same temperature. However, the value of the interfacial tension between segregated liquid phases in partially miscible systems is relatively small, and the phase that is rich in component 1 completely wets the interface between the phase that is rich in component 2 and the vapor at the triple point. Thus, spherical droplets with a high solute concentration exhibit strong surface adsorption of component 1 even at very low supersaturations, as illustrated by the density profiles in Fig. 1 for a typical droplet at low values of $S$. The growth of a droplet in these systems proceeds via the formation of a liquid film on the entire surface of the soluble particle, with a thickness that increases with supersaturation. We have therefore assumed that the geometry of all our droplets is spherical, even at very low supersaturations where one could more realistically expect nucleation to proceed via the formation of microlenses of the liquid on the surface of the soluble particle with a nonzero contact angle. At these low supersaturations, or when the wetting condition is not satisfied, the geometry of the system will not remain spherical.

A. Miscible mixtures

Let us first study the behavior of droplets formed by two species that are fully miscible at all compositions and generate mixtures that deviate little from ideality, as illustrated by the semilinear behavior of the solvent’s thermodynamic activity, $a_1^o=\exp(\mu_1^o/\mu_1)$, as a function of the mole fraction $x_1=\rho_1/(\rho_1+\rho_2)$ for binary solutions with $\Lambda^*=-0.1$ in Fig. 2: $\mu_1^o$ represents the chemical potential of species 1 in...
the binary mixture coexisting with its vapor.

As shown in Fig. 3, the size of droplets formed on a soluble particle of size \( n_2 \) increases monotonically with increasing supersaturation along the branch AB in this figure. The growth factor \( g_j = R/R_o \) is calculated as the ratio of the radius of the droplet \( R \), defined by the location of the outer inflection point in the density profile of species 1 (see Fig. 1), to the radius of the dry soluble particle calculated from the density profile for species 2 in the limit \( S = 0 \). In this type of miscible mixtures, the soluble particle dissolves gradually in the condensing liquid as the supersaturation is increased.

In order to analyze the stability of the droplets at a given supersaturation, we devised a method to estimate the height and shape of the free energy barrier for the formation of the different aggregates. Since a droplet can be thought of as a relatively isolated group of molecules, its free energy should depend mainly on the interactions among the molecules that make it up, but not on the surrounding vapor pressure. Hence, in a first approximation, given the work of formation \( \Delta \Omega^* \) for a droplet with \( n_1 \) and \( n_2 \) molecules in equilibrium with its surrounding vapor, with chemical potentials \( \mu_1^* \) and \( \mu_2^* \), the free energy needed to form the same aggregate at different chemical potentials \( \mu_1 \) and \( \mu_2 \) can be approximated by\(^{35}\)

\[
\Delta \Omega = \Delta \Omega^* + n_1 (\mu_1^* - \mu_1) + n_2 (\mu_2^* - \mu_2).
\]  

In particular, the work of formation of a dry particle of solute with size \( n_2 \) will be given by

\[
\Delta \Omega_{dry} = \Delta \Omega_{dry}^* + n_2 (\mu_{2, dry}^* - \mu_2).
\]  

and the free energy of formation of the droplet on an existing soluble core at any supersaturation \( S = \exp(\mu_1 - \mu_1^*) \) can then be estimated by taking the difference

\[
\Delta \Omega = \Delta \Omega^* - \Delta \Omega_{dry}^*.
\]  

We illustrate in Fig. 4 the behavior of \( \Delta \Omega/kT \) at various supersaturations for droplets with \( n_2 = 250 (R_o = 4.10 r) \). In general, droplets along the branch AB in Fig. 3 correspond to minima of the free energy and represent stable droplets. However, once the value of \( S = 1 \), the aggregates become metastable with respect to the homogeneous solvent phase and the free energy develops a maximum at the size of the critical droplet for nucleation at that value of \( S \). The height of the energy barrier to nucleation is given by the difference between the values of \( \Delta \Omega \) at the two extrema, and the properties of the associated critical cluster correspond to those of the droplet on the branch BC in Fig. 3 with the same supersaturation. Aggregates along this branch are thus in unstable equilibrium with the vapor. The barrier to nucleation vanishes when the supersaturation reaches the value at point B (\( S_B \)). At this supersaturation the soluble particle is “activated,” a term introduced by Köhler\(^3\) to indicate that no energy barrier needs to be surmounted to induce the condensation of the solvent; any droplet will grow spontaneously beyond this point. As can be seen in Fig. 3, the supersaturation needed to activate the soluble particle increases as its size decreases.

This general behavior can be predicted using the conventional Köhler theory of activation based on the capillarity approximation.\(^3,4\) In this theory, the supersaturation over a drop of solution with a radius \( R \) is given by

\[
S = a'_1 \exp \left( \frac{2 \gamma_{lv}}{\rho_1 R k T} \right) = x_1 \exp \left( \frac{2 \gamma_{lv}}{\rho_1 R k T} \right),
\]  

where \( a'_1 \) is the thermodynamic activity of the solvent in the drop, \( \gamma_{lv} \) is the surface tension of the homogeneous solution, \( R \) can be estimated from the volume of the droplet expressed as \( V = 4 \pi R^3/3 = n_1/\rho_1 + n_2/\rho_2 \), and \( \rho_i \) are the number den-
sities of the pure components. The last form in Eq. (17) results from the assumption that the non-volatile component is present in dilute proportion, so that \( a_1^* \) is essentially given by the mole fraction \( x_1 \).

We compare the predictions of both forms of Köhler’s theory with our results from density functional theory for miscible mixtures in Fig. 5, for droplets formed on soluble particles of two different sizes \( n_2 \). The values of the number densities \( \rho_i \), solvent activities \( a_1^* \), and surface tensions for bulk solutions with the same composition as the drop, \( x_1 = n_1/(n_1 + n_2) \), have been calculated in a consistent manner using our theory. As can be seen from this comparison, the classical approach generates good predictions for the condensation on very large soluble particles, but fails to describe the behavior of the smaller systems. Most of the failure in these cases seems to be associated with the assumption of a surface tension that is independent of the droplet’s size. The effect of the nonideality of the mixture is exacerbated at intermediate compositions. The first form of Köhler theory in Eq. (17) always underestimates the growth factor of a droplet at any supersaturation (or, equivalently, overestimates the equilibrium vapor pressure of droplets of a given size) by assuming too high a value for the droplet surface tension. On the other hand, the ideal mixture approximation overestimates \( g_f \) for large droplets at equimolar compositions, where the properties of the real solution dominate the system’s behavior.

**B. Partially miscible mixtures**

For positive values of the mixing parameter \( \Lambda^* \), binary mixtures are no longer miscible at all temperatures and compositions. Phase separation between a solvent-rich phase and a solute-rich phase occurs at a saturation point and the properties of condensing droplets reflect this transition. For these types of mixtures, a gap develops in the composition \( x_1 \) of the mixture at the thermodynamic activity \( a_1^* \) of the coexisting phases. (see Fig. 2 for mixtures with \( \Lambda^* > 0 \)).

In partially miscible mixtures, droplets formed on large particles of the nonvolatile component exhibit a “solubility” transition at a vapor pressure above the vapor pressure of the bulk saturated solution, similar to the deliquescence process for particles of salt dissolved in water. At this transition, the soluble core dissolves spontaneously. We illustrate this phenomenon in Fig. 6 for soluble particles of different sizes in mixtures with \( \Lambda^* = 0.065 \). For these mixtures, the solute mole fraction in the bulk saturated solution is \( x_2 = 0.369 \) and the solution’s vapor pressure corresponds to a supersaturation \( S_{sat} = 0.860 \). The location of the solubility transition is indicated for the three largest soluble particles in Fig. 6 using a horizontal line. We have also labeled in this figure five different reference points on the supersaturation curve for a soluble particle with \( n_2 = 1.5 \times 10^4 \). These labels help distinguish regions of supersaturation and their corresponding boundaries \( (S_B, S_C, \text{and } S_D) \), where different thermodynamic behaviors are observed. Similar points can be identified for each of the other systems.

As we did in the previous section, we analyze the stability of droplets formed on a soluble particle of fixed size \( n_2 \) by studying the behavior of the work of formation \( \Delta \Omega \) at different supersaturations. We present these results in Fig. 7 for a system with \( n_2 = 1.5 \times 10^4 \). Droplets on branches AB and CD in Fig. 6 correspond to minima of the free energy, while those on branches BC and DE are at the
FIG. 7. Work of formation $\Delta \Omega$ as a function of drop size, as measured by the growth factor $g_f$, at different supersaturations $S$ for droplets with a soluble core of size $n_s=1.5\times10^{15}$ ($R_s=14.98\sigma$). $\Lambda^* = 0.065$ in this partially miscible mixture. $S_g$ corresponds to the supersaturation at the solubility transition.  

The solubility transition resembles a drop of a diluted binary solution. In particular, correspond to stable droplets in which the soluble core has not yet dissolved and is coated by a thin layer of the condensing solvent (see Fig. 1); for supersaturation values $S < S_{surf} < 1$, these coated particles are absolute minima of the free energy. As the saturation increases, a new minimum in the free energy develops for saturations larger than $S$ at point $C$ ($S_C$) corresponding to a metastable droplet in which the solution is completely dissolved. At the supersaturation labeled as $S_{eq}$ in Fig. 7, the work of formation of the solvent-coated particle and the work of formation of the fully dissolved particle become equal, but there is a free energy barrier separating both states. This barrier vanishes at a well defined supersaturation, $S = S_R$, where the core particle dissolves spontaneously (solubility transition). For this particular system, the solubility transition occurs at a value of $S = S_R > 1$, and thus for droplets that are metastable with respect to the homogeneous solvent phase. However, the barrier to nucleation is too high at the solubility transition. The barrier to nucleation decreases with supersaturation and vanishes at $S = S_D$ (Köhler activation); droplets grow spontaneously at higher vapor pressures.

The location of the solubility transition shifts to lower supersaturations for larger soluble particles as illustrated in Fig. 6, and thus can occur between states that are fully stable. This shift impacts the nature of the droplet that becomes activated for nucleation. Larger soluble particles dissolve before the barrier to nucleation vanishes and the activated drop for nucleation resembles a drop of a diluted binary solution. For the smaller soluble particles, the nucleation barrier vanishes before the core is dissolved and the dissolution process occurs in a gradual way as the droplet grows.

The solubility transition in fluid mixtures resembles the deliquescence-efflorescence transition of water soluble salts as observed experimentally by several groups and as predicted by Chen and Ming using a capillarity approximation. In particular, the latter authors have proposed that the deliquescence transition occurs when the free energy of the dissolved particle equals that of a wetted particle rather than that of a dry crystal, as initially proposed by Mirabel, Reiss, and Bowles. When a dry particle is considered as the equilibrium state at low supersaturations, the energy cost of creating the dry solid-vapor interface can reverse the observed trend and induce the transition to occur at lower values of $S$ for the smaller particles. In our systems, however, soluble particles exhibit high solvent surface adsorption and low interfacial tensions with the condensing phase. The composition of the drop with a dissolved core at the solubility transition is always similar to that of the bulk saturated solution, and thus the location of the transition is dominated by the curvature of Kelvin effect [exponential term in Eq. (17)].

Our model also predicts that the growth factor, $g_f = R/R_0$, at the solubility transition increases as the size of the soluble particle decreases. This result, however, is opposite to the one observed experimentally or predicted by the aforementioned classical theories for the deliquescence of salt crystals. For the type of fluid mixtures that we can explore with our model, no realistic combination of the interaction parameters results in a different trend. The minimum growth factor at the solubility transition always occurs in the imaginary limit of an infinite soluble particle at the composition and vapor pressure of the bulk saturated solution. We suspect that the different behavior observed in fluid mixtures and soluble salt crystals is associated mainly with the different nature of the liquid-liquid and solid-liquid interfaces, and the electrolytic properties of the salt. The higher energy cost of creating the liquid-crystal interface, associated with the stronger colligative effect on the vapor pressure for an electrolytic solution, should induce the deliquescence transition at lower supersaturations and reduce the impact of particle size, via the Kelvin effect, on its location. These two factors will reduce the value of $g_f$ at the transition, and will have a stronger effect on the properties of smaller particles.

Large soluble particles in all segregating mixtures in our model exhibit a solubility transition at a well defined supersaturation whenever dissolution precedes the disappearance of the barrier to nucleation. Thus, one would expect to observe the same type of hysteresis associated with deliquescence of large salt crystals. The range of supersaturations in which the coated soluble particle is metastable with respect to the dissolved particle becomes wider for the smaller cores and the growth rate in this region becomes less steep. The free energy surface for the smaller soluble particles is flatter than for larger cores in the region where activated solubility can occur, which could prolong the equilibration time for unstable aggregates in this region. However, we did not find any systems for which the dissolution of a nonactivated soluble particle occurs gradually over a finite range of supersaturations. In that sense, our model does not shed light on the physical mechanism that could lead to the experimentally observed gradual deliquescence of small salt crystals.

Increasing the degree of immiscibility of the two com-
components has several effects on the behavior of the system, as shown in Fig. 8 for mixtures with various values of $\Lambda^*$ and a soluble particle with $n_s=5\times10^5$ ($R_o=48.11$). As we can see, higher supersaturations are required to induce the solubility transition in more immiscible systems. The growth factor increases considerably and the metastability regions for coated and dissolved soluble particles become wider as two independent branches develop for these different sets of clusters. The value of $\Lambda^*$ has little impact on the supersaturation required to activate, in the Köhler sense, soluble particles in which the solubility transition precedes the disappearance of the barrier to nucleation; critical clusters for these large soluble particles resemble droplets of a dilute solution. However, activation occurs at considerably higher supersaturations in more immiscible mixtures when the critical aggregate still contains a partially dissolved core.

Finally, Fig. 9 shows the comparison of our results with the predictions of the classical Köhler theory. We include only predictions based on the first form of Eq. (17), given that the mixtures are far from ideal. The classical results are generated using the surface tension of the solution $\gamma_{li}$ as a function of the mole fraction $x_1$, as in the previous section, but the best predictions are based on the assumption that the surface tension remains constant once the concentration of solute in the drop exceeds that of the bulk saturated solution. The classical approach generates good estimates for the vapor pressure for the very large soluble particles, even predicting the existence of a solubility transition. The supersaturation at the transition is close to that predicted using Eq. (17) for a droplet with the properties of the bulk saturated solution. As demonstrated in previous density functional studies of binary mixtures, the accuracy of classical predictions worsens rapidly as the size of the aggregates decreases due to the overestimation of the surface tension and exacerbated nonideal solution effects. As was the case for miscible mixtures, Köhler theory underestimates the growth factor at any given saturation in these types of systems.

IV. CONCLUSIONS

We have used density functional theory to study the structural and thermodynamic properties of droplets formed on soluble and partially soluble particles composed of a fluid with an extremely low volatility. These systems share many features with water soluble salts. Aggregates in which the nonvolatile core is coated by a thin layer of solvent are stable at low supersaturations $S$, but become metastable with respect to the solvent homogeneous phase for $S>1$. The height of the barrier to nucleation on the soluble particles decreases as the vapor pressure of the solvent increases and eventually vanishes; soluble particles then become activated for nucleation in the Köhler sense. The required supersaturation for activated nucleation increases as the size of the soluble particle decreases.

Our results show that droplets formed on partially soluble particles can exhibit a solubility transition at vapor pressures lower than the one required for activated nucleation, but higher than the vapor pressure of the bulk saturated solution. At this transition the energy barrier for total solubilization of the nonvolatile particle vanishes and the soluble particle dissolves spontaneously. The solubility transition shifts to higher supersaturations as the size of the soluble particle decreases and the relative change in the droplet’s size at the transition, or growth factor, increases in the pro-

![FIG. 8. Growth factor $g_f=R/R_o$ at different supersaturations $S$ for droplets with a soluble core of size $n_s=5.0\times10^5$ ($R_o=48.11$) in mixtures with various degrees of immiscibility (as measured by the mixing parameter $\Lambda^*$). The horizontal lines indicate the location of the solubility transition.](image1)

![FIG. 9. Comparison of results from density functional theory and classical Köhler theory for the growth factor at different supersaturations in droplets with a soluble core of size $n_s=2.0\times10^5$ ($R_o=7.87\sigma$), $n_s=1.5\times10^5$ ($R_o=14.98$), and $n_s=5.0\times10^5$ ($R_o=48.11$). $\Lambda^*=0.065$ in this partially miscible mixture.](image2)
cess. For the smaller soluble particles the solubility transition disappears as the solvent-coated particle becomes activated for nucleation.

The solubility transition exhibits various similarities with the deliquescence process of water soluble salts. For example, the solvent-coated and droplet with a dissolved core can exist as metastable states and hysteretic behavior could be expected. However, at least for the simple types of mixtures explored in this work, there are clear differences between the two types of systems. The solubility transition for fluid droplets is expected to occur at a well defined value of supersaturation and the growth factor at the transition increases as the size of the soluble particle decreases. Experimental studies show that the deliquescence of salts can exhibit a completely different behavior. It is clear that more theoretical and experimental studies are needed to better understand the interplay between bulk and interfacial properties in small systems such as the ones just described.

Several authors have studied the formation of droplets on soluble solid particles using various models derived from the capillarity approximation. Some of these studies have identified and analyzed many of the same features described in our work. We have compared our results with the predictions of commonly used forms of the classical approach for droplet formation on soluble particles and shown their limitations in describing the behavior of small systems. However, our results also show that the classical theory seems to be pretty reliable in predicting the properties of very large systems, even in the case of nonideal mixtures.

Extensions of our work to ternary mixtures with a component with different affinity for the solute would help us better understand the behavior of important atmospheric systems and the stability of emulsions. In particular, recent experimental studies of binary heterogeneous gas-liquid nucleation have identified the existence of an interesting soluble-insoluble transition as the concentrations of the components are varied. We will present the predictions of our density functional approach for similar types of systems in a future work.

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