Coil-Globule Transition in Gas-Liquid Nucleation of Polar Fluids

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We report computer simulations of homogeneous gas-liquid nucleation in a model for strongly polar fluids. We find that, in the early stages of the nucleation process, chainlike clusters are formed. Beyond a certain size, these collapse to form compact spherical clusters. However, the interface of the collapsed nuclei differs markedly from the planar interface. Classical nucleation theory underestimates both the size of the critical nucleus and the height of the nucleation barrier. [S0031-9007(98)07436-5]

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The spontaneous condensation of water droplets in the vapor phase is probably the best known example of homogeneous nucleation of a polar fluid. However, best known is not the same as best understood. In fact, recent experiments indicate that classical nucleation theory [1] seriously overestimates the rate of nucleation for strongly polar substances, such as acetonitrile [2], although, surprisingly, it works well for water [3].

The most important factor determining the gas-liquid nucleation rate is the height of the free-energy barrier for the formation of a critical nucleus. Classical nucleation theory (CNT) assumes that the nuclei at the top of the nucleation barrier are compact spherical objects that behave like small droplets of bulk liquid. Recent computer simulations on a nonpolar (Lennard-Jones) fluid support this picture [4]. However, for polar fluids, the nature of the critical nucleus is still under debate. Wright *et al.* [2] suggest that, for polar liquids, the critical nucleus is a prolate spheroid—thus increasing the surface-to-volume ratio, and thereby the nucleation barrier. The orientational distribution of dipoles inside this cluster is assumed to have cylindrical symmetry. Abraham [5] proposed a model in which the dipoles are assumed to be oriented perpendicular to the interface. This would give rise to a size-dependent surface tension due to the effect of surface curvature on the dipole-dipole interaction. However, both pictures are at odds with the findings of a recent density-functional study of the critical nucleus of a dipolar model fluid (the Stockmayer fluid) [6]. This study indicated that the dipoles on the liquid side of the interface of critical nuclei are oriented parallel to the surface, rather than perpendicular. Unfortunately, the applicability of the density-functional theory is limited to relatively weak polar fluids.

In the present Letter, we present direct numerical simulations of the structure and free energy of precritical and postcritical nuclei of a strongly polar Stockmayer fluid. The Stockmayer potential is given by

$$v(\boldsymbol{r}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] - 3(\boldsymbol{\mu}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{\mu}_j \cdot \boldsymbol{r}_{ij})/r_{ij}^5 + \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j/r_{ij}^3 . \quad (1)$$

Here ϵ is the Lennard-Jones well depth, σ is the Lennard-Jones diameter, $\boldsymbol{\mu}_i$ denotes the dipole moment of particle i, and $\boldsymbol{r}_{ij}$ is the vector joining particles i and j.

The equilibrium phase behavior of this system has been studied in detail by computer simulation [7,8] and by theory [9,10]. The simulations suggest that attractive dispersion forces are essential for the existence of liquid-vapor phase coexistence [7]. In the absence of attractive dispersion forces, the vapor does not condense to form a liquid, but generates a "gel" of chains of dipoles that are aligned head-to-tail [11,12].

The system that we study in the present Letter is strongly polar; the reduced dipole moment $\mu^* = \mu/\sqrt{\epsilon\sigma^3} = 4$. Yet, this value of the dipole moment is still well below the threshold value of $\mu^* = 5$ [8], above which gas-liquid phase coexistence is suppressed. In fact, the value $\mu^* = 4$ is comparable to that for the SPC/E model of water ($\mu^* = 3.5$) [13]. All simulations were performed at a reduced temperature $T^* = k_B T/\epsilon = 3.5$ (k_B is the Boltzmann's constant), which is approximately 30% below the critical temperature $T_c^* = 5.07$ [8]. At the temperature and the range of pressures considered in the simulations, the bulk liquid is isotropic.

As the density of clusters in the vapor is low, the interactions between them can be neglected and we need only to simulate one cluster in a grand-canonical ensemble. We compute the excess free-energy $\Delta\Omega$ of a cluster of size n in a volume V, at chemical potential μ and temperature T, from the probability distribution function P_n

$$\beta\Delta\Omega(n, \mu, V, T) = -\ln[P_n] = -\ln[N_n/N] . \quad (2)$$

Here $\beta \equiv 1/k_B T$ is the reciprocal temperature; N_n is the average number of clusters of size n and N is the (average) total number of particles. To identify which particles make up a cluster, we used the geometric criterion

introduced by Stillinger [14]. All particles that are less than a distance $q_c = 1.5\sigma$ apart are considered to be connected and belong to the same cluster. We stress that our approach does not favor a particular cluster shape. In order to sample P_n near the top of the barrier, we used a modified version of the umbrella sampling technique [15]. For details, see Ref. [4].

Figure 1 shows the excess free energy of a cluster as a function of its size, at a supersaturation $S = (P/P_{\mathrm{coex}} \approx \exp[\beta\Delta\mu]) = 1.26$, where $\Delta\mu = \mu - \mu_{\mathrm{coex}}$, with μ (P) the imposed chemical potential (pressure) and μ_{coex} (P_{coex}) the chemical potential (pressure) at coexistence. As long as the interactions between the clusters can be neglected [16], we can obtain the free-energy barrier at any desired chemical potential μ' from the nucleation barrier measured at a given chemical potential μ via

$$\beta\Delta\Omega(n,\mu',V,T) = \beta\Delta\Omega(n,\mu,V,T) - \beta(\mu' - \mu)n + \ln[\rho(\mu')/\rho(\mu)], \tag{3}$$

where $\rho = N/V$ is the total number density. Classical nucleation theory predicts that the height of the nucleation barrier is

$$\beta\Delta\Omega^* = \beta\,\frac{16\pi\gamma^3}{3\rho_l^2\Delta\mu^2}, \tag{4}$$

where ρ_l ($= 0.78$) is the density of the bulk liquid, and γ is the liquid-vapor interfacial tension. The CNT prediction for the size of the critical nucleus is

$$n^* = \frac{32\pi\gamma^3}{3\rho_l^2\Delta\mu^3}. \tag{5}$$

In order to compare our simulation results with CNT, we computed both γ ($\gamma = 1.34\epsilon/\sigma^2$) and μ_{coex} ($\mu_{\mathrm{coex}} = -26.82\epsilon$).

Figure 2 shows the comparison between the simulation results and CNT. Clearly, the theory underestimates both the size of the critical nucleus and the height of the nucleation barrier. As the nucleation rate is dominated by the height of the barrier, our results are in qualitative agreement with the experiments on strongly polar fluids [2], in which it was found that CNT overestimates the nucleation rate. But, unlike the experiments, the simulations allow us to investigate the microscopic origins of the breakdown of classical nucleation theory.

To this end, we studied the structure of the (pre)critical nuclei. We now consider the structure of a relatively large critical cluster ($n \approx 300$). Examination of the distribution functions of the eigenvalues of the moment-of-inertia tensor showed that the cluster is effectively spherical. We find no evidence for a prolate shape of the cluster, of the type suggested in Ref. [2]. Furthermore, both the nematic order parameter P_2 and the ferroelectric order parameter P_1 are zero, indicating that there is no net alignment of the dipoles in the cluster. Singer and co-workers [17] studied Stockmayer clusters consisting of 50 particles with a reduced dipole moment of $\mu^* = \sqrt{3}$, and found that the (liquid) clusters had an oblate shape with a large degree of circulating orientational order up to $T^* = 0.4T_c^*$. This temperature is much lower than in the present simulations ($T^* = 0.7T_c^*$). We applied Singer's analysis and found

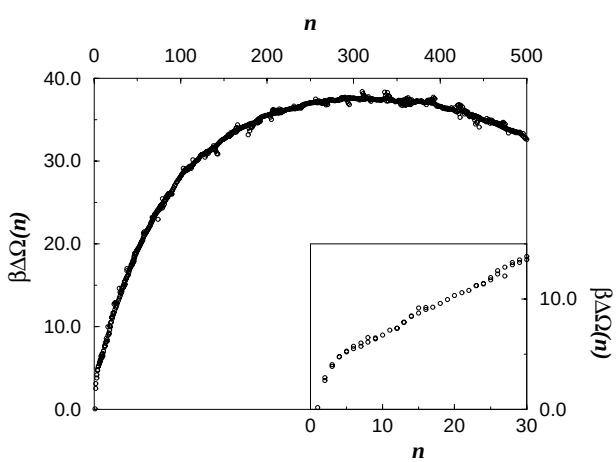

FIG. 1. The excess free energy $\beta\Delta\Omega$ of a cluster as a function of its size n, for a Stockmayer system at $S = 1.26$ and $T^* = 3.5$. The inset shows a magnification for small n.

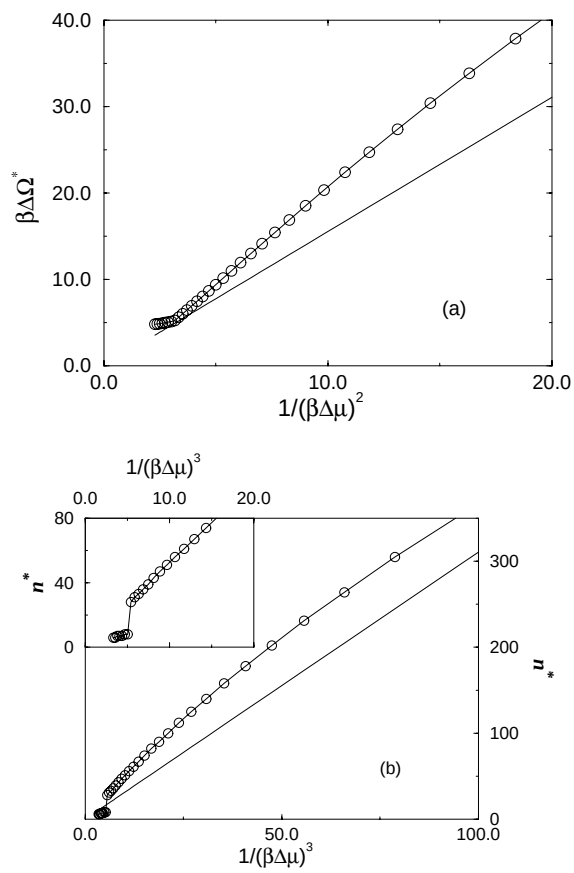

FIG. 2. Comparison of the simulation results (open circles) with classical nucleation theory (straight solid line): (a) Nucleation barrier; (b) size of the critical cluster. The inset shows a magnification for small n.

no circulating orientational order. Hence, the large critical clusters are spherical with no global orientational order.

We also examined the *local* order of these large clusters by computing the degree to which the dipoles are oriented perpendicular to the surface [6]. In agreement with earlier work [6,17,18], we find that the dipoles orient parallel to the interface on the liquid side, but perpendicular on the vapor side. Hence, the assumption that the dipoles are oriented perpendicular to the surface at the *liquid* side of the interface [5] is not justified for this model.

Let us next consider the smaller clusters. At moderate supersaturation these correspond to precritical clusters. But, by increasing the supersaturation, the top of the nucleation barrier may correspond to clusters of this size. In CNT it is assumed that even the smallest droplets are spherical. However, we find that clusters containing up to thirty dipolar particles form chains (see Fig. 3). In fact, we find a whole variety of differently shaped clusters in dynamical equilibrium: linear chains, branched-chains, and ring "polymers." As the cluster size is increased, the polymers become longer. But, beyond a certain size, they collapse to a compact structure. In order to quantify this, we determined the size dependence of the radius of gyration of the cluster, as well as the three eigenvalues of the moment-of-inertia tensor. Figure 3 shows the square

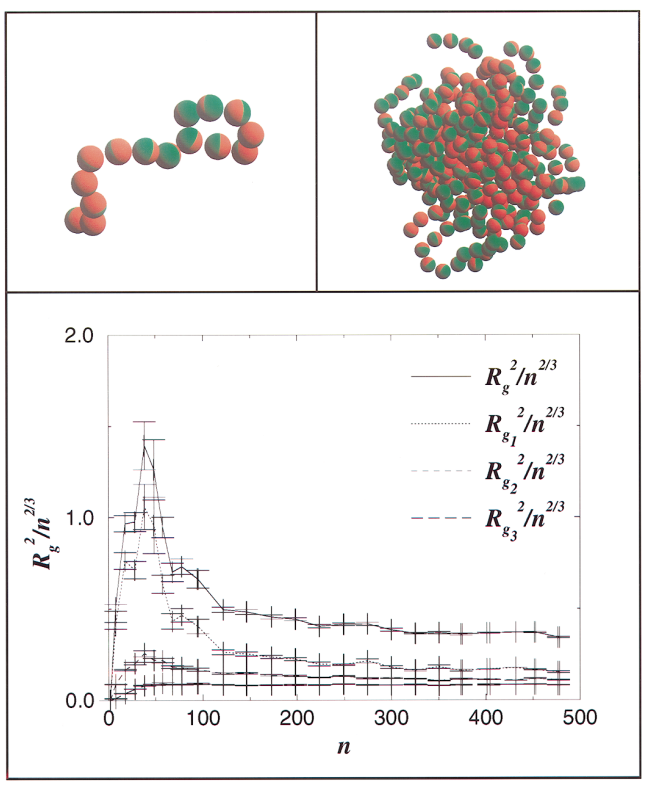

FIG. 3(color). Radius of gyration R_g, and the three eigenvalues of the moment-of-inertia tensor, as a function of cluster size n, at $S = 1.26$ and $T^* = 3.5$. Initially, the clusters are chainlike (snapshot, top left), but at a cluster size of $n \approx 30$ they collapse to compact spherical nuclei (snapshot, top right).

of the radius of gyration, divided by $n^{2/3}$. For a compact spherical object R_g^2 scales with $n^{2/3}$, whereas for chains R_g^2 scales with n^α, where $1.2 < \alpha < 2$, depending on the rigidity of the chain. Hence, for chainlike clusters $R_g^2/n^{2/3}$ should increase with n, while for compact clusters it should approach a constant value.

Figure 3 shows that initially $R_g^2/n^{2/3}$ increases with the size of the cluster. Moreover, one eigenvalue of the moment-of-inertia tensor is much larger than the other two, indicating the tendency of clusters to form chains. However, at a cluster size of $n \approx 30$, $R_g^2/n^{2/3}$ starts to decrease and approaches a constant value at $n \approx 200$. Analysis of the individual eigenvalues shows that at that point the clusters have collapsed to compact objects that fluctuate around a spherical shape.

The existence of chainlike precritical nuclei is more than a mere curiosity: it affects the nucleation barrier. We note that, if the clusters were perfectly rigid chains, the variation in free energy with cluster size would be linear. Indeed, as can be seen from Fig. 1, the initial increase in cluster free energy is very nearly linear with its size. The barrier shape predicted by CNT ($\Delta\Omega \sim c_1 n^{2/3} - c_2 n$) is only recovered after the clusters have collapsed.

The linear regime in the size dependence of the cluster free energy has a remarkable consequence for the dependence of the critical cluster size on supersaturation (see Fig. 2b). When the supersaturation is increased, the critical nucleus size decreases. However, at a supersaturation of $S = 1.8$ $[1/(\beta\Delta\mu)^3 = 5.25]$, the critical clusters have reached a size at which the variation in free energy with cluster size is linear. At this point, the top of the barrier is flat, and a small increase in the supersaturation results in a jump in the critical cluster size (see Fig. 2b, inset).

It is thus clear that at large supersaturation, where the critical nuclei are relatively small, the polymerlike character of the clusters leads to strongly nonclassical nucleation behavior. However, even for the larger collapsed nuclei, we find traces of the tendency to form chains.

A visual inspection of these clusters suggests that loops of dipolar chains stick out of the surface (see Fig. 3). In order to quantify this behavior, we have computed the radial profile of the coordination number for a critical cluster of $n \approx 300$. This is shown in Fig. 4. For comparison we also give the same profile for a critical cluster in the (nonpolar) Lennard-Jones system. Note that the interface for the Stockmayer cluster is more diffuse than for the Lennard-Jones cluster. But, more importantly, it is seen that for the Stockmayer cluster, unlike the Lennard-Jones cluster, the coordination number approaches a value of two at the vapor side of the interface. Such behavior is to be expected if the particles on the vapor side of the interface belong to chains.

In most nucleation theories it is assumed that the surface free energy of a cluster is that of a planar interface at coexistence. It is therefore natural to ask whether protruding chains of dipoles also occur in the planar interface.

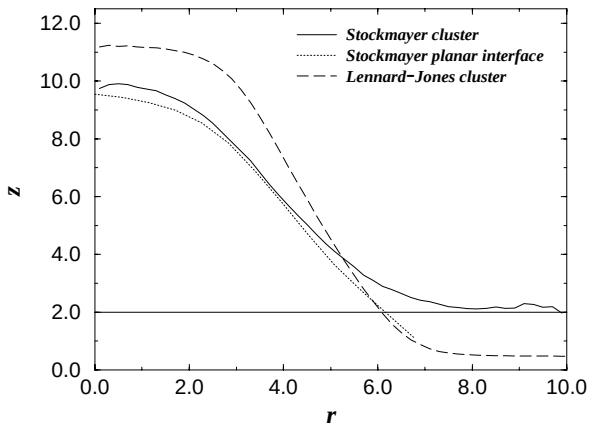

FIG. 4. Radial profile of the coordination number for a Stockmayer critical cluster at $S = 1.26$ and $T^* = 3.5$ (solid line). The coordination number z is defined as the number of particles within a cutoff distance $q_c = 1.5\sigma$. For comparison, we also indicate the coordination number profile for a planar interface (dotted curve) and for a critical cluster in the (nonpolar) Lennard-Jones system (long-dashed curve).

Figure 4 shows that this is not the case. This figure shows the coordination number profile, as obtained from the simulations, for the planar interface between a bulk Stockmayer liquid and its vapor. Clearly, the coordination number on the vapor side of the planar interface drops below two. Inspection of the density profiles shows that the planar interface is sharper than the interface of a critical droplet—the width of the interface of a critical droplet is some 25% larger. Most likely, the planar interface is sharper because the stronger dispersion interaction with the bulk causes the dipole chains to adsorb.

In summary, our simulations show that homogeneous gas-liquid nucleation in a Stockmayer system is initiated by chainlike clusters. When these clusters exceed a certain size, they condense to form compact dropletlike nuclei. However, the interface of these droplets, with a high degree of chain formation, is still markedly different from the planar interface. We note that the persistence of the structure of precritical nuclei at the surface of the critical nuclei appears to be a much more general phenomenon [19]. In highly polar liquids [2], it may be responsible for the discrepancy between the experimentally observed nucleation rates and the predictions of classical nucleation theory. The reason that the agreement with CNT is better for water [3] could be that the hydrogen bonding suppresses the chain formation.

Finally, it is interesting to consider the implications of our findings for the nucleation behavior of polar fluids without attractive dispersion forces. For these fluids the tendency to form chains will be even more pronounced and the point at which the clusters collapse will shift to large cluster sizes. This means that condensation will be preceded (and possibly pre-empted) by the growth of very large, polymerlike clusters. It is tempting to speculate that the gel-like phase observed in the simulations of Refs. [7,12] is, in fact, an interpenetrating network of uncollapsed dipolar chain clusters.

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