Finite-size scaling and particle size cutoff effects in phase separating polydisperse fluids

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We study the liquid-vapor phase behaviour of a polydisperse fluid using grand canonical simulations and moment free energy calculations. The strongly nonlinear variation of the fractional volume of liquid across the coexistence region prevents naive extrapolation to detect the cloud point. We describe a finite-size scaling method which nevertheless permits accurate determination of cloud points and spinodals from simulations of a single system size. By varying a particle size cutoff we find that the cloud point density is highly sensitive to the presence of rare large particles; this could affect the reproducibility of experimentally measured phase behavior in colloids and polymers.

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Many complex fluids such as colloidal dispersions, liquid crystals and polymer solutions are inherently polydisperse in character; their constituent particles have an essentially continuous range of size, shape or charge. Polydispersity is of significant practical importance because it can affect material properties in applications ranging from coating technologies and foodstuffs to polymer processing [1]. However, our understanding of the fundamental properties of polydisperse fluids remains very limited compared with what we know about their monodisperse counterparts. The challenge arises because a polydisperse fluid is effectively a mixture of an infinite number of particle species. Labelling each by the value of its polydisperse attribute $\sigma$, the state of the system (or any of its phases) has to be described by a density distribution $\rho(\sigma)$, with $\rho(\sigma)d\sigma$ the number density of particles in the range $\sigma \ldots \sigma + d\sigma$. The most common experimental situation is that in which the form of the overall or “parent” distribution $\rho^0(\sigma)$ is fixed by the synthesis of the fluid, and only its scale can vary depending on the proportion of the sample volume occupied by solvent. One can then write $\rho(\sigma) = n^0 f^0(\sigma)$ where $f^0(\sigma)$ is the normalized parent shape function and $n^0 = N/V$ the overall particle number density. Varying $n^0$ at a given temperature corresponds to scanning a “dilution line” of the system.

A central issue in the physics of polydisperse fluids is the nature of their phase behaviour: in order to process a polydisperse fluid one needs to know under which conditions it will demix and what phases will result. However, the phase behaviour of polydisperse systems can be considerably richer than that of monodisperse systems, due to the occurrence of fractionation [2–4]: at coexistence, particles of each $\sigma$ may partition themselves unevenly between two or more “daughter” phases as long as–due to particle conservation–the overall density distribution $\rho^0(\sigma)$ of the parent phase is maintained. As a consequence, the conventional fluid-fluid binodal of a monodisperse system splits into a cloud curve marking the onset of coexistence, and a shadow curve giving the density of the incipient phase; the critical point appears at the intersection of these curves rather than at the maximum of either [5].

In this letter we describe a joint simulation and theoretical study of a model polydisperse Lennard-Jones fluid in which the size of the particles influences not only the length-scale but also the strength $\epsilon_{ij}$ of the interparticle potentials, as defined in (2) below. For the case of size-independent interaction strengths, the critical point lies very close to the maximum of the cloud curve [6], whereas for the present model we find that it is substantially below (see Fig. 3), as is observed in many experiments on complex fluids (see e.g. [7]) and simplified theoretical calculations [8]. At the critical temperature, $T_c$, there then exists a finite density range where phase separation occurs on the dilution line. Most results shown below will be at this temperature; note that we will be interested mainly in the low-density part of the coexistence region rather than the critical effects at the other end, using $T_c$ merely as a convenient temperature scale.

The simulations were performed within the grand canonical ensemble (GCE). This is particularly useful for polydisperse systems, where it permits sampling of many different realizations of the particle size distribution while catering naturally for fractionation effects. Operationally, we ensure that the ensemble averaged density distribution always equals the desired parent distribution $\rho^0(\sigma)$ by controlling an imposed chemical potential distribution $\mu(\sigma)$. A combination of novel and existing techniques [9] are required to tune $\mu(\sigma)$ such as to track the dilution line, i.e. to vary the parent density $n^0$ but not its shape $f^0(\sigma)$.

In the GCE simulations, the number density $n$ is a fluctuating variable with average equal to $n^0$. Its distribution $p(n)$, shown in Fig. 1 for a range of parent densities $n^0$ at $T = T_c$, is a key observable. In the coexistence region it has two distinct peaks, which we sample using multi-
canonically preweighted \[10\]. The weight under the low and high density peaks corresponds respectively to the fractional volumes \(v_g\) and \(v_l\) that would be occupied by gas and liquid in the corresponding canonical ensemble. As expected, the peaks separate and the valley between them deepens as we move away from the critical point by decreasing \(n^0\). Concomitant with this is a gradual transfer of weight from the liquid to the gas peak. Finally the liquid peak disappears, at exponentially small values of \(v_l\) visible only on a log scale (Fig. 1(b)).

The observed variation of \(p(n)\) raises the question of how to detect the cloud point \(n_{cl}^0\), defined as the lowest parent density \(n^0\) where stable phase coexistence occurs. In a monodisperse system this is straightforward because the cloud point also gives the density of the gas phase, which remains constant throughout the coexistence region. One then simply detects the point where the gas and liquid peaks have the same weight, i.e. \(r = v_l/v_g = 1\), and measures the gas density there. (The criterion \(r = 1\) has the added advantage of leading to only exponentially small finite-size corrections to the value of \(\mu\) at coexistence \[11\]). However, this method fails in a polydisperse system because fractionation causes the densities and size distributions of the coexisting phases to vary with \(n^0\) \[5\]. One could attempt to locate the cloud point instead by extrapolating in \(n^0\) to the point where \(v_l \rightarrow 0\) \[6\]. But in our system the dependence of \(v_l\) on \(n^0\) is so strongly nonlinear—another effect of fractionation, see inset of Fig. 1—that the resulting cloud point estimates would have very large error bars. Indeed, on a linear plot of \(v_l\) versus \(n^0\) as shown in Fig. 1(a) the effects of the particle size cutoff \(\sigma_c\) which our more careful analysis will reveal (see Fig. 3 below) are essentially invisible.

To make progress, we analyse the finite-size scaling of \(p(n)\). As the linear system size \(L\) grows at fixed \(n^0\) and \(T\), the peaks in \(p(n)\) will narrow around the densities of gas and liquid, respectively, and the size distributions averaged over configurations from each peak will tend to those in the coexisting phases. The ratio \(r = v_l/v_g\) is determined by the difference in the grand potential; this is directly related to the pressure \(P\) so that \(r = \exp(\beta L^d \Delta P)\) for large \(L\) where \(\beta = 1/k_B T\) and \(\Delta P = P_1 - P_g\). The criterion for stable coexistence at given fixed \(n^0\) is that \(r\) must have a finite value as \(L \rightarrow \infty\); the pressure difference then has to scale as \(\Delta P \sim L^{-d}\) except in the special case \(r = 1\) (see above).
ulation data using histogram reweighting, and the peak position then serves as an estimate for \( n_{cl}^0 \). This is shown in the inset of Fig. 2, and gives \( n_{cl}^0 \approx 0.0823 \) from the largest \( L \), consistent with our earlier estimate derived from comparing data for different \( L \).

The above arguments can be formalized using the results of [11], which pertain to the monodisperse case but which we have generalized to polydisperse systems [12]. We find that for large \( L \) the second-derivative plot approaches a universal master curve

\[
- \left( \frac{\partial}{\partial n} \right)^2 \ln r = \frac{z}{(1+z)^3}, \quad \hat{n}_0 = z + \ln z , \quad (1)
\]

parameterized by \( z \). The scaled parent density is defined here as \( \hat{n}_0 = aL^d(n_0^0 - n_{cl}^0) + \ln(bL^dn_{cl}^0) \) with \( a \) and \( b \) system-specific dimensionless scale factors. This scaling implies that the cloud point estimate from the peak position has finite-size corrections of order \( L^{-d} \ln L \), while the peak width and height scale as \( L^{-d} \) and \( L^{2d} \), respectively. Our data are consistent with the width and height scaling and with the dominant \( L^{-d} \) dependence of the peak shifts [12]. The master curve (1), appropriately scaled, is overlaid onto the largest-\( L \) data in Fig. 2 (inset) and shows excellent agreement.

Fig. 1 shows that the metastable liquid peak in \( p(n) \) persists until well below the cloud point \( n_{cl}^0 \). The point at which it disappears marks the so-called mean field spinodal [13] where the liquid is unstable to small density fluctuations. The parent density \( n_{sp}^0 \) where this occurs should tend to an \( L \)-independent value as \( L \) grows large [13], and our data (not shown) are consistent with this. Spinodals in monodisperse systems are conventionally characterized by the density of the phase that becomes unstable, which is located inside the region where phase separation occurs. Here we use instead the density \( n_{sp}^0 \) of the coexisting stable phase, which is outside this region. This is a more meaningful representation in the polydisperse context since only the stable (majority) phase has the parental size distribution, while that of the metastable (minority) phase is determined indirectly via chemical potential equality.

Equipped with a systematic method for determining cloud points, we now consider the overall phase diagram of our system, the interparticle potential of which was assigned the Lennard-Jones form:

\[
u_{ij} = \epsilon_{ij} \left[ \left( \sigma_{ij}/r_{ij} \right)^{12} - \left( \sigma_{ij}/r_{ij} \right)^{6} \right] \quad (2)
\]

with \( \epsilon_{ij} = \epsilon_0\sigma_0 \), \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \) and \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \). The potential was truncated for \( r_{ij} > 2.5\sigma_{ij} \) and no tail corrections were applied. The diameters \( \sigma \) are drawn from a (parental) Schulz distribution \( f^0(\sigma) \propto \sigma^\sigma \exp\left\{ -z^+(1/\sigma) \right\} \), with a mean diameter \( \bar{\sigma} \) which sets our unit length scale. We chose \( z = 50 \), corresponding to a moderate degree of polydispersity: the standard deviation of particle sizes is \( \delta = 1/\sqrt{z+1} \approx 14\% \) of the mean. The distribution \( f^0(\sigma) \) was limited to within the range \( 0.5 < \sigma < \sigma_c \). The upper cutoff \( \sigma_c \) serves to prevent the appearance of arbitrarily large particles in the simulation, but would also be expected in experiment because in the chemical synthesis of colloid particles, time or solute limits restrict the maximum particle size [14].

We complement the simulations with theoretical phase behaviour calculations, following closely our study of the purely size-polydisperse case [6]. An accurate expression for the excess free energy of a polydisperse hard sphere fluid accounts for the repulsive interactions. To this is added a van der Waals term which represents the attractive part of the \( u_{ij} \). It scales as

\[
\int d\sigma \sigma^2 \rho(\sigma)\rho(\sigma') (\sigma\sigma')^3 \quad (3)
\]

where the factors \( \sigma\sigma' \) and \( (\sigma + \sigma')^3 \) arise, respectively, from the size dependence of the interaction amplitude \( \epsilon_{ij} \) and the interaction range \( \sigma_{ij} \). Multiplying out gives an expression involving only the moment densities \( \int d\sigma \rho(\sigma)^i \) with \( i = 1 \ldots 4 \). Since the repulsive part of the excess free energy has a similar moment structure, the moment free energy (MFE) method [15] can be used for accurate numerical prediction of phase behaviour [6].

![FIG. 3: Comparison of cloud curves for \( \sigma_c = 1.4 \) and \( \sigma_c = 1.6 \). The critical points for \( \sigma_c = 1.6 \) (×) and \( \sigma_c = 1.4 \) (+) are marked. Also shown is the spinodal (limit of metastability) for \( \sigma_c = 1.6 \). The inset displays the variation of the gas cloud point density \( n_{cl}^0 \) at \( T = T_c \) as a function of \( \sigma_c \), as obtained from GCE simulations (open symbols) and MFE theory (filled symbols).](image-url)
Despite particle sizes around $\sigma_c$ being very rare in the parent, they occur in significant concentration in the shadow liquid. Physically, since large particles interact more strongly, their presence leads to a substantial free energy gain at the shorter interparticle separations of the liquid.

One is led to enquire whether the gas phase cloud point density would eventually tend to a nonzero limit as $\sigma_c$ is increased. The inset of Fig. 3 shows the simulation results and theoretical predictions. The former exhibit a further strong decrease of $n^0$ by $\approx 25\%$ between $\sigma_c = 1.6$ and 1.8; the latter suggest that this trend continues and that the cloud point density tends to zero for large $\sigma_c$. Such an unusual effect has previously been seen in theoretical studies of polydisperse hard rods with wide length distributions [16] and is also predicted to occur in solid-solid phase separation of polydisperse hard spheres [17], though only for large $\sigma_c$ and distributions with fatter than exponential tails. Here the decrease of $n^0$ is clear even for $\sigma_c$ of $O(1)$, i.e. of the same order as $\sigma$, and scaling estimates suggest that cutoff effects occur for any size distribution with tails heavier than a Gaussian [12].

The physical origin of the decrease of $n^0$ to zero is the appearance (for large $\sigma_c$) of a second peak in the shadow phase size distribution near $\sigma_c$ (Fig. 4, inset). As with the hard rods, we expect this second peak to eventually dominate as $\sigma_c$ increases so that the shadow phase consists of ever more strongly interacting particles whose sizes are concentrated near $\sigma_c$. We speculate that as a consequence, there exists some cutoff for which the shadow phase liquid freezes into a quasi-monodisperse crystal phase. Indeed our simulations provide evidence for this scenario: for the large cutoff $\sigma_c = 2.8$ the liquid spontaneously freezes to an f.c.c. crystal structure [12]. Although we observe this only for small $n^0$ values close to the spinodal point it is conceivable that, for $\sigma_c$ values larger than those presently accessible to simulations, the freezing might occur from the stable liquid phase.

Finally, with regard to the cloud curves as a whole (Fig. 3), we note that significant cutoff-dependent shifts occur only for densities below the critical density. This is consistent with our interpretation above: for higher densities, the shadow phase is a gas of lower density than the parent. In this, the concentration of large particles is suppressed and that of small particles negligibly enhanced because of their weak interactions. The shadow size distributions are therefore concentrated well within the range $0.5 \ldots \sigma_c$ (data not shown) so that no cutoff dependence arises.

In summary, the task of accurately locating cloud points of polydisperse fluids via simulation is severely complicated by fractionation effects. We have presented a generally applicable finite-size scaling method which addresses this problem. Application to a model polydisperse fluid reveals the cloud curve to be highly sensitive to the presence of very rare large particles. Such effects imply that in experiments on polydisperse fluids (see e.g. [4]) it may be important to monitor and control carefully the tails of the size (or charge, etc) distribution. Otherwise undetected differences could lead to large sample-to-sample fluctuations in the observed phase behaviour.

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