Fluid-Solid Phase Separation in Hard-Sphere Mixtures is Unrelated to Bond Percolation

In a recent Letter, Buhot [1] proposes that entropy driven phase separation in hard-core binary mixtures is directly related to a bond-percolation transition. In particular, Buhot suggests that a phase instability occurs when the coordination number n_b, defined as

$$n_b = \rho_l \int_{\sigma_l \leq r \leq \sigma_l(1+R)} g_{ll}(r)\, dr\,, \tag{1}$$

is equal to zp_c, where z is the coordination number of a particular crystal lattice, and p_c is its bond-percolation threshold. Here ρ_l is the number density of the larger particles, $g_{ll}(r)$ is the radial distribution function of the larger particles, and $R = \sigma_s/\sigma_l < 1$ is the ratio of the diameters σ_i. However, for binary hard-sphere mixtures, calculations based on an accurate approximation to $g_{ll}(r)$ demonstrate that n_b varies widely along the phase boundaries calculated directly by simulations, implying that bond percolation is *unrelated* to the phase separation in these systems.

For highly asymmetric binary hard-sphere systems, Dijkstra *et al.* [2] conclusively demonstrated that an effective one-component description based on a depletion potential picture quantitatively describes the fluid-solid transition. This in turn implies that the one-component description should give a fair representation of the radial distribution function $g_{ll}(r)$. Recent simulations [3] of the Asakura-Oosawa (AO) depletion potential [4] show that the Percus-Yevick (PY) approximation quantitatively describes the pair correlations along the fluid-solid transition line. In the inset of Fig. 1, the simple form $g_{ll}(r) = \exp[-\beta V_{\mathrm{dep}}(r)]$, where $V_{\mathrm{dep}}(r)$ is the effective depletion potential, is compared to the more accurate PY integral equation results. Typically, for packing fraction $\eta_l = \pi\rho_l\sigma_l^3/6 \leq 0.25$ along the phase boundaries this form gives near quantitative agreement for $r \leq \sigma_l(1 + R)$, which is not surprising since for small η_l the potential is typically at least $2.5 k_B T$ along the fluid-solid transition line, while the hard-core induced correlations are small so that the exponential form dominates. In fact, Buhot's treatment of binary hard spheres reduces exactly to this simple form, but with an AO depletion potential which is valid only when $\eta_l \to 0$. If one replaces η_s with the η_s^r of small spheres in a reservoir kept at constant chemical potential, the correct form of the AO potential is recovered [2]. In Fig. 1, the metastable fluid-fluid and the stable fluid-solid phase lines taken from simulations [2] are compared to lines of the constant coordination number, which are calculated with Eq. (1) and $g_{ll}(r) = \exp[-\beta V_{\mathrm{dep}}(r)]$, together with the depletion potential used for the simulations as well as the simpler AO potential. The difference between the two is very small, implying that the coordination number is not very sensitive to the exact form of the depletion potential. Also included is the proposed bond-percolation induced fluid-solid line at $n_b = 2.4$ derived from the approximation to $g_{ll}(r)$ used by Buhot.

We find the following: (a) As expected, the approximation used by Buhot for $g_{ll}(r)$ breaks down as η_l increases. (b) The lines of the constant coordination number are not related to either the fluid-fluid or the fluid-solid phase lines, implying that there is no direct relation between bond percolation and phase separation. The same results were found for other size ratios, and it is hard to see how more accurate approximations for $g_{ll}(r)$ could change this picture.

The breakdown of the bond-percolation picture for this archetypical hard-core mixture model implies a similar breakdown for other, more complex, mixtures. The good agreement found [1] at a few state points for hard-square systems probably results from either their 2D nature, the imposed parallel symmetry, or the rather unusual purported second order fluid-solid transition. It does not imply that bond percolation is generally relevant for fluid-solid phase separation in binary hard-core mixtures.

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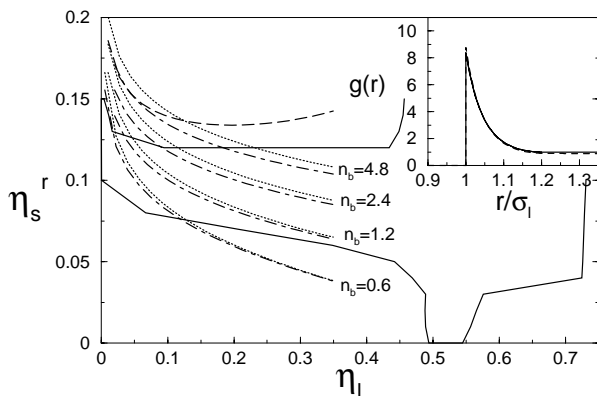 Cambridge CB2 1EW, United Kingdom

FIG. 1. Solid lines: the fluid-solid and fluid-fluid phase lines from the simulations of Dijkstra *et al.* [2] for $R = 1/30$. Dotted lines and dash-dotted lines: the coordination number calculated as in the text using the AO potential and the potential from the simulations, respectively. Dashed line: the $n_b = 2.4$ line proposed by Buhot [1]. Inset: $g_{ll}(r)$ for $R = 0.2$, $\eta_l = 0.25$, $\eta_s^r = 0.25$ with AO potential. Solid line: from $g_{ll}(r) = \exp[-\beta V_{\mathrm{dep}}(r)]$; dashed line: from PY integral equation.

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