Comment on "Reverse Brazil Nut Problem: Competition between Percolation and Condensation"

In a recent paper [1] the Brazil nut problem (BNP), where particles with large diameters rise to the top when exposed to vertical shaking, and the reverse Brazil nut problem (RBNP), where the large particles segregate to the bottom, were investigated. The authors present molecular dynamics (MD) simulations for binary hard sphere mixtures at a *fixed* temperature, which show pronounced BNP and RBNP behaviors depending on the mass and diameter ratios of the two hard sphere species. For an explanation, a new *condensation versus percolation* driven segregation mechanism was put forward, which has attracted much attention in the press [2]. The purpose of this Comment is to show that the proposed mechanism is incorrect. All the effects observed in the MD simulations are understood by simple conventional thermodynamics.
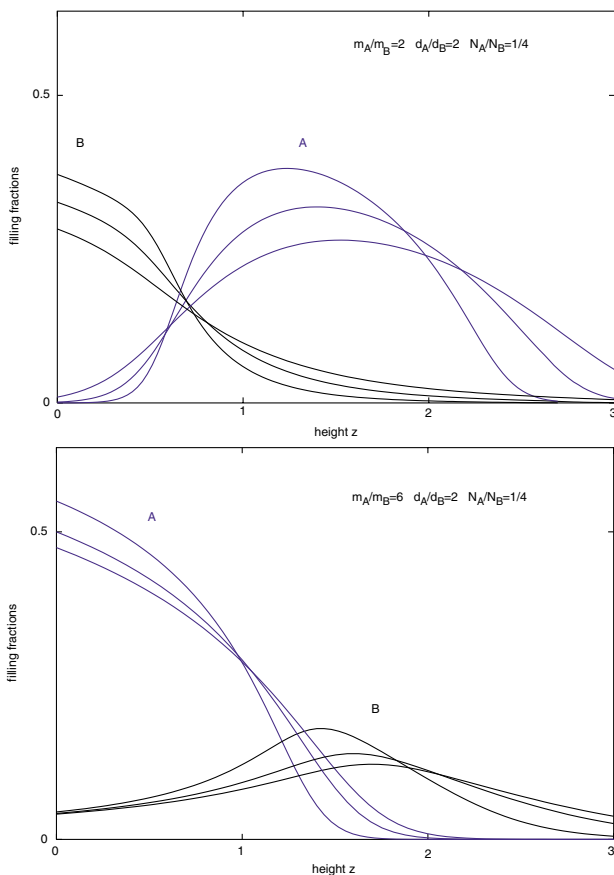

FIG. 1 (color online). Calculated filling fractions of binary hard sphere liquids under gravity for different mass ratios. The length unit equals the container size in the MD simulations of Ref. [1]. With decreasing temperature the profiles are shifted to smaller heights.

Because in the solid phase particles may no longer exchange positions, we conjecture that demixing must happen already in the fluid phase. Therefore we consider a binary hard sphere mixture with species A and B having masses $m_A > m_B$ and diameters $d_A > d_B$ in the liquid phase with an appropriate equation of state, e.g., the Mansoori-Carnahan-Starling-Leland equation [3]. It is then straightforward to compute the Helmholtz free energy [4] under gravity

$$F = E - TS. \tag{1}$$

Variation of F with respect to the particle densities for fixed particle numbers N_A and N_B leads to two coupled nonlinear equations which are solved numerically, and the calculated filling fractions as functions of the height z are depicted in Fig. 1. The density profiles compare very well with the MD simulations presented in [1]. But note that here the temperatures T lie above the temperature where the binary liquid begins to solidify (the total packing fraction lies sufficiently below close packing everywhere), whereas the temperatures used in [1] are supposed to be quenched in a regime where parts of the sample are "frozen."

We must conclude that demixing indeed occurs in the liquid phase. It is clearly due to the competition between *gravity and entropy* rather than to that of *condensation and percolation*. There is nothing mysterious or special going on, and all the effects are understood by conventional thermodynamics. Finally, if the temperature is further decreased, the binary liquid eventually begins to condensate locally according to its filling fractions in the fluid phase. However, there exists no condensation driven demixing. For details see Ref. [5].

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