Residual multiparticle entropy does not generally change sign near freezing

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The residual multiparticle entropy (RMPE) of two- and three-dimensional fluids changes sign near the freezing line, providing a quasiuniversal "one-phase" rule for the location of the liquid-solid transition. We present new simulation results for d-dimensional hard-sphere fluids ($d=1-5$) which show, however, that this freezing criterion fails in other spatial dimensions. The results also call into question the idea that a change in sign of the RMPE implies the emergence of a new kind of local structural order in the fluid. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2916697]

Freezing of a fluid into an ordered solid is a widely studied phenomenon. Yet accurately locating liquid-solid phase boundaries still represents a major challenge even for simple model systems. Molecular simulations can be effectively used to this end,[1] but the computations required are typically demanding. Moreover, errors are introduced not only via the specific methods employed for computing the chemical potentials of the fluid and crystalline phases but also through the use of finite system sizes and interaction cutoffs.[1–3]

Because of these issues, investigators often first turn to heuristic "one-phase" criteria to estimate the location of the freezing line. Several such empirical rules have been introduced and tested.[1,4] Here we focus on one that is straightforward to evaluate and provides surprisingly reliable predictions for a number of systems: The zero residual multiparticle entropy (zero-RMPE) criterion.[5,6] The RMPE of a fluid ($\Delta s=s^{ex}-s_2$) is defined to be the difference between s^{ex}, the total excess entropy per particle relative to an ideal gas with the same temperature, T, and number density, ρ, and s_2, the pair-correlation contribution to s^{ex}. The latter can be expressed as[7]

$$s_2=-\frac{\rho k_B}{2}\int d\mathbf{r}\{g(\mathbf{r})\ln g(\mathbf{r})-[g(\mathbf{r})-1]\}, \quad (1)$$

where k_B is Boltzmann's constant, and $g(\mathbf{r})$ is the radial distribution function of the fluid. The RMPE effectively represents the contribution to s^{ex} due to spatial correlations involving more than two particles.

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The zero-RMPE freezing criterion states that $\Delta s=0$ for the fluid at the liquid-solid transition. This rule semiquantitatively predicts the freezing line for a wide variety of model fluids in both two and three spatial dimensions.[5,6,8–15] Because the criterion does not hinge on system-dependent parameters, it has been argued to be more general than other phenomenological freezing rules (see, e.g., Ref. 12). The change in sign of Δs which occurs at the zero-RMPE condition has previously been interpreted as signaling the emergence of a new kind of local structural order in the fluid.[16,17]

In this Communication, we put the zero-RMPE criterion to a new and stringent test: whether it is consistent with the freezing behaviors of d-dimensional hard spheres for $d=1-5$. To simplify the notation, we nondimensionalize entropies by the Boltzmann constant k_B and lengths by the particle diameter σ.

For the $d=1$ case (i.e., hard rods), there is no freezing transition.[18] Here we examine whether this is consistent with the zero-RMPE criterion using exact analytical results for the excess entropy per particle[19] and the radial distribution function[20] together with Eq. (1). For $d=2-5$, we investigate the freezing criterion by computer simulation. Estimates for the density of the saturated fluid at freezing (ρ_f), obtained in previous simulation studies, are presented in Table I. We compute the excess entropy per particle s^{ex} using an expanded-ensemble implementation[21] of grand canonical transition matrix Monte Carlo simulations.[22,23] In these simulations, we use volumes of 400, 343, 1296, and 1024 for $d=2-5$, respectively. We compute s_2 via the radial distribution function obtained from event-driven molecular dynamics simulations in the microcanonical ensemble.[24] Here we use 2500, 2500, 5000, and 10 000 particles for $d=2-5$, respectively. We employ cubic cells and periodic boundary conditions for both simulation methods. We have verified that the two methods yield statistically indistinguishable equations of

TABLE I. The freezing density, ρ_f, the zero-RMPE density, $\rho(\Delta s=0)$, and the RMPE evaluated at the freezing density, $\Delta s(\rho_f)$, of hard-sphere fluids in d dimensions.

d	ρ_f	$\rho(\Delta s=0)$	$\Delta s(\rho_f)$
1	⋯	0.825	⋯
2	0.88[a]	0.826	0.747
3	0.943[b]	0.948	−0.022
4	1.04,[c]1.00[d]	>1.22 [e]	−0.517
5	1.22,[c]1.16[d]	>1.33 [e]	−0.743

[a]References 34–36.
[b]References 34, 37, and 38.
[c]Reference 39.
[d]Reference 40.
[e]See Fig. 1.

state. We have also confirmed that varying the system size does not significantly affect the simulation results.

Figure 1 displays Δs as a function of ρ for the hard-sphere fluids ($d=1-5$, from top to bottom). Table I contains a summary of the relevant data: the freezing density, ρ_f, the zero-RMPE density, $\rho(\Delta s=0)$, and the RMPE evaluated at the freezing density, $\Delta s(\rho_f)$. For $d=3$, the freezing and the zero-RMPE densities are nearly identical [$\rho_f=0.943$ versus $\rho(\Delta s=0)=0.948$]. This is consistent with previous simulation results for a wide range of three-dimensional fluids.[5,6,8–10,12–15] For $d=2$, the zero-RMPE criterion slightly underpredicts the freezing density [$\rho_f=0.879$ versus $\rho(\Delta s=0)=0.826$]. This slight underprediction is also consistent with the earlier two-dimensional simulations of Saija *et al.*,[11] who speculated that the zero-RMPE criterion is more directly related to the emergence of sixfold orientational order in the fluid, one of the structural precursors[25] to the freezing transition in this system.

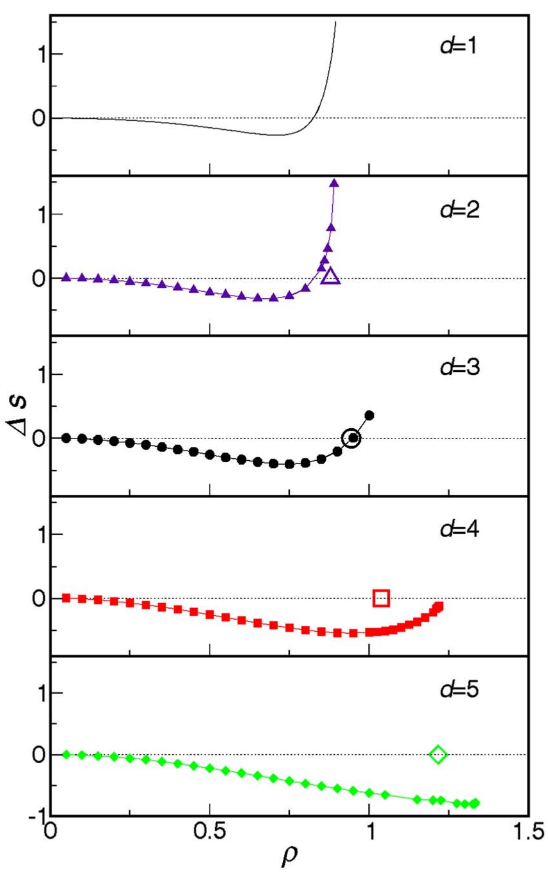

FIG. 1. (Color online) Residual multiparticle entropy $\Delta s=s^{ex}-s_2$ versus density ρ for d-dimensional hard-sphere fluids ($d=1-5$, from top to bottom). The freezing density ρ_f is also indicated as a large open symbol in each plot (see also Table I). Note that there is no freezing transition for $d=1$.

Now we examine the results for the $d=1$ fluid. While it is known that there is no phase transition in this system,[18] note that the zero-RMPE criterion incorrectly predicts one. Specifically, as shown in Fig. 1, the fluid displays a finite zero-RMPE density [$\rho(\Delta s=0)=0.825$]. Given the lack of a phase transition in this system, this result also calls into question the idea that a change in sign of the RMPE necessarily implies the emergence of a new kind of structural order in the fluid.

The failure of the zero-RMPE criterion as a general freezing rule is reinforced by considering the hard-sphere fluid in higher ($d>3$) dimensions. Figure 1 shows that it (at best) significantly overpredicts the freezing density for $d=4$ and 5. In fact, although we were able to study both fluids well above their freezing densities, we were only able to establish lower bounds for the zero-RMPE densities (see Table I).

Based on these results, it is tempting to speculate that the zero-RMPE density may not generally be accessible to high-dimensional fluids upon compression, as they may encounter a glass transition first. Some further insights into this issue can be obtained by considering the theory of Parisi and Slanina,[26] which provides analytic expressions for the equation of state and the radial distribution function for high-dimensional ($d\to\infty$) hard-sphere fluids. The ideal glass transition of these systems has also recently been estimated using the aforementioned theory and the replica method.[27,28] It can be readily verified that these approaches indeed predict that very high-dimensional hard-sphere fluids encounter the glass transition upon compression before the RMPE changes sign. We note, however, that much more work must be done before a comprehensive understanding of freezing and the glass transition in high-dimensional hard-sphere fluids can be obtained. In fact, whether the densest packings are amorphous or crystalline[29,30] and whether a first-order freezing transition even occurs in these systems[31–33] remain important outstanding questions.

In any case, the earlier results for $d=1-5$ clearly demonstrate that the RMPE does not generally change sign near the freezing transition. Of course, our data cannot rule out the possibility of a different, less general, freezing criterion involving the RMPE. For example, perhaps $\Delta s=C_d$ at the freezing line, where C_d is a dimensionality dependent constant. This possibility could be further investigated by studying, e.g., the freezing line of the four-dimensional Lennard-Jones fluid. Nonetheless, the fact that C_3 happens to have a numerical value close to zero—i.e., that the RMPE changes sign near the freezing transition for $d=3$—does not appear to have special physical significance.

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