

Entropy and the freezing of simple liquids

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A criterion for the freezing of a liquid is investigated through an analysis of the contribution of multiparticle correlations to the statistical entropy. Molecular-dynamics results are presented for a Lennard-Jones system at two subcritical isotherms in a range of densities across the freezing line.

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Recently, new attention has been devoted to the multiparticle correlation expansion of the entropy of simple classical fluids which was originally derived by Nettleton and M. S. Green for an infinite open system using graphical techniques [1]:

$$s^{(\text{ex})} = \sum_{n=2}^{\infty} s_n, \quad (1)$$

where $s^{(\text{ex})}$ is the excess entropy per particle in units of Boltzmann's constant. The partial entropies s_n are obtained from the integrated contribution of the spatial correlations between n -tuples of particles. In particular, the pair entropy for a homogeneous and isotropic system reads

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

where ρ is the number density and $g(r)$ is the radial distribution function (RDF). The result obtained by Nettleton and M. S. Green generalizes the expression previously derived by H. S. Green for a finite system [2].

Recent calculations of the pair entropy for liquid sodium and argon using experimental data have been performed by Wallace who has also reconsidered the original H. S. Green's expansion in the canonical ensemble [3-6]. The formal equivalence of the entropy expansion in the canonical ensemble with its grand canonical counterpart, however, was fixed by Baranyai and Evans [7] who carried out a molecular-dynamics (MD) calculation of both the two- and three-particle contributions to the statistical entropy of a Lennard-Jones (LJ) model fluid along two isotherms [8]. The two-body term s_2 is a negative definite quantity. Like s_2 , the three-body contribution s_3 turns out to be a negative, monotonically decreasing function of the density at the temperatures sampled by Baranyai and Evans. They also noted that the partial sum ($s_2 + s_3$) becomes somewhat more negative than the total excess entropy for states of the liquid close to the freezing line. This behavior is already manifest in the residual multiparticle entropy

$$\Delta s \equiv s^{(\text{ex})} - s_2, \quad (3)$$

which, despite of its minor quantitative relevance in the entropic balance, does indeed reflect the changes in phase

behavior undergone by the system. In fact, an analysis of Δs vs ρ for hard spheres (HS) shows that this quantity faithfully records all the borders between distinct packing regimes which are identified by both theory and experiment [9,10]. In particular, $\Delta s_{\text{HS}}(\rho)$ exhibits a nonmonotonic profile with a change of sign from negative to positive values at a density $\rho \approx 0.960$ which lies extremely close to the computer-estimated freezing point $\rho_{\text{HS}}^{\text{f}} \approx 0.943$, in units of the hard-core diameter σ . It thus appears that, beyond this threshold, the loss in entropy due to localization ($s_2 < 0$) becomes tempered by the gain associated with the ordering of the fluid on a local scale ($\Delta s > 0$). This process, which is driven by a requirement of greater efficiency in the packing of the spheres, does show up, as expected, at the level of higher-order correlation functions and leads to an increase of the excess entropy of the system relatively to the prevailing negative value settled by the two-body term. In this respect, the change of sign in $\Delta s_{\text{HS}}(\rho)$ unveils as an underlying signature of the freezing transition within the homogeneous fluid phase of hard spheres [10].

The data reported by Baranyai and Evans for the LJ model refer to systems with a number of particles N ranging from 108 to 2048 at reduced temperatures 1.15 and 1.5 (the same reduced units, scaled to the LJ parameters, will be adopted from now on for all quantities). However, the density range explored did not extend up to the freezing line. The goal of the present calculation is to cover this gap so as to check the validity of the "freezing criterion" discussed above for a more realistic interaction. As the density increases, the long-ranged oscillations in the RDF become more and more enhanced and, correspondingly, the error associated with a finite upper cutoff of the integral in Eq. (2) increases. Therefore, in order to sample a more extended space region, we carried out a series of MD calculations on systems with 6912 particles in the liquid phase with a time step of 0.005 using the Nosé algorithm [11]. The LJ potential was truncated at 2.5. The present MD calculations were performed along two isotherms, i.e., for $T = 0.75$ (just above the estimated triple point temperature $T_t = 0.68 \pm 0.02$) [12], and for $T = 1.15$ (still below the critical point). At such two temperatures, the thermodynamic history of the system from very low densities is supplied by Hansen and Verlet in

TABLE I. Compressibility factor $\beta P/\rho$, excess energy per particle $U^{(ex)}/N$, excess entropy per particle $s^{(ex)}$, and two-body excess entropy s_2 as a function of the reduced density for $T=0.75$ and 1.15. The number of equilibrium configurations $\mathcal{N}_{\text{conf}}$ used to compute the thermal averages is also indicated.

T	ρ	$\mathcal{N}_{\text{conf}}$	$\beta P/\rho$	$U^{(ex)}/N$	$s^{(ex)}$	s_2
0.75	0.84	5000	0.441	-6.024	-3.441	-3.378
0.75	0.85	5000	0.692	-6.084	-3.516	-3.492
0.75	0.86	5000	0.952	-6.134	-3.581	-3.599
0.75	0.87	5000	1.244	-6.192	-3.659	-3.711
1.15	0.75	2500	1.161	-5.107	-2.535	-2.203
1.15	0.85	2500	2.865	-5.664	-3.133	-2.855
1.15	0.92	2500	4.719	-5.951	-3.599	-3.462
1.15	0.93	5000	5.022	-5.986	-3.671	-3.566
1.15	0.94	5000	5.364	-6.013	-3.739	-3.668
1.15	0.95	5000	5.711	-6.039	-3.810	-3.771
1.15	0.96	5000	6.069	-6.063	-3.882	-3.882
1.15	0.97	5000	6.450	-6.082	-3.953	-3.993

Ref. [12]. The range of densities spanned in this work was $0.84 \leq \rho \leq 0.87$ for $T=0.75$ and $0.75 \leq \rho \leq 0.97$ for $T=1.15$. Correspondingly, the RDF was evaluated up to $R_{\text{max}} \sim 10$, where $R_{\text{max}} = L/2$ and $L = (N/\rho)^{1/3}$ is the simulation box length. At such distances the values attained by the RDF do not significantly differ from unity and, therefore, the standard asymptotic correction on the integrals for both the pressure and the internal energy can be safely made. The RDF histogram (with a spatial resolution $\Delta r = 0.01$) was updated after every ten MD time steps. Typical averages were computed on the thermalized system over a number of 2500–5000 configurations. Given the above setup, the value of s_2 was found to converge to four significant figures even at the highest sampled density. This numerical happenstance straightly follows from the asymptotic vanishing of the integrand in Eq. (2) as the square of $[g(r) - 1]$. Actually, it turns out that the above level of convergence in s_2 is already established for $r \approx 8$.

Table I gives the present results for the thermodynamic quantities of the LJ liquid. In order to estimate the statistical uncertainty affecting the values of both s_2 and Δs , we divided the MD trajectory for each set of (T, ρ) values into blocks of 5000 time steps (corresponding to 500 sampling configurations). After verifying the statistical independence of the partial block averages for each quantity through the evaluation of the interblock correlation coefficient, we estimated the error on the cumulative average as the sample standard deviation [13]. The error on the compressibility factor $\beta P/\rho$ does not exceed 0.01 while that on s_2 is lower than 0.004. The corresponding error on Δs is 0.003 for $T=0.75$ and 0.006 for $T=1.15$. However, a residual systematic uncertainty is associated with the estimate of the total excess entropy of the initial reference states at both temperatures, i.e., ($\rho=0.84$, $T=0.75$) and ($\rho=0.75$, $T=1.15$), as obtained after integration of the thermodynamic data by Hansen and Verlet. Given their estimate of the uncertainty affecting $\beta P/\rho$, we conclude that the resulting error on $s^{(ex)}$ should not exceed 0.015.

The residual multiparticle entropies for both isotherms are plotted in Fig. 1 together with the data given in Ref. [8] for $T=1.15$. A spline interpolation of the data locates

the zero of Δs at $\rho=0.856$ for $T=0.75$ and at $\rho=0.960$ for $T=1.15$. In Table II these values are compared with the freezing-point estimates for both a LJ system with 864 particles and liquid argon as reported in Ref. [12]. The largest discrepancy relative to the two-phase free-energy recipe is 2.5%. However, a caveat should be posed on the different size of the two LJ systems. The predicted temperature dependence of the density where $\Delta s=0$ adheres to that followed by the freezing line. Moreover, the resulting values suggestively lie systematically closer to the experimental ones. Given the present evidence we surmise that the change of sign undergone by the residual multiparticle entropy along the *fluid* branch furnishes a one-phase criterion for predicting the *freezing* point of a simple liquid. The ensuing estimate of the freezing line $\rho_{\text{LJ}}^f(T)$ allows the calculation of the slope of the phase equilibrium curve (dP/dT) and, through the Clausius-Clapeyron equation, of the ratio of the latent heat to the volume change at the transition. A rough, straight-line

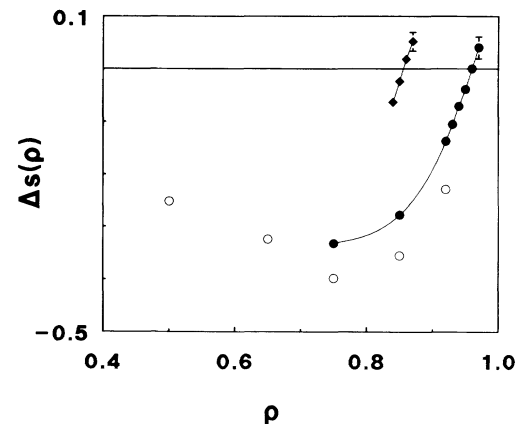


FIG. 1. Residual multiparticle entropy as a function of the reduced density for the LJ liquid. Diamonds: data for $T=0.75$. Solid circles: data for $T=1.15$. Open circles: data from Ref. [8] for $T=1.15$. The solid line represents a spline interpolation of the data. The estimated error is also displayed.

TABLE II. Freezing point densities for the Lennard-Jones liquid: (a) two-phase rule (see Ref. [12]); (b) present, one-phase criterion. The corresponding experimental data for argon are also reported [12].

T	LJ (a)	LJ (b)	Argon
0.75	0.875	0.856	0.856
1.15	0.936	0.960	0.947

estimate of the slope, as can be obtained from the present data which refer to two isotherms only, is 15.4. This result may be compared with the experimental value 12.3 and 15.3 for argon at $T=0.75$ and 1.15, respectively [12].

We have also analyzed Monte Carlo data relative to a model system of 864 soft spheres interacting through a merely repulsive potential $\phi(r)=4\epsilon(\sigma/r)^{12}$ [14,15]. This system undergoes a freezing transition at a reduced density $\rho_{\text{soft}}^f(T)\approx 0.814T^{0.25}$ [16,17]. The calculated behavior of Δs as a function of ρ turns out to be analogous to that reported for hard spheres with a crossover point which overestimates the freezing density by 5% with respect to the numerical simulation datum. This discrepancy (which is larger than that found for both hard spheres and the LJ

system) is still within the error arising from the statistical uncertainty on the tabulated RDF values. In fact, as noted by the authors in Ref. [14], this uncertainty becomes particularly relevant (significantly exceeding 1%) for distances below the position of the first peak, because of the poor statistics in this region. We have verified that the contribution to s_2 that is associated with this interval of distances affects its first decimal place and, therefore, the corresponding error may sensitively weigh in the ultimate balance between the total excess entropy and the two-particle term for densities close to the freezing point.

Molecular-dynamics calculations for the LJ system at supercritical temperatures together with an extension of the analysis to other inverse-power pair potentials will be the object of a forthcoming paper.

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