# Enumeration of random packings for atomic substances

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At fixed density, the number of distinguishable ways that $N$ identical atoms can be packed into a fixed volume is expected to rise exponentially, $\exp(vN)$, when the number $N$ of atoms is very large. Heretofore no satisfactory method has been available to evaluate the positive constant $v$. We propose such a method in classical statistical mechanics, utilizing the formalism and some basic results from the "inherent structure" theory of condensed phases. It requires data concerning (a) the mean potential energy of amorphous packings, (b) the mean logarithm of the normal-mode frequencies for both crystalline and for amorphous packings, and (c) a smooth extrapolation of the liquid-phase thermodynamic energy through the supercooled regime to absolute zero. We have applied this method to the soft-sphere model with $r^{-12}$ pair potentials, drawing upon published computer-simulation results. We find for this model that $v=0.07\pm0.06$, where most of the estimated error arises from uncertainty in the data currently available for (a) above.

## I. INTRODUCTION

An important open problem is to find the number of ways that identical particles or molecules can be arranged in space to form mechanically stable packings. Regular crystalline arrangements offer a few possibilities, but for large numbers of particles the overwhelming majority of the packings would be amorphous. This paper proposes a method for estimating the numbers of particle packings, which is based upon the "inherent structure" formalism for condensed phases of matter.

The inherent structure picture of condensed phases identifies three contributions to the Helmholtz free energy $F(N,V,T)$: the number of minima $\Omega(N,V)$ on the potential-energy hypersurface $\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ of $N$ particles, the (thermally weighted) mean energy $\hat{\Phi}_q$ of the packings corresponding to the respective minima, and the vibrational free energy $F^{\text{vib}}(N,V,T)$, measuring the mean configurational hypervolume available to thermally induced vibrational distortions of each of the packings.[1] Formally, the packings may be found by selection of a representative collection of instantaneous configurations from the equilibrium phase and employment of each one of them as the initial condition for a steepest-descent trajectory. Except for a set of measure zero, these trajectories must terminate at a local minimum of $\Phi$. Experimentally, this procedure corresponds to repeated instantaneous (anneal-free) quenching of the equilibrium phase. An advantage of the inherent structure formalism is that the study of any of the condensed phases, whether crystalline, vitreous, or liquid, may be accomplished within a common conceptual framework.

The three previously identified components of the free energy may differ in their relative importance according to the phase in question. In the crystalline phase at any given density there is usually only one relevant minimum, and in the absence of strong thermal fluctuations, the static crystal energy and the harmonic part of the vibrational free energy are the most important components of the free energy. In the equilibrium liquid, on the other hand, the thermal fluctuations are so strong that the vibrational free energy may make the most important contribution to the free energy.[2] The strongly supercooled liquid presents a circumstance where all three components may make important contributions to the free energy. The supercooled liquid may be subject only to weak vibrational fluctuations, like the crystal, but with an inherent structure composed of not one but many packings, like the equilibrium liquid. The total number of minima (or, equivalently, the number of corresponding packings) $\Omega$ enters into the free energy, as we shall show below, as an entropy $v$, defined on a per-particle basis as $v=\ln(\Omega/N!)/N$. For strongly supercooled simple liquids, we will show that $v$, the "packing entropy," indeed makes a relatively more important contribution to the free energy. Therefore we undertake in this work the enumeration of the packings corresponding to the minima of $\Phi$ for a simple model liquid.

We outline the plan of this work as follows. In Sec. II we review the inherent structure formalism, display explicitly the three components of the free energy, and discuss the physical significance of the packing entropy. In Sec. III we estimate the packing entropy from published thermodynamic data calculated for the liquid and crystalline phases of a soft-sphere model. We conclude this work in Sec. IV with a discussion of other estimates for the packing entropy, and of its relevance for the study of glasses and supercooled liquids.

## II. THE THERMODYNAMIC SIGNIFICANCE OF THE PACKING ENTROPY

The inherent structure analysis of the free energy has been discussed in detail previously.[1] Here, we merely outline the steps in order to define our terms.

The potential-energy hypersurface $\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ may be viewed as the union of basins each containing one of the minima identifiable by the procedure discussed in the

Introduction and elsewhere.[1] Each basin $B_\xi$ contains all the points of $\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ which also lie on a steepest-descent path to the minimum $\Phi_{q,\xi} = \Phi(\mathbf{x}_{1,\xi}, \ldots, \mathbf{x}_{N,\xi})$ contained in $B_\xi$. Every point on $\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ is thus accounted for, except those on the boundaries of $B_\xi$ which constitute a set of zero measure. Normally the canonical classical partition function $Q_{NVT}$ appears as

$$Q_{NVT} = (N!\Lambda^{3N})^{-1} \int d\mathbf{x}_1, \ldots, d\mathbf{x}_N$$
$$\times \exp[-\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N)/k_B T] ,$$

(1)

where $\Lambda$ is the de Broglie wavelength, written as $\Lambda = (h^2/2\pi m k_B T)^{1/2}$. Now we may rewrite $Q_{NVT}$ thus:[1]

$$Q_{NVT} = \Lambda^{-3N} \int d\phi_q \exp\{N[\sigma(\phi_q) - \phi_q/k_B T$$
$$- F^{\text{vib}}(T, \phi_q)/N k_B T]\} ,$$

(2)

where $\phi_q = \Phi_q/N$. The distinguishable potential energy minima are distributed by depth $\phi_q$ according to $\exp[N\sigma(\phi_q)]$. The vibrational free energy is calculated from the partition function of the configurations contained in each basin, averaged arithmetically over all the basins $B_\xi$ encountered with depth $\phi_q$, as follows:[1]

$$\exp[-F^{\text{vib}}(T, \phi_q)/k_B T] = \left\langle \int_{B_\xi} d\mathbf{x}_1 \cdots d\mathbf{x}_N \exp[-(\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_N) - \Phi_{q,\xi})/k_B T] \right\rangle_{\phi_q} .$$

(3)

The free energy of an infinite system ($N$, $V \to \infty$; $\rho = N/V = \text{const}$) may be found by evaluating the integrand in Eq. (2) at its global maximum. We denote by $\hat{\phi}_q$ the choice of $\phi_q$ which equivalently maximizes the expression

$$\sigma(\phi_q) - \phi_q/k_B T - F^{\text{vib}}/N k_B T .$$

In principle, $\hat{\phi}_q$ depends upon both the density and the temperature. However, for a large class of simple atomic liquids (in equilibrium), including the soft-sphere liquid discussed herein, $\hat{\phi}_q$ is in practice essentially temperature independent.[1,3] For these liquids there is substantially a unique inherent structure valid at all temperatures (above freezing) with mean per-particle potential energy $\langle \Phi_{q,\xi}/N \rangle$ equal to $\hat{\phi}_q$. This corresponds to a sharp unimodal distribution $\exp[N\sigma(\phi_q)]$ in $\phi_q$ whose maximum asymptotically for large $N$ equals the distinguishable number of packings $\Omega/N!$. Therefore we can equally well define $\nu$ to be the value of $\sigma$ at this maximum $[\max_{\phi_q} \sigma(\phi_q)]$.[1,4] For the liquid ($\lambda$), the free energy $F_\lambda(N, V, T)$ becomes

$$F_\lambda/N k_B T = 3\ln\Lambda - \nu + \hat{\Phi}_{q,\lambda}/N k_B T + F_\lambda^{\text{vib}}/N k_B T .$$

(4)

The crystalline phase for these systems corresponds configurationally to the basin surrounding a single distinguishable minimum (disregarding crystal defects), namely, the zero-temperature crystal. The contribution of $\sigma(\phi_q)$ to the crystalline free energy $F_\chi(N, V, T)$ therefore vanishes, and we write

$$F_\chi/N k_B T = \hat{\phi}_{q,\chi}/N k_B T + 3\ln\Lambda + F_\chi^{\text{vib}}/N k_B T ,$$

(5)

where $\hat{\Phi}_{q,\chi}$ is the zero-temperature crystal energy. For the low-temperature (harmonic) crystal, the vibrational free energy reduces to the usual expression,[5]

$$F_\chi^{\text{vib}}/N k_B T = \frac{1}{N} \sum_{n=1}^{3N} \ln[\omega_n^0 (2\pi m k_B T)^{-1/2}] ,$$

(6)

where $\omega_n^0$ are the normal-mode frequencies of the crystal, subject to the usual periodic boundary conditions.

The low-temperature crystalline phase serves as a reasonable choice for a reference state for the calculation of $\nu$, since its partition function may be easily calculated from Eqs. (5) and (6) for a large class of simple atomic models. In terms of the entropy difference $\Delta S = S_\lambda - S_\chi$, provided there is a temperature range over which this difference can be defined, we have

$$\Delta S/N k_B = \nu + (\Delta\langle\Phi\rangle - \Delta\hat{\Phi}_q)/N k_B T - \Delta F^{\text{vib}}/N k_B T .$$

(7)

The unsubscripted brackets indicate the usual ensemble average, and $\Delta$ will serve to indicate generally the isothermal difference between a property of the liquid phase ($\lambda$) and the same property of the crystalline phase ($\chi$). In principle we require the above quantities at one temperature only since $\nu$ depends only on density or pressure but not temperature. We admit that the vibrational free energy $F_\lambda^{\text{vib}}$, and therefore $\Delta F^{\text{vib}}$, is at least as difficult to evaluate as $F_\lambda$ itself for the high temperatures encountered by the equilibrium liquid. However, if it is legitimate to extrapolate stable liquid properties to the supercooled liquid, we find that $F_\lambda^{\text{vib}}$ simplifies considerably. In particular, as $T$ approaches zero, we find (classically)

$$F_\lambda^{\text{vib}}/N k_B T = \left\langle \frac{1}{N} \sum_{n=1}^{3N} \ln[\omega_n(2\pi m k_B T)^{-1/2}] \right\rangle_{\phi_q} ,$$

(8)

where $\omega_n$ are the normal-mode frequencies of the packing with per-particle energy $\phi_q$, subject to periodic boundary conditions. The residual excess (over the crystal) entropy of the inherent structure of the liquid is $S^{\text{res}} = \lim_{T\to 0} \Delta S$, and the packing entropy $\nu$ is found from

$$\nu = S^{\text{res}}/N k_B + \Delta\overline{\ln\omega} ,$$

(9)

where

$$\Delta\overline{\ln\omega} \equiv \lim_{T\to 0} \Delta F^{\text{vib}}/N k_B T = \frac{1}{N} \sum_{n=1}^{3(N-1)} (\langle\ln\omega_n\rangle_{\phi_q} - \ln\omega_n^0) .$$

We stress that Eq. (9) is a classical mechanical result only. Stated alternatively, the classical residual excess entropy

contains only a vibrational contribution $(\Delta \overline{\ln\omega})$ and a contribution $(v)$ due to the multitude of packing options. We expect that the packing entropy $v$ will usually make a significant contribution to the residual excess entropy, particularly if the constituent particles have rotational or conformational degrees of freedom.

Our program for evaluating $v$ from Eq. (9) requires both an independent evaluation of $\Delta \overline{\ln\omega}$ from normal mode analysis and of $S^{res}$ from calorimetric data. The latter evaluation follows directly from the relation between the constant-volume heat capacity $C_v$ and the entropy $S$, namely $C_v = T\partial S/\partial T$, which then leads to

$$S^{res}/Nk_B = \Delta S(T_1)/Nk_B - \int_0^{k_B T_1} d(k_B T)\Delta C_v/Nk_B T .$$

(10)

Knowledge of $\Delta S$ for some particular temperature $T_1$ and $\Delta C_v$ for all temperatures between zero and $T_1$ is enough to determine $S^{res}$. Since the heat-capacity data are usually reported only as a discrete function of temperature, we find it convenient to express $\Delta C_v$ as the best fit of a polynomial in $T$ to the relevant data. Nonintegral powers of $T$ are generally required to describe the high-temperature dependence of $C_{v,\lambda}$, but since $T_1$ would not be much higher than the freezing temperature, a polynomial fit should adequately describe the classical $\Delta C_v$ for temperatures below $T_1$. We evaluate $S^{res}$ from an expression of the following form:

$$S^{res}/Nk_B = \Delta S(T_1)/Nk_B - \sum_{l=1}^{L} c_l(k_B T_1)^l .$$

(11a)

This approach is general and may be accomplished experimentally, provided the inherent structure of the liquid can be attained. However, in the next section, we determine $\Delta S(T_1)/Nk_B$ and the coefficients $c_l$ from the thermodynamic properties calculated from computer-simulation data reported by Hoover et al.[6] for a soft-sphere system. For the same system Stillinger and Weber[7] have calculated $\Delta \overline{\ln\omega}$, which allows us to complete our estimation of $v$.

### III. EVALUATION OF $S^{res}$ AND $v$ FOR A SOFT-SPHERE LIQUID

In this section we follow the steps outlined above to find both the residual and packing entropy of the inherent structure of a soft-sphere liquid. We first require $\Delta C_v$ for temperatures between zero and $T_{freezing}$, which therefore requires the heat capacity for the supercooled liquid. Although we do not immediately have such data, we do have accurate internal energies $\langle \Phi \rangle_\lambda$ for the equilibrium liquid at temperatures above $T_{freezing}$ as well as the mean packing energy $\hat{\Phi}_q$, which corresponds to the liquid quenched without annealing to zero temperature. The temperature dependence of $\langle \Phi \rangle_\lambda/N$ in the supercooled region can be approximated[8] by fitting the polynomial

$$P_\lambda(T) = \sum_{m=0}^{M} \alpha_{m,\lambda} T^m$$

to $\langle \Phi \rangle_\lambda$. This requires the constraint $\alpha_{0,\lambda} = \langle \Phi \rangle_\lambda(T=0)/N = \hat{\Phi}_{q,\lambda}/N$ for the known amorphous

packing energy, and a constraint of harmonic mode equipartition $\alpha_{1,\lambda} = \frac{3}{2}k_B$. If in addition we fit

$$P_\chi(T) = \sum_{m=0}^{M} \alpha_{m,\chi} T^m \quad (\alpha_{0,\chi} = \hat{\Phi}_{q,\chi}/N, \ \alpha_{1,\chi} = \frac{3}{2}k_B)$$

to $\langle \Phi \rangle_\chi$, then by

$$C_v/N = \frac{\partial \langle \Phi \rangle/N}{\partial T}$$

the coefficients $c_l$ in Eq. (11a) become

$$c_l = (l+1)\Delta\alpha_{l+1}/l .$$

(11b)

The internal energies of an equilibrium soft-sphere liquid and of the crystalline phases are implicit in the pressure equation-of-state data published by Hoover et al.[6] The potential energy $\Phi$ of $N$ soft spheres is defined by

$$\Phi = \sum_{\substack{i,j=1 \\ i<j}}^{N(N-1)/2} \epsilon \left[ \frac{\sigma}{r_{ij}} \right]^{12} ,$$

(12)

where $\sigma$ is the diameter, $\epsilon$ is the energy for a pair at contact, and $r_{ij}$ is the distance between any pair $i,j$ of particles. Since $\Phi$ is homogeneous in distance, the following special relationship is found between the internal energy $\langle \Phi \rangle$ and the equation of state:[6]

$$\langle \Phi \rangle/Nk_B T = \frac{1}{4}(pV/Nk_B T - 1) .$$

(13)

Another consequence of the distance scaling is that the equation of state may be expressed in terms of a single dimensionless variable $\rho^*$, which Hoover et al. defined as $\rho^* \equiv \rho\sigma^3(\epsilon/4k_B T)^{1/4}$. We define the reduced temperature by $T^* \equiv (\rho^*)^{-4}/4 = k_B T/\epsilon(\rho\sigma^3)^4$, and reexpress the equation-of-state data as a function of $T^*$. Table I shows the reduced internal energy $\langle \Phi \rangle^* \equiv \langle \Phi \rangle/N\epsilon(\rho\sigma^3)^4$ as a function of $T^*$, as deduced from Hoover's equation-of-state data and Eq. (13). The reduced internal energy for the zero-temperature liquid $\hat{\Phi}^*_{q,\lambda}$ is taken from the calculation of Stillinger and Weber,[7] for which they find

TABLE I. Thermodynamic data for the soft-sphere system at constant density. The data for $T^* > 0$ are taken from Tables I and III of Ref. 6. The value for $\Phi^*_{q,\chi} = \langle \Phi \rangle^*_\chi(0)$ is inferred from $\langle \Phi \rangle^*_\chi(T^*) - \frac{3}{2}T^*$ for $T^* = 0.12056$. The value for $\Phi^*_{q,\lambda} = \langle \Phi \rangle^*_\lambda(0)$ is taken from Ref. 7. Except for $\Phi^*_{q,\lambda}$, all the values correspond to the infinite-system equilibrium phase. The freezing temperature is found from Ref. 6 to be, in reduced units, $T^*_{freezing} = 0.57224$.

| $T^*$ | $\langle \Phi \rangle^*_\chi$ | $\langle \Phi \rangle^*_\lambda$ | $\Delta S/Nk_B$ |
|---|---|---|---|
| 1.0412 | | 3.2458 | |
| 0.83371 | 2.6908 | 3.0003 | 0.602 |
| 0.71118 | | 2.8458 | |
| 0.61035 | 2.3666 | 2.7103 | 0.646 |
| 0.38104 | 2.0529 | | |
| 0.25000 | 1.8744 | | |
| 0.12056 | 1.6927 | | |
| 0.0 | 1.5119 | 1.75±0.01 | |

TABLE II. Coefficients of the polynomial fit to internal energy data. The polynomial $P(T^*) = \sum_{m=0}^{M} \alpha_m (T^*)^m$ was fitted to the data $\langle \Phi \rangle^*(T_j^*)$, $j = 1, \ldots, J$ by minimizing the sum $\sum_{j=1}^{J} [P(T_j^*) - \langle \Phi \rangle^*(T_j^*)]^2$. The best fits for both phases were found with $M = 5$. For all cases with $M = 5$, the sum over $j$ is less than $10^{-6}$. The coefficient $\alpha_1$ is equal to $\frac{3}{2}$ in all cases.

|            | $\alpha_{0,\lambda} = 1.74$ | $\alpha_{0,\lambda} = 1.75$ | $\alpha_{0,\lambda} = 1.76$ | $\alpha_{0,\chi} = 1.5119$ |
|------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| $\alpha_2$ | 0.959 015                   | 0.828 270                   | 0.697 620                   | 0.092 606                   |
| $\alpha_3$ | −2.192 336                  | −1.905 855                  | −1.619 648                  | −1.881 561                  |
| $\alpha_4$ | 1.589 868                   | 1.361 418                   | 1.133 221                   | 3.547 898                   |
| $\alpha_5$ | −0.408 254                  | −0.345 452                  | −0.282 726                  | −1.886 303                  |

$\hat{\Phi}_{q,\lambda} = 201 \pm 1$ from the mean energy of 47 independent packings quenched from an $N = 256$ soft-sphere liquid, at density $\rho \sigma^3 = 0.818\,41$.

The relation between the packing entropy and the residual excess entropy was derived for an infinite system, and a consistent calculation of $S^{\text{res}}$ would use infinite-system data. Hoover et al. corrected both their original $N = 500$ equation-of-state and entropy data for system-size effects, and report their data as infinite-system data. However, the $\hat{\Phi}^*_{q,\lambda}$ found from the $N = 256$ calculation of Stillinger and Weber is not subject to the corrections discussed by Hoover et al. There are in principle size corrections to this $T = 0$ quantity, but they are completely unknown at present.

In order to explore the sensitivity of the coefficients $\{\alpha_{m,\lambda}\}$ to the uncertainty of $\Phi^*_{q,\lambda}$, we determined $P_\lambda(T^*)$ over the range of acceptable values for $\Phi^*_{q,\lambda}$. We tabulate the resulting coefficients in Table II. We plot the interpolated $\langle \Phi \rangle$ (minus the harmonic potential energy) for the supercooled liquid in Fig. 1, calling attention thereby to the importance of the anharmonic terms in $\langle \Phi \rangle_\lambda$ even for very low temperatures. The effect of the uncertainty of $\alpha_{0,\lambda}$ on $C_{v,\lambda}(T^*)/Nk_B$ is shown in Fig. 2.

The fits $P_\lambda(T^*)$ and $P_\chi(T^*)$ allow us to calculate $S^{\text{res}}/Nk_B$, when we have $\Delta S$ for a given temperature. Hoover et al. report the entropy for both phases at two common temperatures $T_1$ and $T'_1$. We have listed the entropy difference $\Delta S/Nk_B$ in Table I for the two temperatures. With $\Delta S$, the coefficients listed in Table II, and Eq. (11), we calculate $S^{\text{res}}/Nk_B$, and list their values in Table
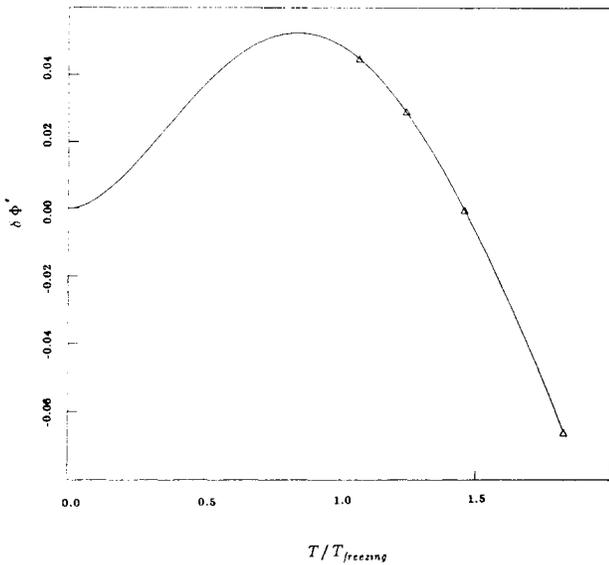


FIG. 1. The anharmonic contribution $\delta \Phi^*$ to the excess (over ideal gas) reduced internal energy for the soft-sphere liquid. The solid line represents $\delta \Phi^*$, defined here by $\delta \Phi^* \equiv \langle \Phi \rangle^*_\lambda - (\Phi^*_{q,\lambda} + \frac{3}{2} T^*)$. The coefficients $\{\alpha_{m,\lambda}\}$ for $P_\lambda(T^*) \cong \langle \Phi \rangle^*_\lambda$ are found in Table II. The plots are essentially the same for all three choices of $\alpha_{0,\lambda}$ found in Table II. The triangles represent the internal energy data for the liquid listed in Table I.
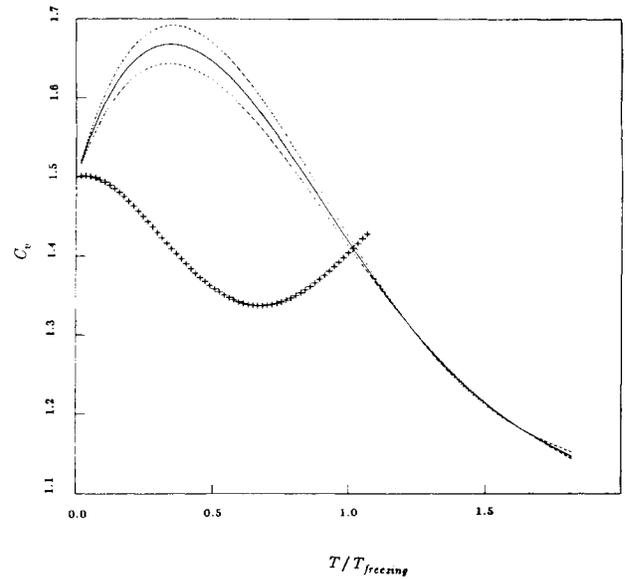
FIG. 2. Excess (over ideal gas) constant-volume heat capacity per particle $C_v/Nk_B$, found from $\partial \langle \Phi \rangle^*/\partial T^*$ $\cong \sum_{m=1}^{5} m \alpha_m (T^*)^{m-1}$. The coefficients $\{\alpha_m\}$ are found in Table II. The crosses represent $C_{v,\chi}/Nk_B$. The solid curve represents $C_{v,\lambda}/Nk_B$, from the $\{\alpha_{m,\lambda}\}$ corresponding to $\alpha_{0,\lambda} = 1.75$. The upper and lower dashed curves depict $C_{v,\lambda}/Nk_B$ calculated from the $\{\alpha_{m,\lambda}\}$ corresponding to $\alpha_{0,\lambda} = 1.74$ and $\alpha_{0,\lambda} = 1.76$, respectively.

TABLE III. Estimates for the residual excess entropy. In each case $S^{res}$ is calculated from Eq. (11) and the data in Tables I and II. The values $S^{res}_{(-)}$, $S^{res}_{(0)}$, and $S^{res}_{(+)}$ correspond to choosing $\Phi^*_{q,\lambda} = 1.74$, 1.75, and 1.76, respectively.

| $T^*_1$ | $S^{res}_{(-)}/Nk_B$ | $S^{res}_{(0)}/Nk_B$ | $S^{res}_{(+)}/Nk_B$ |
|---|---|---|---|
| 0.610 34 | 0.044 | 0.099 | 0.157 |
| 0.833 71 | 0.046 | 0.102 | 0.160 |

III. If there were no uncertainty associated with the fit of the polynomials to the energy data, the residual entropy calculated at $T = T_1$ would equal that at $T = T'_1$. The actual differences are not zero but they are small, in accord with a good fit of the polynomials to the data. The uncertainty in $S^{res}$ due to the uncertainty in $\Phi^*_{q,\lambda}$ is, on the other hand, substantial, overwhelming all other contributions to the uncertainty. We conclude that the residual excess entropy of the inherent structure of this soft-sphere liquid is

$$S^{res}/Nk_B = 0.10 \pm 0.06 \ .$$

To deduce the packing entropy $\nu$ from the residual entropy, we use Eq. (8) and require $\Delta \overline{\ln\omega}$. System-size corrections are absent in this quantity since they are only additive for the respective harmonic free energies. Stillinger and Weber[7] have calculated the harmonic $F^{vib}/Nk_B T$ [Eqs. (6) and (8)] for both the crystal and the liquid, from which we find $\Delta \overline{\ln\omega} = -0.033$ in reduced units. We conclude that the packing entropy of the inherent structure of the soft-sphere liquid is

$$\nu = 0.07 \pm 0.06 \ ,$$

in reduced units. Again, the greatest part of the relatively large uncertainty in $\nu$ is due to the uncertainty in the packing energy $\Phi^*_{q,\lambda}$, which presumably could be substantially diminished by more exhaustive simulation for the soft-sphere liquid.

## IV. DISCUSSION

One immediate use of $\nu$ is for the estimation of $F^{vib}_\lambda$ at any temperature for which $F_\lambda$ and $\hat{\Phi}_{q,\lambda}$ are known [cf. Eq. (4)], or for $\Delta F^{vib}$ when $\Delta S$, $\Delta \langle \Phi \rangle$, and $\Delta \Phi^{vib}$ are known [cf. Eq. (7)]. For example, for $\nu$, Eq. (7) and Table I, we find $-\Delta F^{vib}/Nk_B T = 0.42 \pm 0.07$ for $T^* = 0.610\,35$, ($T^*_{freezing} = 0.572\,24$),[6] which is over a tenfold increase above $-\Delta \overline{\ln\omega} = 0.033$, and which accounts for nearly two thirds of $\Delta S/Nk_B$ at this temperature. This gives us a way to quantify the strong anharmonic distortions of the packings concomitant with the equilibrium soft-sphere liquid. Further, this result indicates that for this model, the difference between the vibrational distortions of, respectively, the crystal and the inherent structure of the liquid present at the freezing temperature makes the largest contribution to the entropy of fusion ($S_{fusion} = 0.89 \pm 0.02$).[6]

There are other approaches to the estimation of the packing entropy. For example, Stillinger and Weber have made rough estimates of $\nu$ for simple atomic systems[9,10]

with short-ranged attractions, and repulsions which asymptotically (in the high-density limit) follow the soft-sphere model of Eq. (12). These estimates were made by directly counting the number of packings found in small ($N = 32$) systems. No system-size corrections were attempted. They found $\nu$ (which for these systems is density-dependent in a nontrivial way) about twice that calculated here for soft spheres, although the large uncertainties in both estimates preclude a decisive quantitative comparison. They also observed that $\nu$ appeared to decrease with increasing density. This finding is consistent with the lower value which we report for the soft-sphere $\nu$, since at high densities the effects of the repulsive forces dominate those of the attractive forces.

In the preceding section we suggested that $\nu$ might be determined by experiment, at least for some suitable substances. We note that $\nu$ must be strongly material dependent. One way to determine the residual entropy [cf. Eq. (10)] for a simple atomic liquid would be to supercool the liquid in steps, down to nearly zero temperature, in order to obtain $\Delta C_v(T)$ directly. The supercooled liquid eventually vitrifies, but as long as the crystal does not nucleate, near zero temperature the amorphous solid should be one of the many typical packings which would have been obtained by an instantaneous quench of the liquid. To the extent that the packings are narrowly distributed about a single mean energy, the properties of the amorphous solid obtained by supercooling should not significantly deviate from those of the inherent structure, which is an ensemble of the typical packings. In any case, systematic corrections could be formulated for the temperature dependence of $\hat{\Phi}_q$ due to the width of the packing distribution, and therefore of any temperature dependence of inherent structures.
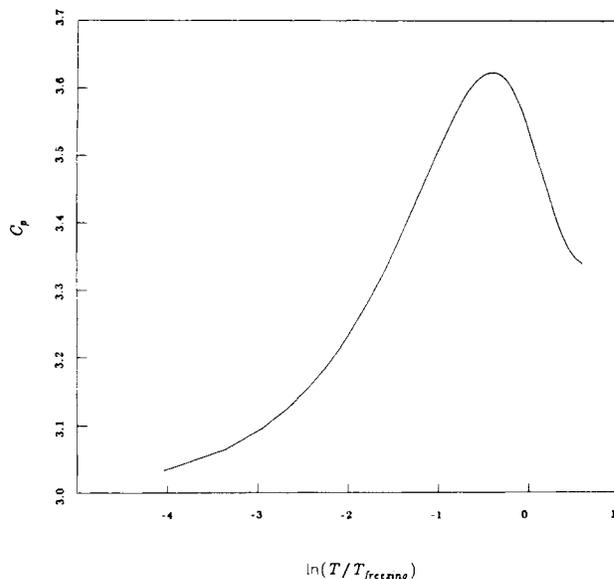


FIG. 3. Constant-pressure heat capacity per particle $C_{p,\lambda}/Nk_B$, including ideal gas contributions, calculated from the solid curve in Fig. 2 and Eq. (14).

Cape and Woodcock have studied the supercooled soft-sphere liquid by computer simulation.[11] Their simulation corresponds substantially to the experiment described above. By integrating the heat capacity (at constant pressure) over the temperature range of the supercooled liquid, they found $S^{res}/Nk_B = 0.29 \pm 0.07$. This gives $\nu = 0.26 \pm 0.07$, according to Eq. (9). Cape and Woodcock apparently did not attempt to quench to a (zero temperature) amorphous potential energy minimum; they do not report a $\Phi_{q,\lambda}$. However, we regard this parameter as an important component in the estimation of $\nu$. We also note that their equation of state for the equilibrium phases varies slightly from the values reported by Hoover et al. As we illustrate in Fig. 2, even small errors in the low-temperature heat capacity are sufficient to induce large uncertainties in $S^{res}$ and therefore $\nu$. For example, an interpolated $C_v$ based on $\Phi_{q,\lambda}^* = 1.77$ would have given $S^{res}$ within the uncertainty bounds reported by Cape and Woodcock; however this packing energy appears to be outside the range suggested by the Stillinger-Weber calculation.

We may also compare our interpolated $C_v$ for the supercooled liquid with the Cape-Woodcock calculation for $C_p$ by exploiting the relation special to the soft-sphere liquid:[11]

$$C_p/Nk_B = C_v/Nk_B + \frac{4(C_v/Nk_B - 5)^2}{(20\langle \Phi \rangle /Nk_BT - 16C_v/Nk_B + 25)} .$$

(14)

Here, both $C_v$ and $C_p$ include ideal gas contributions, whereas we did not include such contributions in Eqs. (10) and (11). Although Cape and Woodcock did not tabulate $C_p$, they plotted it against $\ln(k_BT/\epsilon)$ in Fig. 2 of Ref. 11. We plot our own derived $C_p$ against $\ln(T/T_{freezing})$ in Fig. 3 for comparison. The comparison reveals a strong qualitative similarity between the two estimates for $C_p$. Specifically, we note that the position, height, and breadth of the two peaks are similar. This supports our belief that, in spite of the differing estimates for $\nu$, the interpolation between the mean packing energy of the inherent structure and the internal energy of the equilibrium liquid provides an accurate description of the internal energy of the (rapidly) supercooled liquid for this simple soft-sphere system.

The peaks in the heat capacities reported both here and by Cape and Woodcock are too broad to correspond to the heat-capacity anomalies usually associated with phase transitions. However, they probably indicate a substantial yet smooth increase in the spatial coherence in the supercooled liquid as it vitrifies. This is consistent with our comments in an earlier study of another simple atomic supercooled liquid.[2] In that study, we investigated the energetic behavior of a supercooled liquid as it followed a steepest-descent path leading to a typical stable amorphous packing. There too we saw indications of increasingly collective spatial rearrangements among the particles as the liquid followed the path to its end point.

The nearest physically realizable analogues to the in-herent structure of the soft-sphere system are probably the pure one-component metallic glasses formed from substances whose crystal structure is close packed. Therefore, these glasses should be the best candidates for an experimental determination of $\nu$. Both seem to be best described, by experiment and by computer simulation, as randomly close-packed structures, with predominantly face-centered-cubic or hexagonal-close-packed short-ranged order but no intermediate-ranged microcrystalline order.[12-14] Neither is a true glass former in any conventional sense;[11,15,16] neither exhibits a well-defined sharp glass transition (cf. Figs. 2 and 3). Both seem to produce amorphous solid whose structure and energies are both narrowly and unimodally distributed, corresponding to an underlying temperature-independent inherent structure. The mechanically stable amorphous solids produced by rapid quenches of simple metallic liquids are therefore most likely to be the packings representative of a temperature-independent inherent structure of the metallic liquid. If the configurational residual excess entropy and harmonic free-energy difference can be accurately measured, then we should have in hand an experimental determination of the packing entropy for these disordered materials.

True glass formers are more complex materials which often display a polyamorphism inconsistent with the assumption of amorphous packings narrowly distributed in energy.[15,17-20] Even in a one-component glass former like sulfur, there should be a broad distribution of inherent structures, depending upon the instantaneous distribution of rings and chains of sulfur atoms in the pre-quenched liquid.[21] Peritectic transition-metal glasses may display either a random close-packed structure or an orientationally ordered quasicrystal structure.[22] Equation (9) could not be applied naively to either of such polyamorphic systems. Also, eutectic metal-metalloid glasses may not be polyamorphic in the sense described above, but there is no single reference crystal.[16] An estimation for $\nu$ in this case might require an experimental realization of Eq. (4), a task operationally more difficult than that for Eq. (9).

In conclusion, we have shown in principle how to estimate the packing entropy for amorphous deposits, and therefore, how to estimate the number of packings which constitute the inherent structure of the liquid. This has been applied to the inverse-twelfth-power soft-spheres model. Knowledge of the packing entropy allows us to estimate the vibrational free energy for a wide range of temperatures, and therefore to assess the importance of the anharmonic distortions of the inherent structure present at liquid-phase temperatures. Knowledge of the mean packing energy of the quenched liquid together with the internal energy of the equilibrium liquid allows us to make an interpolation which reproduces the internal energy of the supercooled liquid reasonably well. For simple one-component metallic glasses, an experimental determination of the packing entropy could be accomplished with sufficiently accurate thermodynamic and normal-mode data.

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