

Thermodynamics of binary mixture glasses

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We compute the thermodynamic properties of the glass phase in a binary mixture of soft spheres. Our approach is a generalization to mixtures of the replica strategy, recently proposed by Mezard and Parisi, providing a first principle statistical mechanics computation of the thermodynamics of glasses. The method starts from the interatomic potentials, and translates the problem into the study of a molecular liquid. We compare our analytical predictions to numerical simulations, focusing onto the values of the thermodynamic transition temperature and the configurational entropy.

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I. INTRODUCTION

In this paper we present the generalization to the binary mixture case of a thermodynamic theory of glasses, recently proposed,^{1,2} which allows to deduce equilibrium properties of fragile glasses³ from those of the corresponding liquid phase, computed for a molecular liquid consisting of m clones⁴ of the system with $m < 1$.

The hypothesis at the heart of this strategy is the existence of a liquid-glass thermodynamic transition, driven by the entropy crisis predicted by Kauzmann,⁵ and the scenario is similar to the one described by Adam, Gibbs, and Di Marzio.⁶⁻⁸ The transition considered here can be also explained in terms of a certain type of replica symmetry breaking (called one step replica symmetry breaking – 1RSB). It shares its main features with the glass transition found in some discontinuous spin-glasses model, as first proposed by Kirkpatrick, Thirumalai, and Wolynes.⁹

We identify the mode coupling temperature T_{MCT} ¹⁰ with the dynamical temperature T_D of the discontinuous spin-glasses,¹¹⁻¹³ and we assume that below this temperature the phase space can be partitioned in a very large number of different free energy valleys. These valleys are supposed to be, in terms of free-energy, the equivalent of the so-called inherent structures,¹⁴ which are built from the minima of the potential energy together with their basins of attraction.

In other words, we suppose that, for $T < T_{\text{MCT}}$, a typical equilibrium configuration belongs to one of these valleys. We label the valleys with an index α , and denote for each valley the free energy density as f_α , the subset of equilibrium configurations belonging to the valley as \mathcal{V}_α and the corresponding restricted partition function as Z_α . The canonical partition function can then be written in the following way:

$$Z \approx \sum_{\alpha} Z_{\alpha} = \sum_{\alpha} \int_{\{x\} \in \mathcal{V}_{\alpha}} dx e^{-\beta H(x)} = \sum_{\alpha} e^{-N\beta f_{\alpha}}, \quad (1)$$

where the function H is the Hamiltonian of the system and β is the inverse temperature. The number of valleys with a given value of free energy density is defined as $\mathcal{N}(f) \equiv \sum_{\alpha} \delta(f - f_{\alpha})$, and we assume that in the thermodynamic limit it becomes a continuous function. It is then possible to write the partition function as

$$Z \approx \int df \mathcal{N}(f) e^{-N\beta f} = \int df e^{-N[\beta f - \Sigma(f, T)]}, \quad (2)$$

where we have introduced the complexity $\Sigma \equiv \log \mathcal{N}/N$.

Let us note that the system in equilibrium does not minimize the free energy of the single valleys, but a collective thermodynamic potential $\phi(T)$, that we interpret as the actual free energy in the liquid and glass phases. $\phi(T)$ is defined by

$$\phi(T) \equiv f^* - T\Sigma(f^*, T), \quad (3)$$

where f^* is the temperature dependent free energy which minimizes the function $f - T\Sigma(f, T)$.

In this picture, the total entropy density is the sum of the entropy inside the valley, and of the entropy coming from the very large number of valleys, with the same value of free energy, that the system is allowed to explore:

$$S_{\text{tot}} = S_{\text{valley}} + \Sigma(T, f^*), \quad (4)$$

hence the complexity introduced here is completely equivalent to the usual concept of configurational entropy of a supercooled liquid.

Assuming the existence of this decomposition of phase space into valleys, we will show that there is a finite temperature T_K (the so-called Kauzmann temperature) where the system undergoes a thermodynamic transition with the following features:

- (a) T_K is the temperature where the complexity Σ vanishes.^{1,2} This means that, unlike the liquid phase, in the whole low temperature glass phase, only a nonexponential number of valleys contribute to the partition function, namely the ones with the lowest free energy density f_{\min} .
- (b) At T_K there is a second order transition from the thermodynamic point of view. The free energy is continuous and there is no latent heat. The specific heat jumps from the liquid value to a smaller one, in agreement with the Dulong and Petit law.
- (c) At T_K there is a discontinuity of the order parameter. Below T_K , in the glass phase, the system is an amorphous solid and the thermal average of the local particle density becomes nonuniform, exhibiting peaks at the favored positions where the particles tend to be trapped in some cages. The order parameter is related to the spatial modulation of the density, and it goes discontinuously from zero in the high temperature liquid phase to a finite modulation in the glass phase.

This transition could be experimentally observed only if one would be able to cool the liquid at an infinitely slow rate, and T_K should correspond to the temperature where the viscosity is supposed to diverge [following for instance a generalized Vogel–Fulcher law $\eta \propto \exp(T - T_K)^{-\nu}$].³ In real experiments, infinitely slow cooling is not available, and the correlation time becomes of order of the experimental time at a temperature T_g , which is in general an intermediate temperature $T_K < T_g < T_{MCT}$. The value of T_g could be computed only if we had under control the time dependence of the correlation functions. In this paper we study only static quantities, and we cannot say anything about the value of T_g or the temperature dependence of the viscosity above T_K .

In such an entropy crisis scenario, it has been shown^{15,4} that the thermodynamic properties of the glass phase can be computed in principle by considering m replicas of the original system, constrained to stay in the same valley, by means of a small but extensive coupling term. In this case, the arguments used in the derivation of (3) can be applied again, leading to a replicated version of the same equation:

$$\Phi(m, T) \equiv \text{Min}_f [mf - T\Sigma(f, T)]. \quad (5)$$

Once again, each of the m systems does not reach the lowest possible free energy, but the one which optimizes the balance between the free energy and complexity in (5).

Interestingly enough, one can derive many properties of the system from (5) if one is able to continue it analytically and compute it for any real value of m , thinking about m as a new parameter of the problem. Indeed, $\Phi(m, T)$, considered as a function of m , gives access to the configurational entropy (complexity) $\Sigma(f, T)$ through a Legendre transform. This implies the relations:

$$f = \frac{\partial \Phi(m, T)}{\partial m}, \quad \Sigma = \frac{m^2}{T} \frac{\partial (\Phi(m, T)/m)}{\partial m}, \quad (6)$$

from which it is possible to eliminate m , obtaining $\Sigma(f)$, which measure the number of valleys with a given value of free energy f . Let us underline that (6) gives access to the full

curve of complexity versus free energy, while the equilibrium free energy of the physical system is obtained only after taking the limit $m \rightarrow 1$.

As we shall see, the thermodynamic potential $\Phi(m)/m$ is a convex function of m with a maximum at a point $m^*(T)$, which is an increasing function of T , vanishing at $T=0$. The second equation of (6) is thus well-defined for $m \leq m^*(T)$. At $m = m^*(T)$, the resulting complexity vanishes $\Sigma=0$ and the free energy $\partial \Phi / \partial m$ reaches a value f_{\min} . For $m < m^*(T)$ the complexity Σ is nonzero: it is thermodynamically favorable to select some valleys which have a free energy density larger than f_{\min} because of the corresponding gain in complexity. If one increases m beyond $m^*(T)$, the formula (6) gives an unphysical negative complexity. In fact in the whole region $m > m^*(T)$ the correct value of f is $f = f_{\min}$, and the complexity is zero.

This is easily understood from the physical interpretation of the transition which we now turn to. The above scenario has

- (a) a high temperature phase where $m^*(T) > 1$. In this phase, when the limit $m \rightarrow 1$ is performed and the equilibrium free energy of the original system is recovered, one gets a value $f_{\text{eq}} > f_{\min}$ together with a positive configurational entropy.
- (b) a low temperature phase where $m^*(T) < 1$. In this phase, in the limit $m \rightarrow 1$ the equilibrium free energy is f_{\min} and the configurational entropy is null.

It is quite easy, at this point, to recognize these two thermodynamic phases as the supercooled liquid one (high) and the glass one (low), separated by a thermodynamic transition of second order, driven by the vanishing of the configurational entropy, at the temperature T_K where $m^*(T_K) = 1$. All the thermodynamic quantities in the glass phase can be computed from the replicated free energy (5) at the point m^* , which play the role of the free energy of the glass.

This scenario of the glass transition is identical to the phase transition appearing in discontinuous (1RSB) spin glasses where it was first explained.¹⁶ The simplest example of such a discontinuous spin glass transition is the random energy model¹⁷ which displays a total freezing at $T = T_K$. As first noticed by Kirkpatrick, Thirumalai, and Wolynes,⁹ discontinuous spin glasses provide some well defined mean field systems where the old ideas of Adam–Gibbs–Di Marzio of a real thermodynamic transition driven by entropic reasons are at work. The present approach allows to apply the replica method directly to the structural glasses (in spite of the absence of any quenched disorder in the Hamiltonian). Assuming that the structural glass transition is characterized in the replica language by a 1RSB, as in discontinuous spin glasses,^{8,18} we can compute the thermodynamic properties of the glass phase. The comparison with the numerical results allows then to justify *a posteriori* the main hypothesis.

At this stage, m appears as an auxiliary parameter which may be interpreted as the effective temperature of the valleys; moreover one finds that in the low temperature phase $1 - m$ gives the probability of finding two systems in the same valley.¹⁶

Summarizing, the study of the liquid-glass transition and

the investigation of the low temperature phase can be accomplished by computing the free energy of a replicated system in its liquid phase, or in other words,⁴ the free energy of a molecular liquid where each molecule has m atoms. The thermodynamic properties of the glass phase can be deduced by means of the analytic continuation to arbitrary real values of this parameter.

In the previous works^{1,2} this general approach was applied to a pure soft sphere system. The extension to binary mixtures is particularly important since there are well known examples of glass forming binary mixtures where an appropriate choice of the interaction parameters strongly inhibits crystallization. This allows therefore to get numerical results which can be compared to the analytical ones. Here we will consider in particular a mixture of soft spheres.

After discussing the model in Sec. II, we will present in Sec. III the generalization to binary mixtures both of the small cage expansion and of the harmonic re-summation scheme introduced previously¹ to deal with the molecular fluid. Section IV describes the application of the HNC approximation to the center of mass degrees of freedom of the molecular fluid. In the last section we will discuss our analytic results, together with some strategies for evaluating numerically the glass transition temperature T_K and the configurational entropy behavior, and a comparison between the numerical estimates and those obtained analytically.

II. GENERAL FRAMEWORK

We study mixtures composed of two types of particles called + and -, with pairwise interactions. The Hamiltonian of our problem is

$$H = \sum_{1 \leq i < j \leq N} V^{\epsilon_i \epsilon_j}(x_i - x_j) \quad \epsilon_i \in \{-, +\}, \quad (7)$$

where the N particles move in a volume V of a d -dimensional space, and V^{++} , V^{+-} , V^{--} are arbitrary short range interaction potentials. We call c_+ (respectively, c_-) the fraction of + (respectively, -) particles.

In the explicit computations described in the next section, we have chosen a binary mixture of soft spheres that has been extensively studied in the past through numerical simulations.^{19,20} The potentials are given by

$$V^{\epsilon \epsilon'}(r) = \left(\frac{\sigma_{\epsilon \epsilon'}}{r} \right)^{12}, \quad (8)$$

where

$$\frac{\sigma_{++}}{\sigma_{--}} = 1.2, \quad \sigma_{+-} = \frac{\sigma_{++} + \sigma_{--}}{2}. \quad (9)$$

The concentration is taken as $c_+ = 1/2$, and the choice of the ratio $R \equiv \sigma_{++} / \sigma_{--} = 1.2$ is known to strongly inhibit crystallization. We also make the usual choice of considering particles with average diameter 1 by setting

$$\frac{(\sigma_{++})^3 + 2(\sigma_{+-})^3 + (\sigma_{--})^3}{4} = 1. \quad (10)$$

All thermodynamic quantities depend on the density $\rho = N/V$ and temperature T only through the parameter

$\Gamma \equiv \rho T^{-1/4}$. For Γ larger than $\Gamma_D = 1.45$ (corresponding to lower temperatures) the dynamics becomes very slow and the autocorrelation time is very large. Hence the system enters the aging regime, where violations of the equilibrium fluctuation-dissipation theorem are observed.¹⁸ This value of Γ_D is supposed to correspond to the mode coupling transition below which the relaxation is dominated by activated processes.²¹ If this simple model behaves like a real fragile glass the Kauzmann transition, characterized by a discontinuity in the specific heat, is located below the dynamical transition, and cannot be directly accessed by numerical simulations, maybe with the exception of studies done on very small samples.¹⁹

The application of the theory to a more realistic potential, namely a Lennard-Jones binary mixture, will be treated in detail in a forthcoming paper.²¹

As previously explained, in order to obtain some information about the super-cooled liquid-glass thermodynamic transition, we consider the thermodynamics of a molecular liquid, whose molecules are composed of m atoms, each carrying a different replica index. The tendency to form molecules is forced by a small but extensive coupling term between particles of different replicas.⁴ Unlike the pure case, we are dealing here with a situation where particles are not all indistinguishable: we have particles of the “+” type and of the “-” type. Physically this has an important effect when R is not close to one. At $R \approx 1$, it is clear that the valleys of the mixture are close to those of the pure system. More precisely, taking one given valley of the pure ($R = 1$) system, one can generate $N! / N_+! N_-!$ valleys of the mixture with $R \approx 1$, by choosing at random the positions of the + and the - particles: in this limit the main effect of the mixture is to add a factor to the entropy, whose value is $N \log 2$ when $N_{\pm} = N/2$. On the other hand, when R is very different from one, the valleys of the mixture are very different from those of the pure system; one cannot find a new valley by just exchanging a + particle with a - particle. This physical problem has an exact counterpart in replica space. One could study the case where molecules are formed by one particle of each of the m different replicas, irrespective of their \pm nature. Qualitatively speaking, this would mean that interchanging two particles of different types, the two replicas to which particles belong would remain in the same valley, that is their free-energy would not change. There are two extreme possibilities, corresponding to the two cases discussed above:

- (a) For R very near to one, the system behaves similarly to the system at $R = 1$. One can form molecules with particles of any type, and the exchange of a “+” particle with a “-” one gives a very small change in free energy.
- (b) For R quite different from 1, the exchange of a “+” particle with a “-” one is a process that can be safely neglected, since it gives a variation in energy that is much larger than kT . In this second case the molecules are built up of atoms of the same type.

In each of these extreme cases the computation is simple: in the first case it just reduces to the $R = 1$ computa-

tion. In the second case, we can assume, as we shall do here, that each molecule is built from m atoms which are all of the same type (all “+” or all “-”). Then one only needs considering attractive coupling terms only between particles of the same kind. The computations in the crossover region are rather complex. For our case $R=1.2$, we have decided to neglect this kind of corrections and to consider the molecules consisting only of particles of the same type.

The replicated partition function is

$$Z_m[\omega] = \frac{1}{N_+! N_-!} \sum_{\sigma_a} \sum_{\pi_a} \int \prod_a d^d x_i^a \times \exp\left(-\frac{\beta}{2} \sum_{i \neq j, a} V^{\epsilon_i \epsilon_j} (x_i^a - x_j^a) - \sum_{i \in \{+\}} \sum_{a \neq b} \omega_+(x_{\sigma_a(i)} - x_{\sigma_b(i)}) - \sum_{i \in \{-\}} \sum_{a \neq b} \omega_-(x_{\pi_a(i)} - x_{\pi_b(i)})\right), \quad (11)$$

where the sum over permutations of atoms in each molecule is taken into account, and $N_+ = c_+ N$, $N_- = c_- N$. When relabeling particles, so that particle i of a given type in replica a corresponds to particle i of the same type in replica b (which is supposed to belong to the same molecules) and so on, the sum over permutations gives a factor $(N_+! N_-!)^{(m-1)}$.

As discussed in the preceding section, in the glass phase the replicas becomes correlated, so the study of the transition is accomplished by choosing as order parameters the m -points correlation functions for each of the two different types of particles:

$$\rho_+(r^1, \dots, r^m) = \sum_{i \in \{+\}} \langle \delta(x_i^1 - r^1) \dots \delta(x_i^m - r^m) \rangle, \quad (12)$$

$$\rho_-(r^1, \dots, r^m) = \sum_{i \in \{-\}} \langle \delta(x_i^1 - r^1) \dots \delta(x_i^m - r^m) \rangle. \quad (13)$$

The transition is signaled, then, by the onset of an off-diagonal nontrivial correlation in replica space at T_K , when the coupling functions ω_{\pm} are sent to zero. This feature is studied as usual introducing the Legendre transform of the molecular (replicated) free energy:

$$G[\rho] = \lim_{\substack{m \rightarrow 1 \\ \omega \rightarrow 0 \\ N \rightarrow \infty}} -\frac{1}{\beta m} \log Z_m[\omega] - \frac{1}{m} \int \prod_{a=1}^m d^d r^a \times \sum_{\epsilon = +, -} \rho_{\epsilon}(r^1, \dots, r^m) W_{\epsilon}(r^1, \dots, r^m) \quad (14)$$

with

$$W_{\epsilon}(r^1, \dots, r^m) = \sum_{a < b} \omega_{\epsilon}(r^a - r^b). \quad (15)$$

Performing the limit $\omega_{\pm} \rightarrow 0$ is equivalent to searching a saddle point of the functional $G[\rho]$. In the presence of a glassy transition we expect the following behavior of order parameters and thermodynamic quantities:

- (a) For $T > T_K$ the free energy is the liquid one ($m=1$) and the order parameters are trivial, i.e., $\rho_{\pm}(r^1) = c_{\pm} \rho$.
- (b) For $T < T_K$, the glass free energy is the maximum with respect to m of the replicated free energy, and this maximum is found at $m^* < 1$. The correlations ρ_{\pm} become non trivial. From the free energy at the maximum we can compute all the thermodynamic quantities.

The free energy and his first derivatives are continuous at T_K , while the heat capacity falls suddenly from liquidlike to solidlike values when the temperature is decreased through T_K . The transition, then, is of second order from the point of view of thermodynamics, but it is discontinuous in the order parameter which abruptly becomes a nontrivial function of positions in different replicas.

It is natural to describe the particle positions in term of center of mass coordinates r_i and relative displacements u_i^a with $x_i^a = z_i + u_i^a$ and $\sum_a u_i^a = 0$. A useful simplification is the choice, for the polarising potentials ω_{\pm} , of a quadratic coupling that allows to rewrite (11) as

$$Z_m = \frac{1}{N_+! N_-!} \int \left(\prod_{i=1}^N d^d z_i \right) \left(\prod_{a=1}^m \prod_{i=1}^N d^d u_i^a \right) \times \left[\prod_{i=1}^N \left(m^d \delta \left(\sum_{a=1}^m u_i^a \right) \right) \right] \times \exp\left(-\beta \sum_{a=1}^m \sum_{i < j} V^{\epsilon_i \epsilon_j} (z_i - z_j + u_i^a - u_j^a) - \frac{1}{4\alpha_+} \sum_{a,b} \sum_{i \in +} (u_i^a - u_i^b)^2 - \frac{1}{4\alpha_-} \sum_{a,b} \sum_{i \in -} (u_i^a - u_i^b)^2\right). \quad (16)$$

In the absence of the interacting potential V , the $\{u_{i\mu}^a\}$ for a given i are Gaussian random variables with a vanishing first moment and a second moment given by

$$\langle u_{i\mu}^a u_{iv}^b \rangle = \left(\delta^{ab} - \frac{1}{m} \right) \delta_{\mu\nu} \delta_{ij} \frac{\alpha_{\epsilon_i}}{m}. \quad (17)$$

III. REPLICATED FREE-ENERGY

A. Harmonic resummation

We are interested in the regime of low temperatures, where the molecules are expected to have a small radius, justifying a quadratic expansion of V in the partition function (16). After integrating over these quadratic fluctuations, one obtains

$$Z_m = \frac{m_i^{Nd/2} \sqrt{2\pi}^{Nd(m-1)}}{N_+! N_-!} \int \prod_{i=1}^N d^d z_i \times \exp\left(-\beta m \sum_{i < j} V^{\epsilon_i \epsilon_j} (z_i - z_j) - \frac{m-1}{2} \text{Tr} \log(\beta M)\right), \quad (18)$$

where the matrix M , of dimension $Nd \times Nd$, is given by

$$M_{(i\mu)(j\nu)}^{\epsilon_i\epsilon_j} = \delta_{ij} \left(\sum_k V_{\mu\nu}^{\epsilon_i\epsilon_k}(z_i - z_k) + \frac{m}{\alpha_{\epsilon_i}} \right) - V_{\mu\nu}^{\epsilon_i\epsilon_j}(z_i - z_j) \quad (19)$$

and $v_{\mu\nu}(r) = \partial^2 v / \partial r_\mu \partial r_\nu$ (the indices μ and ν , running from 1 to d , denote space directions). We have thus found an effective Hamiltonian for the centers of masses z_i of the molecules, which basically looks like the original problem at the effective temperature $T^* = 1/(\beta m)$, complicated by the contribution of vibration modes. We shall proceed by using the same set of approximations which was proposed in the previous papers.^{1,2} We first perform a quenched approximation, which amounts to neglecting the feedback of vibration modes onto the centers of masses, substituting thus the term $\text{Tr} \log(\beta M)$ in (18) by its expectation value, for center of mass positions z_i equilibrated at the temperature T^* . This approximation becomes exact close to the Kauzmann temperature where $m \rightarrow 1$.

Let us introduce the mean values of the diagonal terms of the matrix M :

$$r_\epsilon = \sum_{\epsilon'} c_{\epsilon'} \rho \int d^d r g^{\epsilon\epsilon'}(r) \frac{1}{d} \Delta V^{\epsilon\epsilon'} + \frac{m}{\alpha_\epsilon}, \quad (20)$$

where the $g^{\epsilon\epsilon'}(r)$ are the pair correlation functions. We neglect the fluctuation of these diagonal terms (an approximation which should be valid at high densities) and normalize the off diagonal matrix elements as follows:

$$C_{(i\mu)(j\nu)}^{\epsilon\epsilon'} \equiv \sqrt{\frac{c_\epsilon c_{\epsilon'}}{r_\epsilon r_{\epsilon'}}} V^{\epsilon\epsilon'}(z_i - z_j). \quad (21)$$

The replicated free energy per particle, $\phi(m, T) \equiv \Phi(m, T)/m$, can be expanded in series:

$$\begin{aligned} \beta\phi(m, \beta) = & -\frac{d}{2m} \log(m) - \frac{d(m-1)}{2m} \log(2\pi) \\ & - \frac{1}{mN} \log Z_{\text{liq}}(\beta m) + \frac{d(m-1)}{2m} (c_+ \log(\beta r_+) \\ & + c_- \log(\beta r_-)) + \frac{1}{N} \frac{(m-1)}{2m} \sum_{p=2}^{\infty} \left\langle \frac{\text{Tr} C^p}{p} \right\rangle, \end{aligned} \quad (22)$$

where the p th order term depends as usual on the p points correlation function

$$\begin{aligned} \langle \text{Tr} C^p \rangle = & \sum_{\epsilon_1 \dots \epsilon_p \in \{+, -\}} \sum_{\mu_1 \dots \mu_p} \int d^d z_1 \dots d^d z_p \\ & \times \rho^p g^{\epsilon_1 \dots \epsilon_p}(z_1 \dots z_p) C_{\mu_1 \mu_2}^{\epsilon_1 \epsilon_2}(z_1 - z_2) \dots \\ & C_{\mu_{p-1} \mu_p}^{\epsilon_{p-1} \epsilon_p}(z_{p-1} - z_p) C_{\mu_p \mu_1}^{\epsilon_p \epsilon_1}(z_p - z_1). \end{aligned} \quad (23)$$

We use a ‘‘chain’’ approximation in the computations of traces, where terms with two equal indices are neglected, and the so-called superposition approximation for the p points correlation functions $g^{(p)}(z_1 \dots z_p) = g(z_1 - z_2) \dots g(z_p - z_1)$. With these hypotheses we arrive at

$$\begin{aligned} \langle \text{Tr} C^p \rangle = & \int d^d z_1 \dots d^d z_p \rho^p \sum_{\mu_1 \dots \mu_p} \sum_{\epsilon_1 \dots \epsilon_p} g^{\epsilon_1 \epsilon_2}(z_1 - z_2) \\ & \times C_{\mu_1 \mu_2}^{\epsilon_1 \epsilon_2}(z_1 - z_2) \dots g^{\epsilon_{p-1} \epsilon_p}(z_{p-1} - z_p) \\ & \times C_{\mu_{p-1} \mu_p}^{\epsilon_{p-1} \epsilon_p}(z_{p-1} - z_p) g^{\epsilon_p \epsilon_1}(z_p - z_1) \\ & \times C_{\mu_p \mu_1}^{\epsilon_p \epsilon_1}(z_p - z_1). \end{aligned} \quad (24)$$

The convolutions are computed in Fourier space, introducing the tensor:

$$D_{\mu\nu}^{\epsilon\epsilon'}(k) \equiv \int d^d r g^{\epsilon\epsilon'}(r) C_{\mu\nu}^{\epsilon\epsilon'}(r) e^{ikr}, \quad (25)$$

which can be decomposed into its diagonal (longitudinal) and traceless (transversal) parts with respect to the spatial (μ, ν) indices:

$$D_{\mu\nu}^{\epsilon\epsilon'}(k) = \delta_{\mu\nu} a^{\epsilon\epsilon'}(k) + \left(\frac{k_\mu k_\nu}{k^2} - \frac{\delta_{\mu\nu}}{d} \right) b^{\epsilon\epsilon'}(k). \quad (26)$$

The last step consists in the diagonalization of D in the space of the particles types (ϵ, ϵ') . For each k , there are four distinct eigenvalues, the two longitudinal ones, corresponding to that of the 2×2 matrix

$$D_{\parallel}^{\epsilon\epsilon'}(k) = a^{\epsilon\epsilon'}(k) + \frac{d-1}{d} b^{\epsilon\epsilon'}(k), \quad (27)$$

and the two transverse eigenvalues of the matrix

$$D_{\perp}^{\epsilon\epsilon'}(k) = a^{\epsilon\epsilon'}(k) - \frac{1}{d} b^{\epsilon\epsilon'}(k). \quad (28)$$

The eigenvalues are

$$\begin{aligned} \lambda_{\parallel} = & \frac{1}{2}(D_{\parallel}^{++} + D_{\parallel}^{--} + \sqrt{(D_{\parallel}^{++} - D_{\parallel}^{--})^2 + 4(D_{\parallel}^{+-})^2}), \\ \mu_{\parallel} = & \frac{1}{2}(D_{\parallel}^{++} + D_{\parallel}^{--} - \sqrt{(D_{\parallel}^{++} - D_{\parallel}^{--})^2 + 4(D_{\parallel}^{+-})^2}), \\ \lambda_{\perp} = & \frac{1}{2}(D_{\perp}^{++} + D_{\perp}^{--} + \sqrt{(D_{\perp}^{++} - D_{\perp}^{--})^2 + 4(D_{\perp}^{+-})^2}), \\ \mu_{\perp} = & \frac{1}{2}(D_{\perp}^{++} + D_{\perp}^{--} - \sqrt{(D_{\perp}^{++} - D_{\perp}^{--})^2 + 4(D_{\perp}^{+-})^2}). \end{aligned} \quad (29)$$

Using these approximations, the expression of the binary mixture free energy per particle is

$$\begin{aligned} \phi(m, \beta) = & -\frac{d}{2m} \log(m) - \frac{d(m-1)}{2m} \log(2\pi) + \frac{d(m-1)}{2m} \\ & \times (c_+ \log(\beta r_+) + c_- \log(\beta r_-)) + \frac{(m-1)}{2m} \frac{1}{\rho} \\ & \times \int d^d k \{ L_3(\lambda_{\parallel}(k)) + L_3(\mu_{\parallel}(k)) + (d-1) \\ & \times [L_3(\lambda_{\perp}(k)) + L_3(\mu_{\perp}(k))] \} - \frac{(m-1)}{4m} \int d^d r \rho \\ & \times \sum_{\epsilon\epsilon'} g^{\epsilon\epsilon'}(r) \sum_{\mu\nu} (C_{\mu\nu}^{\epsilon\epsilon'}(r))^2 - \frac{1}{mN} \log Z_{\text{liq}}(\beta m), \end{aligned} \quad (30)$$

where the function L_3 is $\log(1-x) + x + x^2/2$.

Let us notice that the condition for identifying the Kauzmann temperature, $\partial\beta F_m/\partial m|_{m=1}=0$, reads in our harmonic approximation:

$$S_{\text{liq}} = \frac{d}{2} \log(2\pi e) - \frac{1}{2} \langle \text{Tr} \log(\beta M) \rangle \quad (31)$$

S_{liq} is the entropy of the liquid at the effective temperature T_{eff} , which is equal to T for $m=1$. The right-hand side of this equation is nothing but the entropy S_{sol} of an harmonic solid with a matrix of second derivatives given by M . Thus, we find

$$\Sigma(\beta) = m^2 \frac{\partial\beta F_m}{\partial m} \Big|_{m=1} = S_{\text{liq}} - S_{\text{sol}}. \quad (32)$$

If $S_{\text{liq}} < S_{\text{sol}}$ the system is in the glassy phase ($T < T_K$), while in the other case $S_{\text{liq}} > S_{\text{sol}}$, the temperature is greater than T_K (and of course less than T_D if the spectrum of M is positive). The complexity is then $\Sigma = S_{\text{liq}} - S_{\text{sol}}$, as expected on general grounds.¹⁵

Formula (30) allows to compute the free energy $\Phi(m, T) = m \phi(m, T)$ which is the main quantity needed to investigate the thermodynamics of the low temperature glass phase, using (6). It should be emphasized that within the approximations we used here, the only properties of the liquid phase which are needed to get Φ are the pair correlation $g(r)$ and the free energy. Beside usual thermodynamic quantities (energy, entropy, heat capacity,...), we are interested in the two new parameters describing the glassy phase:

- (a) The square cage radii A_ϵ , defined as $A_\epsilon = \frac{1}{3}(\langle x_i^2 \rangle - \langle x_i \rangle^2)$ for type ϵ particles. This square cage radii are obtained by differentiating the free energy with respect to coupling terms and by sending couplings to zero in the end:

$$A_\epsilon = \frac{2}{d(m-1)N_\epsilon} \frac{\partial(\beta F)}{\partial(1/\alpha_\epsilon)} \quad (\alpha_\epsilon = \infty). \quad (33)$$

The square cage radii are nearly linear in temperature in the whole glassy phase, which is natural since nonharmonic effects have been neglected.

The effective temperature $T_{\text{eff}} = T/m$ of the molecular liquid. This temperature varies very little and it remains close to the Kauzmann temperature when T spans the whole low temperature phase, confirming the validity of our description of the glass by means of a system of molecules remaining in the liquid phase. It is worth to stress that the linear behavior of the parameter m as a function of T is a feature shared by every 1RSB system to our knowledge.

The harmonic expansion makes sense only if M has no negative eigenvalues, which is natural since it is intimately related to the vibration modes of the glass. Notice that here we cannot describe activated processes, and therefore we cannot see the tail of negative eigenvalues [with number decreasing as $\exp(-C/T)$ at low temperatures], which is always present.²² It is known however that the fraction of negative eigenvalues of M becomes negligible below the dynamical transition temperature T_D .²³ So our harmonic expansion makes sense if the effective temperature T_{eff} is less than T_D .

B. Small cage expansion

It is possible to introduce a slightly different way to compute the molecular liquid free-energy, in order to take into account:

- (a) Nonharmonic terms.
(b) Corrections to the quenched approximation.

Starting from the expansion of the potential in powers of the relative variables u , if one expands also the exponential of the corrective term, one obtains an expansion of Z_m as a power series in α_+ and α_- . This is the generalization to mixtures of the small cage expansion scheme utilized in the pure case.^{1,2} This expansion is not equivalent to computing perturbatively quartic and higher order corrections to the Gaussian approximation represented by the harmonic resummation. Indeed, in this α_\pm expansion we are using a truncated version of the series in (22). On the other hand, this direct expansion allows to take into account the annealed fluctuations of the matrix M which were neglected in the harmonic approximation. Therefore these two types of approximations are complementary. In this paper we consider the harmonic resummation and the small cage approximation as distinct schemes of approximation and we compare results obtained independently in both them. However, it is clear that a better approximation of the replicated free energy could be obtained by adding corrections from the small cage approximation, treated in some systematic way, to the harmonic resummation. A first attempt in this direction will be found in a following work.²¹

The leading term of (16) in the $\alpha_+, \alpha_- \rightarrow 0$ limit is

$$Z_m^{(0)} = \sqrt{\frac{2\pi\alpha_+}{m}}^{dN^+(m-1)} \sqrt{\frac{2\pi\alpha_-}{m}}^{dN^-(m-1)} \times m^{dN/2} Z_{\text{liq}}(\beta m). \quad (34)$$

Accordingly, the zero-order free-energy is

$$\begin{aligned} \beta\phi^{(0)}(\alpha_+, \alpha_-, m, \beta) \\ = -\frac{1}{mN} \log Z_m^{(0)} = d_0 + a_0(c_+ \log \alpha_+ + c_- \log \alpha_-), \end{aligned} \quad (35)$$

with

$$\begin{aligned} d_0 &= \frac{d(1-m)}{2m} \log \frac{2\pi}{m} - \frac{d}{2m} \log m - \frac{1}{mN} \log Z_{\text{liq}}(\beta m), \\ a_0 &= \frac{d(m-1)}{2}. \end{aligned} \quad (36)$$

The first-order term is

$$\begin{aligned}
 Z_m^{(1)} &= \frac{1}{N+!N-!} \int \left(\prod_{i=1}^N d^d z_i \right) \left(\prod_{a=1}^m \prod_{i=1}^N d^d u_i^a \right) \\
 &\times \left[\prod_{i=1}^N \left(m^d \delta \left(\sum_{a=1}^m u_i^a \right) \right) \right] \cdot \exp \left(-\frac{1}{4\alpha_+} \right. \\
 &\times \sum_{a,b} \sum_{i \in +} (u_i^a - u_i^b)^2 - \frac{1}{4\alpha_-} \sum_{a,b} \sum_{i \in -} (u_i^a - u_i^b)^2 \\
 &\left. - \beta m \sum_{i < j} V^{\epsilon_i \epsilon_j}(z_i - z_j) \right) \cdot \left(1 - \frac{\beta}{2} \sum_{i < j} \sum_{a=1}^m \sum_{\mu, \nu}^d (u_{i\mu}^a - u_{j\mu}^a) \right. \\
 &\times (u_{i\nu}^a - u_{j\nu}^a) V_{\mu\nu}^{\epsilon_i \epsilon_j}(z_i - z_j) \left. \right) \\
 &= Z_m^{(0)} \left(1 - \frac{\beta}{2} \left\langle \sum_{i < j} \sum_{a=1}^m \sum_{\mu, \nu}^d (u_{i\mu}^a - u_{j\mu}^a) \right. \right. \\
 &\left. \left. \times (u_{i\nu}^a - u_{j\nu}^a) V_{\mu\nu}^{\epsilon_i \epsilon_j}(z_i - z_j) \right\rangle \right), \quad (37)
 \end{aligned}$$

from which we get the first-order contribution to the free energy:

$$\beta\phi^{(1)}(\alpha_+, \alpha_-, m, \beta) = c_+ a_1^+ \alpha_+ + c_- a_1^- \alpha_-, \quad (38)$$

where we define the first-order coefficients as

$$\begin{aligned}
 a_1^+ &= \frac{d(m-1)}{2m^2} \left[c_+ \int d^d r \rho g^{++}(r) \sum_{\mu} V_{\mu\mu}^{++}(r) \right. \\
 &\left. + c_- \int d^d r \rho g^{+-}(r) \sum_{\mu} V_{\mu\mu}^{+-}(r) \right], \\
 a_1^- &= \frac{d(m-1)}{2m^2} \left[c_- \int d^d r \rho g^{--}(r) \sum_{\mu} V_{\mu\mu}^{--}(r) \right. \\
 &\left. + c_+ \int d^d r \rho g^{-+}(r) \sum_{\mu} V_{\mu\mu}^{-+}(r) \right]. \quad (39)
 \end{aligned}$$

Up to first order, the harmonic resummation and the small cage expansion give the same results. Differences appear at the second-order level, which is presented in Appendix. In fact, the second-order term in the harmonic resummation is

$$\frac{(m-1)}{4m} \int d^d r \rho \sum_{\epsilon\epsilon'} g^{\epsilon\epsilon'}(r) \sum_{\mu\nu} (C_{\mu\nu}^{\epsilon\epsilon'}(r))^2, \quad (40)$$

while the second-order term in the small cage approximation adds two new kinds of term (see the Appendix):

- (a) Those involving fourth derivatives of potential, which are anharmonic corrections, are proportional to $(m-1)^2$, unlike any other term up to second order. This means that they are less important near T_K where $m \approx 1$, and more important at very low temperatures.
- (b) Those expressing the fluctuations of the diagonal terms of M . These are corrections to the quenched approximation.

The free energy per particle, up to second order, is then

$$\begin{aligned}
 &\beta\phi(\alpha_+, \alpha_-, m, \beta) \\
 &= d_0 + \frac{a_0}{m} (c_+ \log \alpha_+ + c_- \log \alpha_-) + c_+ a_1^+ \alpha_+ \\
 &\quad + c_- a_1^- \alpha_- + c_+ a_2^{++} \alpha_+^2 + c_- a_2^{--} \alpha_-^2 \\
 &\quad + c_+ c_- a_2^{+-} \alpha_+ \alpha_-, \quad (41)
 \end{aligned}$$

where the coefficients $a_2^{\epsilon\epsilon'}$ are given in the Appendix.

The free energy ϕ should be studied in the zero coupling limit, that is $\alpha_+, \alpha_- \rightarrow \infty$. This cannot be done directly with a powers series of α_+, α_- truncated at a finite order. Therefore one must first take the Legendre transform of ϕ , as previously discussed, getting the thermodynamic potential G as an expansion in powers of different cage sizes A_ϵ , defined by means of (33). Within this formulation, the free energy ϕ in the vanishing coupling limit is obtained by looking for possible minima of G with respect to A^+, A^- .

The Lagrange transformed free energy is, at first order:

$$\begin{aligned}
 \beta G(A^+, A^-, m, \beta) &= \gamma_0 + \frac{d(1-m)}{2m} (c_+ \log(A^+) \\
 &\quad + c_- \log(A^-)) + c_+ \gamma_1^+ A^+ \\
 &\quad + c_- \gamma_1^- A^-, \quad (42)
 \end{aligned}$$

$$\gamma_0 = a_0 + \frac{d(1-m)}{m}, \quad \gamma_1^+ = a_1^+, \quad \gamma_1^- = a_1^-,$$

and the saddle points equations read

$$\begin{aligned}
 \frac{\partial G}{\partial A^+} = 0 &\Rightarrow A^{+*} = -\frac{d(1-m)}{m} \frac{1}{\gamma_1^+} = \frac{1}{\beta r_+}, \\
 \frac{\partial G}{\partial A^-} = 0 &\Rightarrow A^{-*} = -\frac{d(1-m)}{m} \frac{1}{\gamma_1^-} = \frac{1}{\beta r_-}, \quad (43)
 \end{aligned}$$

$$\begin{aligned}
 r_+ &= c_+ \int d^d r \rho g_{\text{liq}}^{++}(r) \frac{1}{d} \Delta V^{++}(r) \\
 &\quad + c_- \int d^d r \rho g_{\text{liq}}^{+-}(r) \frac{1}{d} \Delta V^{+-}(r), \\
 r_- &= c_- \int d^d r \rho g_{\text{liq}}^{--}(r) \frac{1}{d} \Delta V^{--}(r) \\
 &\quad + c_+ \int d^d r \rho g_{\text{liq}}^{-+}(r) \frac{1}{d} \Delta V^{-+}(r).
 \end{aligned}$$

The first-order free energy in the vanishing coupling limit is correspondingly given by

$$\begin{aligned}
 \beta G(A^{+*}, A^{-*}, m, \beta) \\
 &= \frac{d(1-m)}{2m} \log \left(\frac{2\pi}{m} \right) - \frac{d}{2m} \log(m) - \frac{1}{mN} \log Z_{\text{liq}}(\beta m) \\
 &\quad - \frac{d(1-m)}{2m} (c_+ \log(\beta r_+) + c_- \log(\beta r_-)). \quad (44)
 \end{aligned}$$

This expression for G looks quite reasonable. First of all one may note that in the $m \rightarrow 1$ limit it reproduces the liquid free energy density $\beta f = -\log Z_{\text{liq}}(\beta)/N$, as it should. Moreover,

in the limit in which the “+” and “-” particles are no more distinguishable, this expression for G coincides with the one found in the pure case.^{1,2} (More precisely, the two generalized free energy would coincide in this limit if the liquid free energies at inverse temperature βm were the same, which would be true if one would forget about the mixture entropy contribution $\propto c_+ \log c_+ + c_- \log c_-$).

The computation of the second-order terms can be carried out in a very similar way. One gets (see the Appendix):

$$\begin{aligned} \beta G(A^+, A^-, m, \beta) &= \gamma_0 + \gamma_3(c_+ \log(A^+) + c_- \log(A^-)) \\ &+ c_+ \gamma_1^+ A^+ + c_- \gamma_1^- A^- \\ &+ c_+ \gamma_2^{++} (A^+)^2 + c_- \gamma_2^{--} (A^-)^2 \\ &+ c_+ c_- \gamma_2^{+-} A^+ A^- \end{aligned} \quad (45)$$

with

$$\gamma_3 \equiv \frac{d(1-m)}{2m}. \quad (46)$$

In evaluating the formulas of the appendix one needs to know the three particles correlation function. This correlation function can be computed starting from a generalized HNC expansion.¹ Here we follow the simpler route of evaluating the three point function using the superposition principle, i.e., $g_3(x, y, z) = g(x-z)g(x-y)g(y-z)$. When looking for the minimum $\partial G/\partial A^+ = 0$, $\partial G/\partial A^- = 0$, one faces the problem that the second-order corrections are very important (this happens also in the pure case). In this case the solution can be found only through a perturbation around the first-order solution. In this way one gets

$$\begin{aligned} A^{+*} &= A_1^{+*} + \delta A_2^{+*}, \\ A^{-*} &= A_1^{-*} + \delta A_2^{-*}, \end{aligned} \quad (47)$$

$$G(A^{+*}, A^{-*}, m, \beta) = G_1 + \delta G_2$$

and, by writing $m = m_1 + \delta m_2$, the stationarity condition reads

$$\begin{aligned} \frac{\partial G_1}{\partial m}(m_1) &= 0, \\ m_2 &= -\frac{\partial G_2}{\partial m}(m_1) \left(\frac{\partial^2 G_1}{\partial m^2}(m_1) \right)^{-1}. \end{aligned} \quad (48)$$

Therefore, one looks for the value m_1^* which maximizes G_1 , which is nothing but the first-order free energy, and then one computes the second order corrections at $m = m_1^*$. The result is

$$\begin{aligned} A_2^{+*} &= \frac{2\gamma_2^{++}}{(\gamma_1^+)^3} + c_- \frac{\gamma_2^{+-}}{(\gamma_1^+)^2 \gamma_1^-}, \\ A_2^{-*} &= \frac{2\gamma_2^{--}}{(\gamma_1^-)^3} + c_+ \frac{\gamma_2^{+-}}{(\gamma_1^-)^2 \gamma_1^+}, \end{aligned} \quad (49)$$

$$\begin{aligned} G_2 &= c_+ \left(\frac{\gamma_3}{\gamma_1^+} \right)^2 \gamma_2^{++} + c_- \left(\frac{\gamma_3}{\gamma_1^-} \right)^2 \gamma_2^{--} \\ &+ c_+ c_- \frac{\gamma_3^2}{\gamma_1^+ \gamma_1^-} \gamma_2^{+-}. \end{aligned}$$

Finally, the second-order correction to m_1 is obtained by (48).

IV. HNC FOR BINARY MIXTURES

In evaluating the liquid free energy f_{liq} and the $g^{\epsilon\epsilon'}$ at the effective temperature T/m we use the so-called hypernetted chain approximation (HNC), a simple closure approximation that consists in neglecting the bridge diagrams in the Mayer expansion.²⁴⁻²⁷ For homogeneous fluids, apart from the constant $s_{\text{misc}} = -c_+ \log(c_+) - c_- \log(c_-)$, the free energy of the liquid in the HNC approximation is given by

$$\begin{aligned} &\frac{1}{N} \beta F[\{g^{\epsilon\epsilon'}(r)\}] \\ &= \log \rho - 1 + \frac{\rho}{2} \int d^d r \sum_{\epsilon, \epsilon'} c_\epsilon c_{\epsilon'} \{g^{\epsilon\epsilon'}(r) \\ &\quad \times [\log g^{\epsilon\epsilon'}(r) + \beta V^{\epsilon\epsilon'}(r) - 1] + 1\} - \frac{1}{2\rho} \\ &\quad \times \int \frac{d^d k}{(2\pi)^d} \left\{ \log \mathcal{D} - \sum_{\epsilon} \rho c_\epsilon h^{\epsilon\epsilon}(k) \right. \\ &\quad \left. + \sum_{\epsilon, \epsilon'} c_\epsilon c_{\epsilon'} \frac{(\rho h^{\epsilon\epsilon'}(k))^2}{2} \right\}, \end{aligned} \quad (50)$$

where

$$h^{\epsilon\epsilon'}(r) = g^{\epsilon\epsilon'}(r) - 1, \quad (51)$$

and \mathcal{D} is the determinant of the matrix

$$\begin{pmatrix} 1 + \rho c_+ h^{++}(k) & \rho c_+ h^{+-}(k) \\ \rho c_- h^{+-}(k) & 1 + \rho c_- h^{--}(k) \end{pmatrix}. \quad (52)$$

The closed set of HNC equations for the two point correlations can be derived as a stationarity condition of the functional F with respect to these correlation: they are solved using the same numerical technique utilized in the pure case.²

HNC is expected to be a good starting point for our study since both f and the mean values of quantities that involve only two particles correlation functions seem to be evaluated with an error smaller than 10% in the temperature region we are interested in, as we verified by comparing the analytical estimations with simulation results. The terms involving the three point correlation functions, when evaluated by the superposition approximation and the HNC pair correlations, are reproduced with errors which seem to be smaller than 30%.

V. RESULTS AND DISCUSSION

Before discussing the analytical and numerical results on the soft sphere binary mixture, let us pay attention, for a

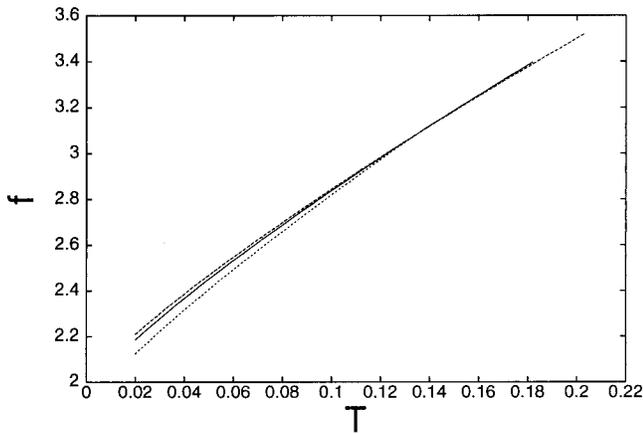


FIG. 1. The free energy of the pure soft sphere model versus temperature. The three curves are the results obtained from the small cage expansion at the first order (dotted line) and at the second order (dashed line), and those from the HNC resummation scheme (continuous line).

while, to the soft sphere model (9) with the particular value $R = 1$ (i.e., the pure case). This allows to compare thermodynamic quantities obtained within the small cage expansion up to second order (evaluating the three point function by the superposition approximation) with those computed at the same order in the replicated HNC resummation scheme.¹

In Figs. 1 and 2(a), 2(b) we show the free energy, the effective inverse temperature βm and the cage radius A for the pure soft sphere model both at the first order, that gives the same results in the two cases, and at the second one. As already outlined, when starting from the generalized HNC expression, the second order coefficient γ_2 is obtained without further approximations than the one related to the use of HNC. On the other hand, these results confirm that evaluating the three point correlation function which appears in γ_2 by the superposition approximation is a rather good approximation. In particular we get very similar values for the thermodynamic transition point, $\Gamma_K \approx 1.53$ from the HNC resummation scheme and $\Gamma_K \approx 1.49$ when using small cage expansion, i.e., an error less than 3%.

Now we come back to the soft spheres binary mixture with the interaction parameters described in (9), taking in particular the value $R = 1.2$ of the ratio between the effective diameters in order to obtain analytical results comparable to the numerical ones. We consider both the small cage expansion to second order and the harmonic re-summation, finding results in very good agreement as is shown in Fig. 3, where the glassy phase free energy computed in the two different schemes of approximation is plotted as a function of T (for simplicity we take in the following $\rho = 1$).

The evaluations of the thermodynamic critical temperature obtained by the two analytic methods nearly coincide: we get $\Gamma_K \equiv T_K^{-1/4} \approx 1.65$, which is in agreement with the numerical estimates that we are going to discuss. For the sake of comparison, let us remember that the mode coupling critical value for this model²⁰ is $\Gamma_D \approx 1.45$. Let us note that the ratio T_D/T_K is usually found to be between 1.2 and 1.6.

We stress that the parameter m and cages size, A^+ and A^- , plotted in Figs. 4(a) and 4(b) are nearly linear with temperature. This means, in particular, that the effective tem-

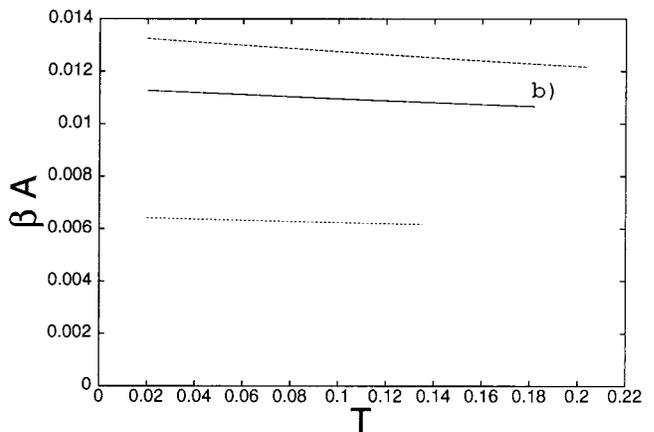
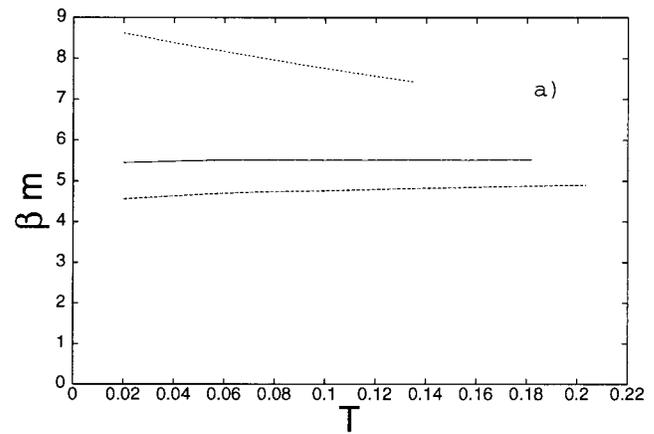


FIG. 2. βm (a) and βA (b) of the pure soft spheres model versus temperature. The three curves are the results obtained from the small cage expansion at the first order (dotted line) and at the second order (dashed line), and those from the HNC resummation scheme (continuous line).

perature T/m is always close to T_K , so in our theoretical computation we need only the mean values of observables in the liquid phase, at temperatures where the HNC approximation still works quite well.

One can also observe that the specific heat [see Fig. 5(a)] shows an evident jump at T_K , remaining close to the crystal-

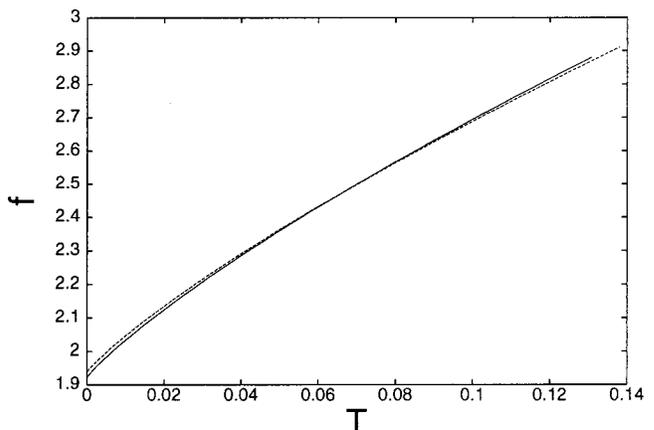


FIG. 3. Free energy of the soft sphere mixture vs temperature. The continuous line is the result of the harmonic resummation scheme and the dashed line is the result of the small cage expansion to second order.

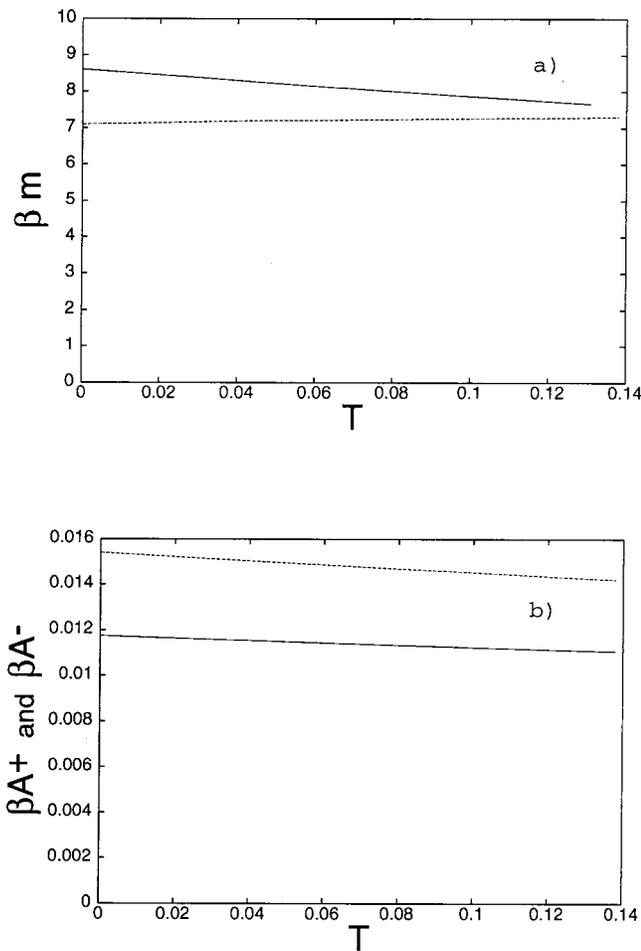


FIG. 4. In (a) we plot βm vs temperature, from the harmonic resummation scheme (continuous line) and from the low temperature expansion to second order (dashed line). In (b) we present βA^+ (continuous line) and βA^- (dashed line) computed in the low temperature expansion to second order. Note that, quite reasonably, the smallest cage radius corresponds to particles with the largest effective diameter.

like value, $3/2$ (we have not included the kinetic energy), in the whole glassy phase. The qualitative behavior of thermodynamic quantities, apart from the presence of the two distinct radii, is very similar to that observed in the pure case^{1,2} and it corresponds to a second-order transition from the thermodynamic point of view.

The harmonic resummation scheme suggests an intriguing approach for evaluating the thermodynamic critical temperature by simulations, starting from (32). Here the liquid entropy can be obtained for instance by numerically integrating the energy

$$\begin{aligned} S_{\text{liq}}(\beta) &= \beta(E_{\text{liq}}(\beta) - F_{\text{liq}}(\beta)) \\ &= S_{\text{liq}}^0 + \beta E_{\text{liq}}(\beta) - \int_0^\beta d\beta' E_{\text{liq}}(\beta'), \end{aligned} \quad (53)$$

where S_{liq}^0 is the entropy of the perfect gas in the $\beta \rightarrow 0$ limit, i.e., in the binary mixture case

$$S_{\text{liq}}^0 = N(1 - \log \rho - c_+ \log c_+ - c_- \log c_-). \quad (54)$$

Moreover, one can think of directly numerically evaluating the ‘‘harmonic solid’’ entropy

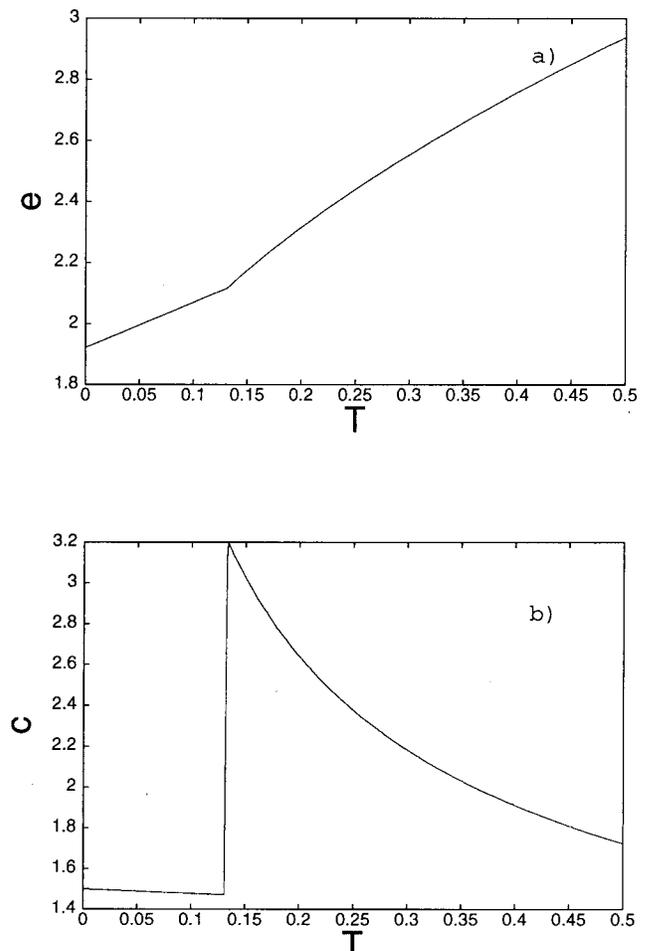


FIG. 5. The energy (a) and the specific heat (b) of the soft sphere mixture versus temperature, both in the liquid and in the glassy phase, from the harmonic resummation scheme.

$$\frac{S_{\text{sol}}(\beta)}{N} = \frac{d}{2} (1 + \log(2\pi)) - \frac{1}{2N} \langle \text{Tr} \log(\beta \mathcal{M}) \rangle, \quad (55)$$

by diagonalizing the instantaneous Hessian and by averaging over different configurations. The knowledge of S_{liq} and S_{sol} allows to obtain a numerical estimate of T_K as the temperature where the two entropies become equal, and to measure the complexity

$$\Sigma(\beta) = \frac{1}{N} [S_{\text{liq}}(\beta) - S_{\text{sol}}(\beta)]. \quad (56)$$

When attempting to obtain such evaluations, we face two kinds of problems.

- (a) The well-known hard task of thermalizing glass-forming liquids at low temperatures. Here we choose to perform a simulated annealing run of a quite large system, using data on the liquid energy down to the temperature where the equilibrium was still reachable in a reasonable CPU time ($\Gamma \sim 1.5$). Then we extrapolate the liquid entropy behavior at lower temperatures by fitting data in the interval $\Gamma \in [1, 1.5]$ with the power law

$$S_{\text{liq}}(T) = aT^{-2/5} + b. \quad (57)$$

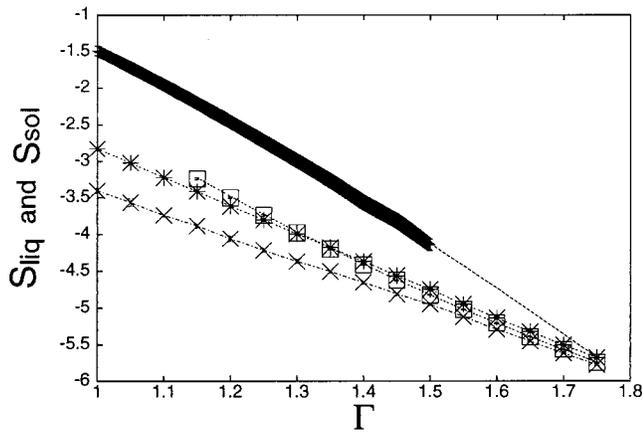


FIG. 6. The entropy of the liquid (+) and the different evaluations (see text) of the amorphous solid entropy, $s_{\text{sol}}^{(a)}$ (x), $s_{\text{sol}}^{(b)}$ (*), and $s_{\text{sol}}^{(c)}$ (□), as functions of Γ , obtained in the numerical simulation. In the liquid entropy case the line is the best fit to the power law $s_{\text{liq}} = a\beta^{2.5} + b$, otherwise lines are only interpolations between neighboring points. The liquid and solid entropies seem to cross around $\Gamma_K \sim 1.75$, which is the corresponding estimation of the thermodynamic liquid-glass transition.

In fact, it has been shown²⁸ that the potential energy of simple liquids at high densities and low temperature must follow this law, and we find that our numerical data are in a very good agreement with it.

The correct evaluation of the solid entropy, which is a subtle task. Beyond the mean field approximation there always exists a non zero number of negative eigenvalues, which decreases as $\exp(-C/T)$ at low temperatures²³ and is expected to be negligible below the mode coupling temperature. An estimate of the error on S_{sol} can be found by doing the following two measurements. (a) One includes in the computation of $\text{Tr} \log(\beta\mathcal{M})$ only the N_{pos} positive eigenvalues. (b) One includes all eigenvalues, but one takes the absolute values of the negative ones:

$$\frac{S_{\text{sol}}^{(a)}}{N} = \frac{d}{2} \left[\left(1 + \log \left(\frac{2\pi}{\beta} \right) \right) - \left\langle \frac{1}{N_{\text{pos}}} \sum_{i=1}^{N_{\text{pos}}} \log \lambda_i \right\rangle \right], \quad (58)$$

$$\frac{S_{\text{sol}}^{(b)}}{N} = \frac{d}{2} \left[\left(1 + \log \left(\frac{2\pi}{\beta} \right) \right) - \left\langle \frac{1}{dN} \sum_{i=1}^{dN} \log |\lambda_i| \right\rangle \right]. \quad (59)$$

The percentage of nonpositive eigenvalues that we find by diagonalizing the instantaneous Hessian is still about 20% at $\Gamma \sim 1$, it decreases to less than 10% at $\Gamma \sim 1.2$ and in the region definitely below T_D , i.e., above $\Gamma \sim 1.5$, it is $\sim 4\%$. On the other hand, nearly all the negative eigenvalues are less than one in absolute value. Therefore, particularly at temperatures $T \gtrsim T_D$, we find a sizable difference between $S_{\text{sol}}^{(a)}$ and $S_{\text{sol}}^{(b)}$ (we disregard in both cases the very few $|\lambda| < 10^{-4}$), as is shown in (Fig. 6). One should note that $S_{\text{sol}}^{(b)}$ seems to display the most regular behavior as a function of Γ . The presence of negative eigenvalues is possibly related also to the fact that when diagonalizing the instantaneous Hessian the system can be far from the center of the minimum, in positions where higher order corrections to a harmonic approximation of the energy landscape are important.

A more extensive study should be performed in order to better understand these subtleties of the computation of the solid entropy. However we would like to mention here a third way for evaluating numerically the solid entropy. Starting from an equilibrium configuration at a given Γ value, we performed a Monte Carlo run at $T=0$, allowing only quite small displacements to each particle. The percentage of non-positive eigenvalues becomes very rapidly $< 2\%$ in the whole temperature range considered and correspondingly the two different ways of evaluating the solid entropy give compatible results. The obtained $S_{\text{sol}}^{(c)}$ is near to the one evaluated from the ‘instantaneous’ Hessian by using also the absolute values of negative eigenvalues in the region $T \sim T_D$ but it decreases slightly faster when lowering the temperature (see Fig. 6).

More precisely, we performed a simulated annealing run of a system of $N=258$ particles, in a cubic box with periodic boundary conditions, starting from $\Gamma=0.05$ and performing up to 2^{22} MC steps at each $\Delta\Gamma=0.05$, the maximum shift δ_{max} permitted to each particle in one step being chosen such as to get an acceptance rate ~ 0.5 . The energy and its fluctuation were measured in the last half of the run at a given Γ value.

Just for decreasing the error on the evaluation of S_{liq} , we fit the very high temperature data on the energy, up to $\Gamma_0 = 0.2$, by using $\Gamma^3 E(\Gamma) = a\Gamma^2 + b\Gamma + c$, obtaining correspondingly $F(\Gamma_0) = 4a\Gamma_0^3/3 + 2b\Gamma_0^2 + 4c\Gamma_0$ that turns out to be perfectly compatible with the HNC value (i.e., we are still in the region where no differences are observable between numerical data and the HNC approximation). The integration is subsequently performed by interpolating with a standard numerical subroutine the simulation data in order to get a result independent on the integration interval.

In order to evaluate $S_{\text{sol}}^{(a)}$ and $S_{\text{sol}}^{(b)}$ we considered 16 different configurations in the last half of the run at each Γ value, while $S_{\text{sol}}^{(c)}$ was measured from the configurations obtained by these ones with 5000 MC steps at $T=0$ (starting from $\delta_{\text{max}}=0.1$ and decreasing it up to 0.02 during the run). One should note that at a given Γ value the obtained evaluations of $S_{\text{sol}}^{(c)}$ seem to depend weakly on the starting equilibrium configuration i.e., fluctuations are very small). Moreover we get perfectly compatible results both halving and doubling the number of MC steps (in the last case we find practically only positive eigenvalues).

We plot in Fig. 6 both $s_{\text{liq}}(\Gamma)$ and the obtained evaluations of $s_{\text{sol}}(\Gamma)$ by the different ways considered, $s_{\text{sol}}^{(a)}$, $s_{\text{sol}}^{(b)}$, and $s_{\text{sol}}^{(c)}$ are very close to each other when approaching the thermodynamic liquid-glass transition, giving similar estimates of $\Gamma_K \sim 1.75$.

The study of the system coupled to a reference configuration x_{ref} , which is an equilibrium configuration of the system itself at the considered temperature, allows to measure the complexity by an alternative route. One considers

$$\beta\mathcal{H} = \beta\mathcal{H}_0 + \epsilon(x - x_{\text{ref}})^2, \quad (60)$$

where

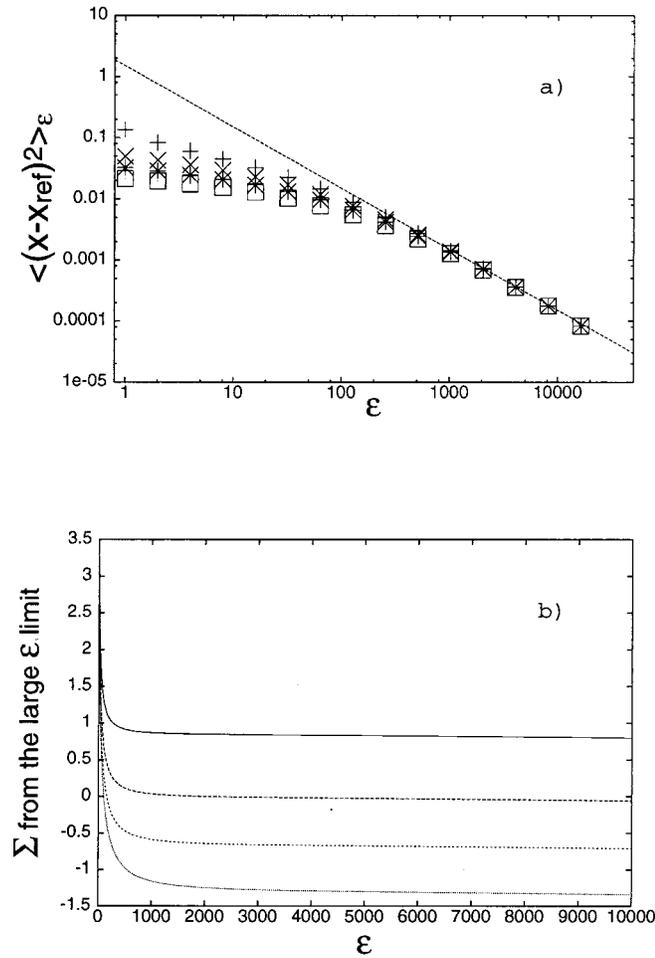


FIG. 7. In (a) we plot $\langle (x-x_{\text{ref}})^2 \rangle_{\epsilon}$ as a function of ϵ at the considered values $\Gamma=1.4$ (+), 1.6 (x), 1.8 (*), and 2.0 (□). Here we show also $3/(2\epsilon)$ (the dashed line) in order to make evident the reaching of the asymptotic behavior. In (b) we present the evaluations (see text) of $\Sigma \approx s_{\text{liq}}^0 + \int_0^{\epsilon} d\epsilon' \langle (x-x_{\text{ref}})^2 \rangle_{\epsilon'} - 3(\log(\epsilon/2\pi) - 1)/2$ in the large ϵ limit (the different curves, from top to bottom, correspond to $\Gamma=1.4, 1.6, 1.8$, and 2.0 , respectively). The complexity turns out to be compatible with zero at $\Gamma_K = 1.6$ which is therefore the evaluation of the thermodynamic liquid-glass transition temperature.

$$(x-x_{\text{ref}})^2 \equiv \sum_{i=1}^N \sum_{\mu=1}^d (x_i^{\mu} - x_{\text{ref},i}^{\mu})^2 \quad (61)$$

is the squared distance between the configurations (note that the coupling breaks the rotation-translation-permutation invariance). Therefore

$$\beta f(\epsilon, \beta) = \beta f_0(\beta) + \int_0^{\epsilon} d\epsilon' \langle (x-x_{\text{ref}})^2 \rangle_{\epsilon'}, \quad (62)$$

where in the region $T \leq T_D$

$$\beta f_0(\beta) = \lim_{\epsilon \rightarrow 0^+} f(\epsilon, \beta) \approx \beta e(\beta) - \Sigma(\beta). \quad (63)$$

On the other hand, one has

$$\lim_{\epsilon \rightarrow \infty} \beta f(\epsilon, \beta) = \beta f_{\infty}(\beta) = \beta e(\beta) + \frac{d}{2} \left(\log \left(\frac{\epsilon}{2\pi} \right) - 1 \right). \quad (64)$$

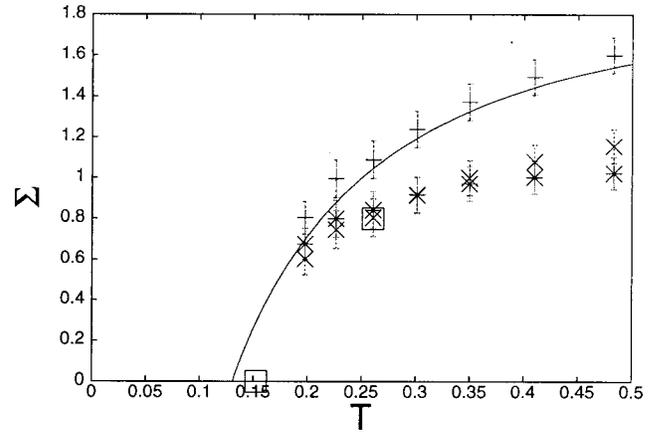


FIG. 8. The complexity $\Sigma(T)$ computed in the harmonic re-summation scheme (continuous line) and the different numerical evaluations, i.e., $s_{\text{liq}} - s_{\text{sol}}^{(a)}$ (+), $s_{\text{liq}} - s_{\text{sol}}^{(b)}$ (x), $s_{\text{liq}} - s_{\text{sol}}^{(c)}$ (*). The □ correspond to the Σ values obtained by studying the coupled system at $\Gamma=1.4$ and 1.6 .

This means that one can obtain an evaluation of the configurational entropy as

$$\Sigma(\beta) \approx s_{\text{liq}}^0 + \int_0^{\epsilon} d\epsilon' \langle (x-x_{\text{ref}})^2 \rangle_{\epsilon'} - \frac{d}{2} \left(\log \left(\frac{\epsilon}{2\pi} \right) - 1 \right), \quad (65)$$

in the large ϵ limit, taking into account as usual the perfect gas binary mixture entropy.

Here we considered a large system of $N=2000$ particles in a cubic box with periodic boundary conditions and we put a cut-off on the potentials, i.e., $\tilde{V}^{\epsilon\epsilon'}(r) = V^{\epsilon\epsilon'}(R_{\text{max}})$ for $r > R_{\text{max}}$, choosing $R_{\text{max}}=1.7$ that means a practically negligible $V^{\epsilon\epsilon'}(R_{\text{max}} \sim 10^{-3})$. The algorithm is then implemented in such a way that for each particle the map of the ones which are at distance lower than $R_{\text{max}} + 2\delta_{\text{max}}$ is recorded and updated during the run.

We performed up to $\mathcal{N}=2^{21}$ MC steps at each considered $\Gamma=1.4, 1.6, 1.8, 2.0$. At the end of the run, the configuration was copied in the reference one and subsequently a run of $\mathcal{N}/16$ MC steps was performed on the coupled system for different ϵ values, $\epsilon=1, 2, 4, 8, \dots$ up to very large $\epsilon \sim 10^4$, measuring the squared distance. We note that perfectly compatible results were obtained for $\mathcal{N}=2$.¹⁹ The integrals were evaluated by interpolating with a standard numerical subroutine between the simulation data in order to obtain results independent on the integration interval.

We plot in Fig. 7(a) both the data on $\langle (x-x_{\text{ref}})^2 \rangle_{\epsilon}$ at different Γ as function of ϵ and $3/(2\epsilon)$. The asymptotic behavior seems to be reached around $\epsilon=2000$, though also at larger ϵ there are very weak deviations from it. When looking at the difference between the corresponding integrals and $d(\log(\epsilon/2\pi) - 1) - s_{\text{liq}}^0$ in the large ϵ limit [see (Fig. 7(b))], one finds that the complexity is compatible with zero at $\Gamma_K \sim 1.6$, a value slightly lower than the previously obtained $\Gamma_K \sim 1.75$ (the analytical estimation being $\Gamma_K \approx 1.65$). On the other hand, the errors on these estimations are difficult to evaluate but they might be quite large, a more extensive

numerical analysis being necessary in order to improve these results.

At last we plot in Fig. 8 the different numerical estimations of the configurational entropy Σ as a function of the temperature and the behavior obtained analytically in the harmonic resummation scheme. In spite of the uncertainties in the measures of Σ and in the analytical approximations (first of all related to the use of the HNC closure for evaluating liquid quantities), the agreement between theory and simulation looks quite satisfactory. We leave for future work both more extensive numerical studies and the improvement of the analytical results, that should allow a more careful comparison.

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APPENDIX: SECOND-ORDER COEFFICIENTS

The second-order expression of replicated partition function in small cage approximation is

$$\begin{aligned}
 a_2^{++} &= \frac{\beta}{4} \frac{(1-m)^2}{m^4} \left[c_+ \int d^d r \rho g^{++}(r) \sum_{\mu\nu} V_{\mu\nu}^{++}(r) + \frac{c_-}{2} \int d^d r \rho g^{+-}(r) \sum_{\mu\nu} V_{\mu\nu}^{+-}(r) \right] - \frac{\beta^2}{4} \frac{(m-1)}{m^3} \\
 &\times \left[c_+^2 \int d^d r_1 d^d r_2 \rho^2 g^{+++}(r_1, r_2) \sum_{\mu\nu} V_{\mu\nu}^{++}(r_1) V_{\mu\nu}^{++}(r_2) + 2c_+ c_- \int d^d r_1 d^d r_2 \rho^2 g^{++-}(r_1, r_2) \right. \\
 &\times \sum_{\mu\nu} V_{\mu\nu}^{++}(r_1) V_{\mu\nu}^{+-}(r_2) + c_-^2 \int d^d r_1 d^d r_2 \rho^2 g^{+--}(r_1, r_2) \sum_{\mu\nu} V_{\mu\nu}^{+-}(r_1) V_{\mu\nu}^{+-}(r_2) \left. \right] - \frac{\beta^2}{2} \frac{(m-1)}{m^3} \\
 &\times \left[c_+ \int d^d r \rho g^{++}(r) \sum_{\mu\nu} V_{\mu\nu}^{++}(r) V_{\mu\nu}^{++}(r) + \frac{c_-}{2} \int d^d r \rho g^{+-}(r) \sum_{\mu\nu} V_{\mu\nu}^{+-}(r) V_{\mu\nu}^{+-}(r) \right], \\
 a_2^{+-} &= \frac{\beta}{4} \frac{(1-m)^2}{m^4} \int d^d r \rho g^{+-}(r) \sum_{\mu\nu} V_{\mu\nu}^{+-}(r) - \frac{\beta^2}{2} \frac{(m-1)}{m^3} \int d^d r \rho g^{+-}(r) \sum_{\mu\nu} V_{\mu\nu}^{+-}(r) V_{\mu\nu}^{+-}(r),
 \end{aligned}
 \tag{A4}$$

and the expression of a_2^{--} is obtained by changing the + in the coefficient a_2^{++} .

To obtain the Legendre transform one must solve the system of linear equations

$$\begin{aligned}
 \frac{\partial \phi}{\partial(1/\alpha_+)} &= -\frac{d(1-m)}{2} A^+ c_+, \\
 \frac{\partial \phi}{\partial(1/\alpha_-)} &= -\frac{d(1-m)}{2} A^- c_-,
 \end{aligned}
 \tag{A5}$$

$$\begin{aligned}
 Z_m^{(2)} &= Z_m^0 \left[1 - \frac{\beta}{4} \left\langle \sum_{i \neq j} \sum_{\mu\nu} V_{\mu\nu}^{\epsilon_i \epsilon_j}(z_i - z_j) \sum_a (\mu_{i\mu}^a - u_{j\mu}^a) \right. \right. \\
 &\times (u_{i\nu}^a - u_{j\nu}^a) \left. \right] - \frac{\beta}{2 \cdot 4!} \left\langle \sum_{i \neq j} \sum_{\mu\nu\eta\tau} V_{\mu\nu\eta\tau}^{\epsilon_i \epsilon_j}(z_i - z_j) \right. \\
 &\times \sum_a (u_{i\mu}^a - u_{j\mu}^a)(u_{i\nu}^a - u_{j\nu}^a)(u_{i\eta}^a - u_{j\eta}^a) \\
 &\times (u_{i\tau}^a - u_{j\tau}^a) \left. \right] + \frac{\beta^2}{2 \cdot 16} \left\langle \left(\sum_{i \neq j} \sum_{\mu\nu} V_{\mu\nu}^{\epsilon_i \epsilon_j}(z_i - z_j) \right. \right. \\
 &\times \sum_a (u_{i\mu}^a - u_{j\mu}^a)(u_{i\nu}^a - u_{j\nu}^a) \left. \right)^2 \left. \right\rangle,
 \end{aligned}
 \tag{A1}$$

where distinction between terms which involve sums over particles of a given kind is required. Taking the logarithm of partition function, one finds the second order contribution to ϕ

$$\begin{aligned}
 \beta \phi^{(2)}(\alpha_+, \alpha_-, \beta) &= c_+ \alpha_2^{++} \alpha_+^2 + c_- \alpha_2^{--} \alpha_-^2 \\
 &+ c_+ c_- \alpha_2^{+-} \alpha_+ \cdot \alpha_-.
 \end{aligned}
 \tag{A2}$$

The second-order coefficients also depend on the three points correlation functions

$$\begin{aligned}
 g^{\epsilon\epsilon'\epsilon''}(r_1, r_2) &= \frac{1}{c_\epsilon c_{\epsilon'} c_{\epsilon''} \rho^2 N} \left\langle \sum_{i \in \epsilon, j \in \epsilon', k \in \epsilon''} \delta(x_i - x_j - r_1) \right. \\
 &\times \delta(x_i - x_k - r_2) \left. \right\rangle.
 \end{aligned}
 \tag{A3}$$

One has

and substitute the solutions into

$$\begin{aligned}
 \beta G(A^+, A^-, m, \beta) &= \phi(\alpha_+, \alpha_-, m, \beta) + \frac{d(1-m)}{2} c_+ \frac{A^+}{\alpha_+} \\
 &+ \frac{d(1-m)}{2} c_- \frac{A^-}{\alpha_-}
 \end{aligned}
 \tag{A6}$$

getting

$$\begin{aligned} \beta G(A^+, A^-, m, \beta) = & \gamma_0 + \gamma_3(c_+ \log A^+ + c_- \log A^-) \\ & + c_+ \gamma_1^+ A^+ + c_- \gamma_1^- A^- \\ & + c_+ \gamma_2^{++} (A^+)^2 + c_- \gamma_2^{--} (A^-)^2 \\ & + c_+ c_- \gamma_2^{+-} A^+ \cdot A^- \end{aligned} \quad (\text{A7})$$

with

$$\begin{aligned} \gamma_0 = & c_0 - a_0(1 + \log m)/m, \quad \gamma_3 = -a_0/m, \\ \gamma_1^+ = & m a_1^+, \quad \gamma_1^- = m a_1^-, \\ \gamma_2^{++} = & m^2 a_2^{++} + m^3 (a_1^{++})^2 / (2a_0), \\ \gamma_2^{--} = & m^2 a_2^{--} + m^3 (a_1^{--})^2 / (2a_0), \\ \gamma_2^{+-} = & m^2 a_2^{+-}. \end{aligned} \quad (\text{A8})$$

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