Lennard-Jones binary mixture: a thermodynamical approach to glass transition

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We study the liquid-glass transition of the Lennard-Jones binary mixture introduced by Kob and Andersen from a thermodynamic point of view. By means of the replica approach, translating the problem in the study of a molecular liquid, we study the phase transition due to the entropy crisis and we find that the Kauzmann’s temperature $T_K$ is $\sim 0.32$. At the end we compare analytical predictions with numerical results.
I. INTRODUCTION

The aim of this paper is to study the liquid-glass transition and investigate the glass phase of a binary mixture of particles which describes a fragile liquid. We consider a binary mixture interacting via a Lennard-Jones potential, introduced by Kob and Andersen\(^1\). This model is suitable for such problems because of the lack of a crystalline state. This allows a detailed comparison between analytical results and numerical simulations.

The proposed theory relies on the following assumptions, discussed in detail in previous papers\(^2\)–\(^5\):

- In the supercooled liquid phase, the phase space can be partitioned in an exponentially high number of potential energy minima separated by energy barriers of order \(O(1)\) (the barriers will diverge at a low temperature, at the Kauzmann temperature where the viscosity diverges). The basins of attractions of these minima are the so-called 'inherent structures'\(^6\). A growing number of numerical studies are supporting this picture\(^7\)–\(^10\). Choosing the thermodynamic point of view, we focus mainly on free-energy landscape. We assume that below the dynamical (Mode Coupling\(^11\)) critical temperature, \(T_D\)\(^12\), \(13\), the supercooled liquid at equilibrium is almost always trapped in one of the exponentially large number of local free energy minima, which we will call 'valleys'. This picture is very similar to the one which describes generalized mean field models of spin-glasses displaying a one step replica symmetry breaking transition\(^14\)–\(^17\). The free-energy minima in short range systems are not separated by infinite barriers, so different valleys with the same free energy can be explored by the system during its evolution. This is what is supposed to happen in the liquid phase.

We write the partition function as a sum of contributions from different minima:

\[
Z = e^{-N\beta \phi(T)} = \int df e^{-\beta N f} \mathcal{N}(f),
\]

where \(\mathcal{N}(f, T)\) is the number of minima of the free energy at temperature \(T\) as function of the free energy density \(f\). We can show that the system does not choose the configuration with minimal free-energy, but instead minimizes the generalized free energy density, namely:

\[
\phi(T) \sim \min_f [f - T \Sigma(f, T)].
\]

The total entropy density is given by the sum of the entropy density of a typical minimum and of the complexity, or configurational entropy \(\Sigma \sim \log \mathcal{N}/N\), taking into account the number \(\mathcal{N}\) of these minima.

- In the glass phase, the system is described, to a first approximation, as an amorphous solid, where the only degrees of freedom are small displacements around disordered centers of oscillation. We assume further that thermodynamic quantities are self-averaging with respect to the disorder.
The main hypothesis relies on old Adam-Gibbs-Di Marzio scenario where the liquid-glass thermodynamic transition is related to an ‘entropy crisis’, that is the existence of a finite temperature where ergodicity breaks and the configurational entropy vanishes. Within this picture, the transition temperature, $T_K$, corresponds to the temperature where the viscosity diverges with a generalized Vogel-Fulcher law, \( \eta \propto \exp(T - T_K)^{-\nu} \). In other words, the typical singular behaviour of experimental measures of thermodynamic quantities (e.g. specific heat) at a somewhat arbitrary $T_g$ is related at a ‘true’ second order transition which occurs at a lower temperature. The internal energy is continuous at $T_K$, there is no latent heat and the specific heat suddenly falls from the liquid value to a definitely smaller one, in agreement with the Dulong and Petit law. Nevertheless, from the point of view of an appropriate order parameter, we find that the transition is discontinuous. Indeed, while in the glass phase each particle is confined in a ‘cage’ of finite size due to interactions with its neighbors, in the liquid, because of diffusion, there is no cage, i.e. there is no thermodynamically stable cage, but only some metastable ‘caging’ effect.

The glass phase is studied by generalizing a recently proposed theory to binary mixture, allowing one to obtain equilibrium properties of fragile glasses from those of liquid phase, computed for a molecular liquid consisting of $m$ ‘clones’ of the system with $m < 1$. This extension has been accomplished so far only for a soft sphere binary mixture model, while in the present paper we address the more realistic model of a Lennard-Jones binary mixture. Due to the different nature of the system and to the presence of a liquid-gas transition, the simple Hyper-Netted-Chain approximation previously used is not enough precise. We must introduce some slightly different approximation in investigating liquid and glass phases which will be discussed in detail later.

After first introducing the model (section II), we present and discuss approximations needed to compute replicated free-energy (sections III-IV), we then describe a way to study supercooled liquid phase (section V) and finally we present analytical results and comparisons with numerical simulations (VI).

II. LENNARD-JONES BINARY MIXTURES

We study mixtures of two types of particles with different radii, here called + and −, with pairwise interactions. The Hamiltonian of our problem is:

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

where the particles move in a volume $V$ of a $d$-dimensional space, and $V^{++}, V^{+-},$ and $V^{--}$ are arbitrary short range potentials.

The so-called soft sphere (SS) model, where the potentials $V(r)$ are short ranged and purely repulsive (i.e. proportional to $R^{-12}$), was studied in a previous work. In that paper one:

- demonstrated the feasibility of extending the thermodynamic theory of liquid-glass transition recently presented to binary mixtures;
- compared analytical results to numerical simulations;
• compared different methods of approximation proposed\textsuperscript{2,4} to compute ‘molecular’ or replicated free-energy.

The free energy in the uncorrelated liquid phase and in the correlated glass phase were there computed\textsuperscript{2} using the framework of HNC closure\textsuperscript{23}. By the HNC approximation the computed entropy in liquid phase was found correct to within 10%. Other approximations were introduced to compute the entropy in glass phase, namely the ‘quenched’ approximation, which neglects the feedback of vibrational modes on center of masses, and the ‘superposition’ approximation, where \( p \)-point correlation functions are expressed as ‘chain’ products of two-point correlation functions. When more realistic potentials are introduced, it is sometimes necessary to use more sophisticated integral equations than those based on the HNC.

In this paper we study a model of binary mixture introduced by Kob and Andersen\textsuperscript{1}, where potentials are of the Lennard-Jones (LJ) type:

\[
V^{\epsilon\epsilon'}(r) = 4\eta^{\epsilon\epsilon'} \left[ \left( \frac{\sigma^{\epsilon\epsilon'}}{r} \right)^{12} - \left( \frac{\sigma^{\epsilon\epsilon'}}{r} \right)^{6} \right].
\] (4)

The concentrations used are \( c_+ = \frac{4}{5} \) and \( c_- = \frac{1}{5} \). With the choice of parameter values \( \sigma_{++} = 1.0, \sigma_{+-} = 0.8, \sigma_{-+} = 0.88, \eta_{++} = 1.0, \eta_{+-} = 1.5 \) and \( \eta_{-+} = 0.5 \) it is possible to prevent both crystallization and separation in two phases with particles of different type. For the sake of clarity we underline that the symbols + and − correspond to A and B of the Kob and Andersen paper and, more importantly, here we do not use any cut-off on the potentials.

The main effect of the introduction of an attractive term in potential \( V(r) \) is the appearance of a density-dependent temperature, \( T_{GL}(\rho) \), where the system undergoes a separation into a liquid and gaseous phases with different densities.

This model has been extensively studied numerically in the past\textsuperscript{1,24–26,7,27}. In particular, at density \( \rho = 1.2 \), it has been shown that a ‘dynamical’ transition occurs at temperature \( T_D = 0.435 \). Below this temperature aging phenomena\textsuperscript{15,28,29} and violation of the fluctuation-dissipation theorem\textsuperscript{27,30} are observed.

In this paper, the same model is studied from a ‘thermodynamic’ point of view, showing the existence of a temperature, \( T_K = 0.32 (< T_D) \), where the system undergoes a real liquid-glass transition.

As a preliminary step, let us note that we have to go beyond HNC approximation to study the model in the fluid phase. Indeed, within this closure, integral equations at density \( \rho = 1.2 \) show a singularity at \( T_{GL} \sim 0.5 \), overestimating the true \( T_{GL} \). We are forced, then, to introduce some more reliable approximation in order to study this model. The correlation functions used in this paper are computed solving an integral equation which continuously interpolates between the HNC approximation at long distances and the Mean Spherical Approximation (MSA) at short distances, as proposed by Zerah and Hansen\textsuperscript{31}. The details are described below.

### III. GENERAL FRAMEWORK

The basic ideas used to study the glassy phase are the ones discussed in the introduction and in previous papers\textsuperscript{3,3}. We briefly review here how to use them for explicit computations.
Letting $f_{eq}$ be the equilibrium free energy, which minimizes $\phi$, the system enters the glass phase when the complexity $\Sigma(f_{eq}, T)$ vanishes. Therefore the computation of $\Sigma(f, T)$ it is the first fundamental topic of our investigation.

This issue can be settled by using the method proposed by Monasson\cite{Monasson}, where $m$ identical replicas of the original system are considered. By introducing a small but extensive and attractive coupling term among them, these replicas are forced to be in the same valley, so that they become strongly correlated. In the limiting case of no coupling term, two arbitrary replicas in the liquid phase are always found in two different valleys, because of the exponentially large number of them, which makes the probability of finding any two systems in the same valley negligible. The transition to glass phase is supposed to be related to an ergodicity breaking, where the free-energy barriers become infinitely large. In the glass phase replicas remain correlated even after sending the coupling term to zero. In a sense, the coupling term acts like, for example, the external magnetic field in the Ising model, exposing the transition. Moreover, the crucial point is that using the same argument as for (2) the free energy of the replicated system $\Phi(m, T)$ is related to the complexity $\Sigma(f, T)$ by the simple formula:

$$\Phi(m, T) \sim \min_f [mf(T) - T\Sigma(f, T)],$$

(5)

It is clear from this formula that if we are able to compute this thermodynamic potential for an arbitrary, non-integer value of the parameter $m$, we can obtain all the values available for free energy, $f$, and complexity, $\Sigma$, simply by varying this parameter $m$ in the following formulas:

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

(6)

By eliminating $m$ from these formulas one obtains the complexity as a function of the free energy $\Sigma(f)$. Obviously, the physical free-energy and configurational entropy are obtained in the limit $m \to 1$.

Because the function $\Phi(m, T)/m$ should be a convex function of parameter $m$, a physically possible situation is described only in the interval $m \in [0, m^*]$, where $m^*$ is the point of maximum. Indeed, $m^*$ corresponds to the minimum value $f_{min}$ available for free-energy. For greater values of $m$, the second equation in (6) implies that complexity is negative, which cannot be accepted on physical grounds.

The region of temperatures where $m^* > 1$ is the liquid phase, where equilibrium complexity is positive and the free energy is that which minimizes the balance between $\beta f$ and $\Sigma(f, T)$. In the low temperature glass phase, $m^* < 1$ instead, and in the whole region $m \in [m^*, 1]$ the replicated free energy (per replica) has the value $\Phi(m, T)/m = f_{min}(T)$. In particular we have that the equilibrium free energy $\Phi(1, T) = f_{min}(T)$. From this free-energy it is possible to get all the other thermodynamic quantities, internal energy, specific heat and so on in the usual ways.

It is useful to think about replicated free-energy as the free energy of a molecular liquid, whose molecules are composed of $m$ atoms, each in a different replica of the liquid. The tendency to form molecules is forced by a small but extensive coupling term between particles of different replicas\cite{Monasson}.

In the case of binary mixtures, one may ask if these molecules can be formed by particles of different kind. For the soft sphere binary mixture model\cite{Monasson} the point is quite subtle because
the particles (and interactions between them) are different only because of their effective size, and the ratio of their radii is not so different from 1. In the Lennard-Jones binary mixture model the situation is more clear. Beside the sizes of particles, there are three different values of the potential well for the three different kinds of interaction (+ +, −−, +−). In this case, the energy depends much more strongly on the type of particles involved. In fact, we expect that even the substitution of a single particle of a given type with a particle of different type, at low temperature, substantially increases the total energy of the system, lowering the probability of such a configuration which can then be safely neglected.

Since replicated (or molecular) free energy must describe the free energy of $m$ systems in the same state, we introduce attractive coupling terms only between particles of the same kind, neglecting molecules formed by atoms of different types. The replicated partition function is then:

$$Z_m[\omega] = \frac{1}{N_+!N_-!} \sum_{\sigma_a} \sum_{\pi_a} N^a \prod_i d^3 x^a_i \exp \left( -\frac{\beta}{2} \sum_{i\neq j,a} V^{\epsilon_{ij}} (x^a_i - x^a_j) \right)$$

$$- \sum_{i \in \{+\}} \sum_{a \neq b} \omega_+ (x_{\sigma_a(i)} - x_{\pi_a(i)}) - \sum_{i \in \{-\}} \sum_{a \neq b} \omega_- (x_{\pi_a(i)} - x_{\pi_a(i)})$$

where $\omega$ is the attractive potential among replicas and we must sum over the permutation ($\sigma_a$ and $\pi_a$) of the particles in each replica. When relabeling particles, so that to particle $i$ of a given kind in replica $a$ corresponds particle $i$ of the same kind in replica $b$ (which is supposed to belong to the same molecules) and so on, the sum over permutations can be eliminated leaving a multiplicative factor $(N^+!N^-!)^{m-1}$.

The phase transition we are investigating is equivalent to that shown by generalized spin glasses. The main idea is that in the glass phase there are only few states, not linked by trivial symmetry transformations, which contribute to integral (1). Below $T_K$ these states are mutually inaccessible because of ergodicity breaking. In replica space, this spontaneous one-step replica symmetry breaking is signaled by the onset of an off-diagonal non trivial correlation, when couplings are sent to zero.

The study of the thermodynamic phase, where replicas are correlated, is accomplished by choosing the probability distribution (after selecting a permutation) of the $m$ particles inside the same molecule for both kinds of particles as order parameters:

$$\rho_+(r^1, ..., r^m) = \sum_{i \in \{+\}} \langle \delta(x^1_i - r^1)...\delta(x^m_i - r^m) \rangle$$

$$\rho_-(r^1, ..., r^m) = \sum_{i \in \{-\}} \langle \delta(x^1_i - r^1)...\delta(x^m_i - r^m) \rangle$$

where a permutation is already selected, and introducing the Legendre trasformate of molecular (replicated) free energy:

$$G_m[\rho] = \lim_{\omega \to 0} \left( \frac{1}{\beta m} \log Z_m[\omega] + \frac{1}{m} \int \prod_{a=1}^m d^3 r^a \sum_{\epsilon=\{+,-\}} \rho_\epsilon (r^1, ..., r^m) W_\epsilon (r^1, ..., r^m) \right)$$
with

\[ W_\epsilon(r^1, ..., r^m) = \sum_{a<b} \omega_\epsilon(r^a - r^b) \]  

Performing the limit \( \omega \to 0 \) is equivalent to search for a non-trivial saddle point, with respect to the order parameters, of the functional \( G_m[\rho] \). In the presence of a glass transition we expect the order parameters and thermodynamic quantities to show the following behaviours:

- For \( T > T_K \) the density free energy is the liquid one \( (m = 1) \) and the order parameters are trivial, i.e. \( \rho_+ = c_+ \rho \) and \( \rho_- = c_- \rho \) (where the \( c \)’s are the different concentrations).
- For \( T < T_K \), the density free energy of glass is the maximum of function \( f_m \equiv \Phi(m, T)/m \), that is found at \( m^* < 1 \). From \( f_m \) we can compute all the thermodynamic quantities.

The free energy and its first derivatives are continuous at \( T_K \), while the heat capacity falls suddenly to solid-like values. The transition, then, is of second order from thermodynamics point of view, but it is discontinuous in the order parameter which abruptly becomes a non trivial 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 \( u^a_i \) with \( x^a_i = z_i + u^a_i \) and \( \sum_a u^a_i = 0 \). A useful simplification is the choice of quadratic coupling among replicas, that allows rewriting (7) as:

\[ Z_m = \frac{1}{N^+! N^-!} \int \left( \prod_{i=1}^N d^d z_i \right) \left( \prod_{a=1}^m \prod_{i=1}^N d^d u^a_i \right) \left[ \prod_{i=1}^N \left( m^d \delta(m \sum_{a=1}^m u^a_i) \right) \right] \]

\[ \cdot \exp \left( -\beta \sum_{a=1}^m \sum_{i < j} V^{\epsilon_i \epsilon_j} (z_i - z_j + u^a_i - u^a_j) \right) \]

\[ - \frac{1}{4\alpha_+} \sum_{a, b} \sum_{i \in +} (u^a_i - u^b_i)^2 - \frac{1}{4\alpha_-} \sum_{a, b} \sum_{i \in -} (u^a_i - u^b_i)^2 \right), \]

where the \( \{u^a_{i \mu}\} \) for a given \( i \) (the indices \( \mu \) and \( \nu \), running from 1 to \( d \), denote space directions) turn out to be Gaussian random variables with a vanishing first moment and a second moment given by

\[ \langle u^a_{i \mu} u^b_{i \nu} \rangle = \left( \delta^{ab} - \frac{1}{m} \right) \delta_{\mu \nu} \delta_{ij} \frac{\alpha_{\epsilon_i}}{m}. \]

IV. REPLICAED FREE-ENERGY

Three different ways to compute the ‘molecular’ free energy of a replicated system were introduced. In a previous paper on binary glasses, free energy was computed by two of these schemes of approximation, namely harmonic resummation and small cage approximation; both gave similar results. Here we want to unify these two approximations in a single framework.
In the glass phase molecules are expected to have a small radius, so our starting point is a quadratic expansion of $V$ in the partition function (11). The integration over these quadratic fluctuations gives:

$$Z_m = \frac{m^{Nd/2} \sqrt{\frac{N^d}{2\pi}}}{N! N^{-1}} \int \prod_{i=1}^{N} d^d z_i \exp \left( \beta m \sum_{i<j} V_{\epsilon_i \epsilon_j} (z_i - z_j) - \frac{m - 1}{2} Tr \log (\beta M) \right)$$

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

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

and $V_{\mu \nu}(r) = \partial^2 V/\partial r_{\mu} \partial r_{\nu}$. We have then an effective Hamiltonian where the centers of masses $z_i$ of the molecules interact at effective temperature $T^* = 1/(\beta m)$ by means of a pair potential, complicated by the contribution of vibration modes. We proceed by using a 'quenched approximation', i.e. neglecting the feedback of vibration modes onto the centers of masses:

$$Z_m \sim m^{Nd/2} \sqrt{\frac{N^d}{2\pi}} Z_{liq}(\beta m) \exp \left( -\frac{m - 1}{2} \langle Tr \log (\beta M) \rangle_{\beta m} \right).$$

This approximation becomes exact when close to the Kauzmann temperature where $m \to 1$. We normalize matrix elements as follows:

$$C_{\epsilon \epsilon'}^{\epsilon' \epsilon} \equiv \sqrt{c_{\epsilon} c_{\epsilon'}} V^{\epsilon \epsilon'} (z_i - z_j).$$

introducing the mean values of diagonal terms:

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

The replicated free energy is:

$$\beta \phi(m, \beta) = -\frac{d}{2m} \log (m) - \frac{d(m - 1)}{2m} \log (2\pi) - \frac{1}{mN} \log Z_{liq}(\beta m) + \frac{d}{2m} \left( c_+ \log (\beta r_+) + c_- \log (\beta r_-) \right) + \frac{1}{N} \frac{(m - 1)}{2m} \left( \langle Tr \log \left[ \delta_{ij} \sum_k C_{\epsilon \epsilon'}^{\epsilon' \epsilon} (\gamma_{\mu \nu}) - C_{\epsilon \epsilon'}^{\epsilon' \epsilon} (\gamma_{\mu \nu}) \right] \right).$$

We consider fluctuations of diagonal term $\sum_k C_{ik}$ up to second order, while the whole non-diagonal contribution $C_{ij}$ is resummed by means of a kind of chain approximation. The free-energy to compute is, then:
\[ \beta \phi(m, \beta) = -\frac{d}{2m} \log(m) - \frac{d(m - 1)}{2m} \log(2\pi) - \frac{1}{mN} \log Z_{\text{liq}}(\beta m) + \frac{d}{2m} (c_+ \log(\beta r_+) + c_- \log(\beta r_-)) - \frac{1}{2N} \left( \langle \text{Tr} C^{\mu'}_{(i\mu)}(k\nu) C^{\nu'}_{(i\mu)(k'\nu)} \rangle - dN \right) + \frac{1}{N} \left( \frac{m - 1}{2m} \sum_{p=2}^{\infty} \int \frac{\text{Tr} C^p}{p} \right) . \] (19)

The \( p \)-th order term depends, as usual, on the \( p \)-point correlation function

\[ \langle \text{Tr} C^p \rangle = \sum_{\epsilon_1, \ldots, \epsilon_p \in \{+, -\}} \sum_{\mu_1 \ldots \mu_p} \int d^dz_1 \ldots d^dz_p \rho^p g^{\epsilon_1 \ldots \epsilon_p} \rho^p C^{\epsilon_1 \epsilon_2}_{\mu_1 \mu_2} (z_1 - z_2) \ldots C^{\epsilon_{p-1} \epsilon_p}_{\mu_{p-1} \mu_p} (z_p - z_1) . \] (20)

The 'chain' approximation in the computation of the traces neglects contributions coming from the terms where two indices coincide and utilizes the superposition approximation to obtain \( p \)-point correlation functions \( g^{(p)}(z_1 \ldots z_p) = g(z_1 - z_2) \cdots g(z_p - z_1) \). With these hypotheses we arrive at:

\[ \langle \text{Tr} C^p \rangle = \int d^dz_1 \ldots d^dz_p \rho^p \sum_{\mu_1 \ldots \mu_p} \sum_{\epsilon_1, \ldots, \epsilon_p} g^{\epsilon_1 \epsilon_2} (z_1 - z_2) C^{\epsilon_1 \epsilon_2}_{\mu_1 \mu_2} (z_1 - z_2) \ldots g^{\epsilon_{p-1} \epsilon_p} (z_p - z_1) C^{\epsilon_{p-1} \epsilon_p}_{\mu_{p-1} \mu_p} (z_p - z_1) . \] (21)

Traces are computed in Fourier space, where the matrix is diagonal with respect to particle indices, by introducing

\[ D^{\epsilon \epsilon'}_{\mu \nu}(k) \equiv \int d^d \rho_e \epsilon' (r) C^{\epsilon \epsilon'}_{\mu \nu}(r) e^{ikr} , \] (22)

which can be decomposed in its diagonal (longitudinal) and traceless (transversal) parts with respect to spatial indices

\[ D^{\epsilon \epsilon'}_{\mu \nu}(k) = \delta_{\mu \nu} \ a^{\epsilon \epsilon'}(k) + \left( \frac{k_\mu k_\nu}{k^2} - \frac{\delta_{\mu \nu}}{d} \right) b^{\epsilon \epsilon'}(k) . \] (23)

The last step consists in the diagonalization of \( D \) in the space of components. For each \( k \), one has four distinct eigenvalues, the two 'longitudinal' ones, corresponding to those of

\[ D^{\epsilon \epsilon'}_\parallel(k) = a^{\epsilon \epsilon'}(k) + \frac{d-1}{d} b^{\epsilon \epsilon'}(k) , \] (24)

and the two 'transverse' eigenvalues of the matrix

\[ D^{\epsilon \epsilon'}_\perp(k) = a^{\epsilon \epsilon'}(k) - \frac{1}{d} b^{\epsilon \epsilon'}(k) . \] (25)

The eigenvalues are:
\[ \begin{align*}
\lambda_\parallel &= \frac{1}{2} \left( D_{\parallel\parallel}^++ D_{\parallel\parallel}^- + \sqrt{(D_{\parallel\parallel}^+ - D_{\parallel\parallel}^-)^2 + 4(D_{\parallel\parallel}^-)^2} \right) \\
\mu_\parallel &= \frac{1}{2} \left( D_{\parallel\parallel}^+ + D_{\parallel\parallel}^- - \sqrt{(D_{\parallel\parallel}^+ - D_{\parallel\parallel}^-)^2 + 4(D_{\parallel\parallel}^-)^2} \right) \\
\lambda_\perp &= \frac{1}{2} \left( D_{\perp\perp}^++ D_{\perp\perp}^- + \sqrt{(D_{\perp\perp}^+ - D_{\perp\perp}^-)^2 + 4(D_{\perp\perp}^-)^2} \right) \\
\mu_\perp &= \frac{1}{2} \left( D_{\perp\perp}^+ + D_{\perp\perp}^- - \sqrt{(D_{\perp\perp}^+ - D_{\perp\perp}^-)^2 + 4(D_{\perp\perp}^-)^2} \right).
\end{align*} \] (26)

The higher order terms involving the fluctuation of \( \sum_k C_{ik} \) cannot be resummed in a systematic way similar to the one introduced for the off-diagonal terms \( C_{ij} \). In any event, neglecting them is not likely to dramatically change the final result, because the sum of all terms higher than order two contributes just a small correction to second order computation for non-diagonal matrix elements. This is confirmed by comparison to simulations.

In addition, the second order term from these calculations is equal to the second order term computed in the small cage approximation when non-harmonic corrections due to higher derivative are neglected. Summarizing:

- The harmonic resummation scheme allows us to resum the whole contribution coming from off-diagonal matrix elements, but it misses contributions from non harmonic corrections and from thermal fluctuation of diagonal elements of \( M \).
- Both kinds of correction are accounted by the small cage approximation, but in that case we are unable to systematically resum either the terms of the series:
  \[ \sum_{p=2}^\infty \left\langle \frac{\text{Tr} C^p}{p} \right\rangle. \] (27)
  or the contributions from non-harmonic corrections, and one has to truncate the expansion at some order (up to now we truncated at the second order).
- It is possible to partially merge second order contributions from the small cage computation in the harmonic resummation scheme, obtaining the whole resummed series plus fluctuations of diagonal elements up to second order.

The final expression we get for the binary mixture free energy within this scheme is:

\[ \begin{align*}
\phi(m, \beta) &= -\frac{d}{2m} \log(m) - \frac{d(m-1)}{2m} \log(2\pi) + \frac{d(m-1)}{2m} (c_+ \log(\beta r_+) + c_- \log(\beta r_-)) \\
&\quad - \frac{(m-1)}{2m} \frac{1}{\rho} \int \frac{d^d k}{2\pi^d} \sum_{e'e''} d \alpha^{e'}(k) \alpha^{e''}(k) h^{e''\epsilon}(k) + \left( 1 - \frac{1}{d} \right) b^{e'}(k) b^{e''}(k) h^{e''\epsilon}(k) \\
&\quad + \frac{(m-1)}{2m} \frac{1}{\rho} \int \frac{d^d k}{2\pi^d} \left\{ L_3(\lambda_\parallel(k)) + L_3(\mu_\parallel(k)) \right\} (d-1) \left[ L_3(\lambda_\perp(k)) + L_3(\mu_\perp(k)) \right]\} \\
&\quad - \frac{(m-1)}{2m} \int dr \rho \sum_{e'e''} g^{e'e''}(r) \sum_{\mu\nu} \left( C^{e'e''}_{\mu\nu}(r) \right)^2 - \frac{1}{mN} \log Z_{\text{liq}}(\beta m). \end{align*} \] (28)
where the function $L_3$ is $\log(1 - x) + x + x^2/2$. Let us point out that the term in the second line is just the contribution, to lowest order, due to fluctuations of the diagonal elements of the Hessian matrix.

It is now simple to compute the equilibrium complexity $\Sigma_{eq}$:

$$\Sigma_{eq}(\beta) = m^2 \frac{\partial \beta F_m}{\partial m} \bigg|_{m=1} = S_{liq} - S_{sol},$$

(29)

where $S_{liq}$ is the entropy of the liquid at the effective temperature $T_{eff}$, which equals $T$ for $m = 1$, and $S_{sol}$ is the entropy of a harmonic solid with a matrix of second derivatives given by $M$, i.e:

$$S_{sol} = \frac{d}{2} \log(2\pi) - \frac{1}{2N} \langle Tr \log(\beta M) \rangle.$$

(30)

The condition for identifying the Kauzmann temperature, $\Sigma_{eq}(\beta) = 0$, reads in our approximation simply:

$$S_{liq} = S_{sol},$$

(31)

as expected on general grounds.32

If from our computation we find that $S_{liq} < S_{sol}$, we are already in the glass phase ($T < T_K$) and the computation in the liquid does not make sense, while in the other case $S_{liq} > S_{sol}$, the temperature is greater than $T_K$ (and of course less than $T_D$ if the spectrum of $M$ is positive).

With (28) we have a tool to investigate the thermodynamics of the low temperature glass phase. It should be emphasized that only the liquid phase $g(r)$ and free-energy are needed in order to compute the glass phase thermodynamics. Beyond the usual thermodynamic quantities (energy, entropy, heat capacity...), we are interested in the two new parameters describing the glass phase:

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

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

(32)

This expression gives square cage radii nearly linear in temperature in the whole glass phase (see figure [6b]), which is natural since non-harmonic effects have been neglected. The values of $A_\epsilon$ at the Kauzmann temperature are of the same order of those obtained for the soft sphere model, i.e. $\sim 10^{-3}$.

- The effective temperature $T_{eff} = T/m^*$ of the molecular liquid. This varies very little and remains close to the Kauzmann temperature throughout the low temperature phase, confirming the hypothesis that glass can be successfully described by means of a system of molecules remaining in the liquid phase. We stress that the linear behaviour of parameter $m^*$ as a function of $T$ is a feature shared by every 1RSB system to our knowledge. This static parameter should be equivalent to the dynamical parameter that measures violation of the fluctuation-dissipation theorem33, as it is observed in short range spin-glasses.34

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The harmonic expansion makes sense only if $M$ has no negative eigenvalues. This is natural since it is intimately related to the vibration modes of the glass. Notice that we cannot describe activated processes here, and so we cannot see the tail of negative eigenvalues (with number decreasing as $\exp(-1/T)$ at low temperatures), which is always present. It is known however that the fraction of negative eigenvalues of $M$ becomes negligible below the dynamical transition temperature, $T_D$. Therefore our harmonic expansion makes sense if the effective temperature, $T_{\text{eff}}$, is less than $T_D$.

V. INTEGRAL EQUATIONS FOR BINARY MIXTURES

Unlike simpler models such as the soft sphere model, the glass transition for the considered Lennard-Jones binary mixture cannot be described in the simple framework of well-known approximations of nonlinear integral equations for liquids: the Hypernetted Chain approximation (HNC); the Mean Spherical Approximation (MSA); the Percus-Yevick Approximation (PY). Within all the classical approximation HNC, PY and MSA, the compressibility, computed as an integral of correlation functions:

\[
\rho \chi_1 = \beta + \rho \beta \int d^3 r h(r),
\]  

(33)

diverges at a finite temperature $T_{GL}$ which depends on the chosen approximations [fig. 1]. We draw two conclusions from these computations. Our first conclusion is that this singularity corresponds to the liquid-gas phase separation which is typical of simple systems. To convince the reader, in [fig. 2] we show the phase diagram in the plane $\rho - T$ computed within HNC approximation, where the region of phase coexistence is shown.

Hence, our claim is that HNC and PY, in this model, badly overestimate the real liquid-gas phase separation temperature, $T_{GL}$, while MSA approximation allows to get far closer to this transition. This is confirmed by our numerical simulations (see below) placing $T_{GL}$ for $\rho = 1.2$ at $\sim 0.3$. 

\[
\begin{array}{c}
\text{HNC} \\
\text{MSA} \\
\text{PY}
\end{array}
\]
FIG. 1. Compressibility, $\chi$, as a function of temperature, $T$, computed by HNC (filled line), PY (dashed line) and MSA (dotted line) approximations.

FIG. 2. Projection of the phase diagram in the $\rho - T$ plane computed by HNC approximation. In the region on the left of the line, a thermodynamically stable homogeneous phase does not exist and the system undergoes a liquid-gas phase separation.

A simple procedure for improving the integral equations has been proposed by Zerah and Hansen. It mixes the HNC and MSA closures by means of a single parameter, $\alpha$, that is chosen in order to reduce thermodynamic inconsistencies between the two different routes for computing the compressibility:

$$\rho \chi_1 = \beta + \rho \beta \int d^3r h(r)$$

$$\rho \chi_2 = \left(\frac{dP}{d\rho}\right)^{-1}$$

where the pressure, $P$, is computed via the virial equation:

$$\frac{\beta P}{\rho} = 1 - \frac{2}{3} \pi \beta \rho \int dr \, r^3 V'(r) g(r)$$

Briefly, we recall that HNC approximation consists of neglecting the 'bridge' diagrams in the cluster Mayer expansion, while MSA treats the attractive term of the potential as a correction to the repulsive term.

The 'mixed' integral equation which we have resort to is, then:

$$\epsilon \epsilon' \rho^2 g_{\epsilon \epsilon'}(r) = \exp\left(-\beta V_{(R)}(r)\right) \left(1 + \frac{\exp\{f_{\epsilon \epsilon'}(r)[w_{\epsilon \epsilon'}(r) - \beta V_{(A)}(r)]\}}{f_{\epsilon \epsilon'}(r)} - 1\right)$$

(36)
where $V_A(r)$ and $V_R(r)$ are, respectively, attractive and repulsive contribution to potential:

$$
V_R \equiv \begin{cases} 
V(r) - V_{\text{min}} & r \leq r_{\text{min}} \\
0 & r \geq r_{\text{min}}
\end{cases}
$$

$$
V_A \equiv \begin{cases} 
V_{\text{min}} & r \leq r_{\text{min}} \\
V(r) & r \geq r_{\text{min}}
\end{cases}
$$

(37)

and the function $W(r)$ is $h(r) - c(r)$, with $c(r)$ the direct correlation function.

In the Zerah and Hansen scheme the function $f^{p\epsilon}(r)$ is introduced, allowing continuously interpolation between HNC and MSA, simply by choosing:

$$
f^{p\epsilon}(r) = 1 - \exp \left(-\frac{r}{\sigma^{p\epsilon} \alpha} \right).
$$

(38)

Let us stress that for $f(r) \to 1$ the closure (36) reduce to HNC, while in the opposite limit, $f(r) \to 0$, MSA is recovered. The choice of (38) implies that we obtain correlation functions which are HNC-like at large $r$ and MSA-like at short $r$.

We have chosen to utilize this scheme in a different fashion, since we are mainly interested to obtain pair correlation functions which very accurately reproduce the observed liquid behaviour in order to study the effects of the used approximations in describing the liquid-glass transition. The HNC closure is exact at very high temperatures and, within this model, significant deviations from it of the numerical data of the energy appear yet in the region $\beta \in [10^{-4}, 0.1]$. On the other hand, the MSA approximation turns out to be more correct when the liquid-gas coexistence region is approached, both in reproducing the numerical data and in reducing the inconsistencies between the two different compressibilities. We have chosen as a starting value $\alpha = 1.5$ at $\beta = 0.1$, which fits very well the numerical data in the whole region $\beta \in [10^{-4}, 0.1]$ and we increased it linearly in such a way to have a MSA value ($\alpha = 5$) at the liquid-gas transition.

The result is a very good agreement between internal energy computed with the $g(r)$ obtained by solving (36) and the results of numerical simulations [fig.3]. These will be discussed in detail in the following. Let us remind that the pure HNC and MSA closure have an error up to 10%, while, with interpolated integral equations, it is greatly reduced.
FIG. 3. Internal energy vs. inverse temperature, $\beta$. The points are obtained by simulated annealing runs, the solid line by interpolated integral equation.

VI. RESULTS AND DISCUSSION

We have studied a binary mixture where particles interact by means of a Lennard-Jones type potential. This model has been introduced and extensively studied as a good glass former. For density $\rho = 1.2$, numerical simulations show evidence for a 'dynamical' transition at temperature $T_D = 0.4351$. This kind of transition does not correspond to a real thermodynamic transition with singularities in thermodynamic quantities, but rather seems related to changes in the relaxation processes of the system in the free-energy landscape. Mean field theory of supercooled liquid, Mode Coupling Theory, describes this dynamical transition.

Complementary to this 'dynamical' picture of the glass transition is the investigation of the free-energy of a 'molecular' liquid, where 'molecules' are formed by $m$ replicas of the particles in the original system, as recently proposed and studied in this paper for a Lennard-Jones model.

Following this strategy, we show that at the temperature $T_K = 0.32$ (see the figures below) the complexity, i.e. the entropy due to the large number of minima in potential energy as a function of particle positions, vanishes. In our 'thermodynamic' picture, $T_K$ corresponds to the Kauzmann temperature, where the supercooled liquid undergoes a true thermodynamic transition and the system enters a new phase, where it behaves as an amorphous solid.

A. Thermodynamic quantities

From the thermodynamic point of view, the transition is second order. Indeed, the free energy and the internal energy have no singularity [fig. 4], while one can observe that the
specific heat [fig. 5] shows an evident ‘jump’ at \( T_K \), remaining close to 3/2, in agreement with the Dulong-Petit law, throughout the glass phase.

**FIG. 4.** The free energy (a) and the internal energy (b) of the Lennard-Jones model as a function of the temperature, in both the liquid and the glass phase.

**FIG. 5.** The specific heat of the Lennard-Jones as a function of the temperature.

### B. New thermodynamic parameters

In the framework of replica theory of structural glasses two new parameters are introduced, analogous to those used to describe the glass phase in spin-glass models: the parameter \( m \), plotted in [fig. 6a] and cages size, \( A^+ \) and \( A^- \), plotted in [fig. 6b]. Both are nearly linear with temperature. In particular, this means that the effective temperature, \( \beta m \), is always close to the transition value, so in our theoretical computation we need only the mean values of observables at temperatures \( T > T_{GL} \).
C. Comparisons with MC simulations

Before discussing the numerical results on the complexity and the evaluation of the transition temperature, let us pay some attention to the possible presence of a liquid-gas phase separation at a non zero $T_{GL}$. We identify this temperature as the one where the liquid pressure $P_{liq}$ equals the gas pressure $P_{gas}$. At low enough temperatures, the coexistence is between liquid and gas at very small density, where $P_{gas} \approx \rho/\beta$ is negligible. Therefore, as a first approximation, we evaluate $T_{GL}$ as the temperature where the liquid pressure becomes compatible with zero. This pressure is computed via the virial equation:

$$\frac{P}{\rho} = \frac{1}{\beta} - \frac{1}{6N} \left( \sum_{i \neq j} r_{ij} \frac{dV_{ij}}{dr_{ij}} (r_{ij}) \right).$$

(39)

We present in [Fig 7] data on the behaviour of $\frac{1}{6} \langle rdV/dr \rangle$, that seems very well fitted by the power law $aT^{3/5} + b$, usually encountered in liquids. By extrapolating data at temperatures lower than the ones where we succeeded in thermalizing the system, we get a definitely non zero $T_{GL} \sim 0.3$. 
FIG. 7. The numerical evaluation of $T_{GL} \sim 0.3$ as the temperature where the extrapolation of data on $\frac{1}{6} (r dV/dr)$ equals $1/\beta$, i.e. the liquid pressure becomes compatible with zero.

Though more extensive investigations are needed to confirm this result, our data are in good agreement with the existence of a liquid-gas phase separation. Moreover, they strongly support our hypothesis that approximation schemes like HNC and PY overestimate the transition temperature. Therefore, introducing the Zerah and Hansen scheme of interpolation is necessary to analytically evaluate liquid quantities near the transition point. Let us recall that this closure gives $T_{GL} \approx 0.25$, a slightly lower value than numerical simulations.

Details of the simulations will be discussed below but we would like to emphasize here that the model we considered is the LJ binary mixture described in (4) without any cutoff on the potentials, taking into account the small correction due to finite size effects. The presence of a cutoff (it is usual to take $V^{c'}(r) = 0$ for $r > 2.5 \sigma^{++}$) would obviously influence both the energy and the pressure behaviour and we expect a lower value for $T_{GL}$.

In order to evaluate the complexity and the thermodynamic temperature by simulations, we consider the numerical approach suggested by the harmonic resummation scheme, first utilized for the soft spheres binary mixture model. We measure both the liquid and the amorphous solid entropy, whose difference gives $\Sigma$. $T_{K}$ is the temperature where the entropies become equal.

The liquid entropy can be obtained by numerically integrating the energy density

$$S_{liq}(\beta) = \beta (e_{liq}(\beta) - f_{liq}(\beta)) = S_{liq}^0 + \beta e_{liq}(\beta) - \int_0^\beta d\beta' e_{liq}(\beta')$$

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

$$S_{liq}^0 = 1 - \log \rho - c \log c - (1 - c) \log(1 - c).$$

As it has been discussed in the previous paper, the numerical computation of the 'harmonic solid' entropy is a more subtle task. One has
\[ S_{\text{sol}}(\beta) = \frac{d}{2} \left( 1 + \log(2\pi) \right) - \frac{1}{2N} \langle \text{Tr} \log(\beta M) \rangle , \]  

but the measure of \( S_{\text{sol}} \) from the 'instantaneous' Hessian is complicated by the negative eigenvalues, always present beyond the mean field approximation, though their number decreases as \( \exp(-1/T) \) at low temperatures and it is expected to be negligible below the Mode Coupling temperature.\[ \text{[1]} \] 

We consider three different ways of evaluating \( S_{\text{sol}} \):

- We measure it from only the \( N_{\text{pos}} \) positive eigenvalues
  \[ S_{\text{sol}}^{(a)} = \frac{d}{2} \left[ \left( 1 + \log\left( \frac{2\pi}{\beta} \right) \right) - \frac{1}{N_{\text{pos}}} \sum_{i=1}^{N_{\text{pos}}} \log \lambda_i \right] . \]  

- We consider also the absolute values of the negative ones (we are disregarding both here and in the previous case the very few \( |\lambda| < 10^{-4} \),
  \[ S_{\text{sol}}^{(b)} = \frac{d}{2} \left[ \left( 1 + \log\left( \frac{2\pi}{\beta} \right) \right) - \frac{1}{dN} \sum_{i=1}^{dN} \log |\lambda_i| \right] . \]  

- Starting from an equilibrium configuration at a given \( \Gamma \) value, we perform a Monte Carlo run at \( T = 0 \), allowing only small displacements to each particle. The percentage of non-positive eigenvalues becomes very rapidly \( < 2\% \) in the whole temperature range considered and, correspondingly, we get compatible results on \( S_{\text{sol}}^{(c)} \) when using only the positive eigenvalues or also the negative ones.

As shown in [fig. 8], there is not a small difference between \( S_{\text{sol}}^{(a)} \) and \( S_{\text{sol}}^{(b)} \), particularly at temperatures \( T \gtrsim T_D \). This is also related to the fact that nearly all the negative eigenvalues are less than one in absolute value. On the other hand, \( S_{\text{sol}}^{(c)} \) definitely appear nearer to the 'instantaneous' Hessian entropy evaluated by taking all the eigenvalues in absolute value. This has also been observed\[ \text{[3]} \] in the case of the soft sphere binary mixture and it suggests that \( S_{\text{sol}}^{(b)} \) is a more reasonable estimation of the solid entropy.

The other problem that we face is the well-known and difficult task of thermalizing glass-forming liquids at low temperatures. We choose to perform a simulated annealing run of a rather large system, using data on the liquid energy down to the temperature where the equilibrium was still reachable in a reasonable CPU time (\( \beta \sim 2.5 \)).

Then we extrapolate the liquid entropy behaviour at lower temperatures by fitting data in the interval \( \beta \in [1, 2.5] \) with the power law

\[ S_{\text{liq}}(T) = a T^{-2/5} + b. \]  

This corresponds to the assumption of a low temperature liquid energy behaviour \( e \sim T^{3/5} \), a theoretical prediction that seems to be well-followed in many simple liquids\[ \text{[5]} \] and that we find in very good agreement with our data, both in this case and in the previously discussed data on the pressure.
In more detail, we performed a simulated annealing run of a system of \( N = 260 \) particles, in a cubic box with periodic boundary conditions, starting from \( \beta^{1/4} = 0.02 \) and performing up to \( 2^{22} \) MC steps at each \( \Delta \beta^{1/4} = 0.02 \), the maximum shift \( \delta_{\text{max}} \) allowed to each particle in one step being chosen in order to get an acceptance \( a \sim 0.5 \). The energy and its fluctuation were measured in the last half of each run at a given \( \beta \) value while the pressure was obtained from about 200 configurations in the same interval. We take into account the small finite size effects by adding to the energy and pressure the appropriate corrections evaluated analytically by means of \( \int_{\Lambda} v(r) d^3r \), where \( \Lambda \) is the volume obtained as difference between the volume of the whole space and the volume of the box containing the particles. Just for decreasing the error on the evaluation of \( S_{\text{liq}} \), we fit the very high temperature data on the energy, up to \( \beta_0^{1/4} = 0.1 \), by using \( \beta^{3/4} e(\beta) = a\beta^{1/2} + b\beta^{3/4} + c \), obtaining correspondingly \( f(\beta_0) = 4a\beta_0^{3/4}/3 + 2b\beta_0^{1/2} + 4c\beta_0 \), that turns out to be perfectly compatible with the analytical value (i.e. we are still in the region where no differences are observable between numerical data and analytical approximations). The integration is subsequently performed by interpolating the simulation data with a standard numerical subroutine in order to get a result which is independent of 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 \( \beta \)-value, while \( S_{\text{sol}}^{(c)} \) was measured from the configurations obtained from these by 10000 MC steps at \( T = 0 \) (starting from \( \delta_{\text{max}} = 0.05 \) and decreasing it up to 0.005 during the run).

![FIG. 8. The entropy of the liquid (+) and the different evaluations (see text) of the amorphous solid entropy, \( S_{\text{sol}}^{(a)} \) (×), \( S_{\text{sol}}^{(b)} \) (∗) and \( S_{\text{sol}}^{(c)} \) (□), as functions of \( \beta \). The lines are the best fit to the power law, \( S_{\text{liq}} = a\beta^{2/5} + b \).](image)

In [fig. 8] we plot both \( S_{\text{liq}}(\beta) \) and the different measurements of \( S_{\text{sol}}(\beta) \) considered. \( S_{\text{sol}}^{(b)} \) and \( S_{\text{sol}}^{(c)} \) are very close and give similar estimations of \( T_K \sim 0.3 \), whereas \( S_{\text{sol}}^{(a)} \) gives the slightly lower value \( T_K \sim 0.26 \). It seems therefore reasonable to get the mean value \( T_K \sim 0.28 \) as our
numerical evaluation of the Kauzmann temperature.

![Graph showing the comparison between analytical and numerical results]

FIG. 9. Analytical $S_{\text{liq}}$ (upper line) compared with the numerical values (points), and analytical $S_{\text{sol}}$ computed in the harmonic resummation scheme (lower line) compared with the three different numerical results, i.e. $S_{\text{sol}}^{(a)}$ (×), $S_{\text{sol}}^{(b)}$ (∗), $S_{\text{sol}}^{(c)}$ (□).

We note that this value of the Kauzmann temperature, to be compared with the analytical $T_K \approx 0.32$, is close to the previously discussed numerical estimation of $T_{GL}$. Our numerical data are inadequate for clarifying this situation, which is intriguing and deserves a more careful study. Here we only suggest that there could be a glass-gas phase coexistence in the low temperature region.

Finally, [fig. 9] illustrates the comparisons between $S_{\text{liq}}$ and $S_{\text{sol}}$ as functions of the temperature $T$ computed analytically (lines) and the same quantities determined by our numerical simulations (points), as discussed above. In this plot we added both the correct normalization constant, giving $S = 0$ when the volume of phase space is equal to $\hbar^3$, and the thermal contribution which had been neglected in the previous figure. Obviously these terms do not affect the thermodynamical glass transition. We used the physical parameters appropriate to argon ($\sigma_{++} = 3.405 \, \text{Å}, \epsilon_{++}/k_B = 125.2K$), plotting the entropies per particle.

The reliability of the approximations introduced is clarified by these comparisons:

- the numerical points of $S_{\text{liq}}$ are very close to the corresponding analytical quantity computed by means of the interpolation between HNC and MSA closures

- the three different ways to numerically evaluate $S_{\text{sol}}$ are in various agreement with the analytical curve, but it is important to note that in the low temperature region (below the dynamical temperature), none of them is further than $\sim 10 - 20\%$ from the theoretical prediction.
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1 W. Kob and H.C. Andersen, *Phys. Rev. Lett.* **73**, 1376 (1994); *Phys. Rev. E* **51**, 4626 (1995); *Phys. Rev. E* **53**, 4134 (1995).
2 M. Mézard and G. Parisi, *Phys. Rev. Lett.* **82**, 747 (1988).
3 M. Mézard, *How to compute the thermodynamics of a glass using a cloned liquid*, cond-mat/9812024.
4 M. Mézard and G. Parisi, *J. Chem. Phys.* **111**, 1076 (1999).
5 B. Coluzzi, M. Mézard, G. Parisi and P. Verrocchio, *J. Chem. Phys.* **111**, 9039 (1999).
6 F.H. Stillinger and T.A. Weber, *Phys. Rev. A* **25**, 2408 (1982). F.H. Stillinger, *Science* **267**, 1935 (1995) and references therein.
7 S. Sastry, P.G. Debenedetti and F.H. Stillinger, *Nature* **393**, 554 (1998).
8 K.K. Bhattacharya, K. Broderix, R. Kree, A. Zippelius *Energy Landscape and Overlap Distribution of Binary Lennard-Jones Glasses*, cond-mat/9903120.
9 L. Angelani, G. Parisi, G. Ruocco and G. Viliani, *Phys. Rev. Lett.* **81**, 4648 (1998).
10 F. Sciortino and P. Tartaglia, *Phys. Rev. Lett.* **78**, 2385 (1997).
11 For a review see W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).
12 S. Franz and G. Parisi, *Phys. Rev. Lett* (in press) and *Effective potentials in glassy systems: theory and simulations*, cond-mat/9806027.
13 M. Cardenas, S. Franz and G. Parisi, *J. of Chem. Phys.*, **110**, 1726 (1999) *J. Phys. A: Math. Gen.* **31**, L163 (1998).
14 T.R. Kirkpatrick and P.G. Wolynes, *Phys. Rev. A* **34**, 1045 (1986). For a review see also T.R. Kirkpatrick and D. Thirumalai, *Transp. Theor. Stat. Phys.* **24**, 927 (1995)
15 L.F. Cugliandolo and J. Kurchan, *Phys. Rev. Lett.* **71**, 173 (1993).
16 A. Crisanti and H.-J. Sommers, *J. Phys. I (France)* **5**, 805 (1995); A. Crisanti, H. Horner and H.-J. Sommers, *Z.Phys.* **B 92**, 257 (1993).
17 For a careful analysis of the free energy landscape see A. Cavagna, I. Giardina and G. Parisi, *J. Phys. A: Math. Gen.* **30**, 7021 (1997), and references therein.
18 A.W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).
19 J.H. Gibbs and E.A. Di Marzio, *J. Chem. Phys.* **28**, 373 (1958).
20 G. Adam and J.H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
21 G. Parisi, *On the mean field approach to glass systems*, Lecture given at the Sitges conference (1996), cond-mat/9701034. *On the replica approach to glass*, Proceedings of the ACS meeting, Orlando (1996), cond-mat/9701068. *Slow dynamics in glass systems*, Lectures given at the Varenna summer school (1996), cond-mat/9705312. *On the replica method for glassy systems*, Contribution to the Conference in Honour of Giovanni Paladin, Rome (1997), cond-mat/9806008.
22 For a recent review see C.A. Angell, *Science* **267**, 1924 (1995) and P. De Benedetti, *Metastable liquids*, Princeton University Press (1997).
23 J.P. Hansen and I.R. Macdonald, *Theory of Simple Liquids*, Academic (London, 1986).
24 W. Kob, C. Donati, S.J. Plimpton, P.H. Poole and S.C. Glotzer *Phys. Rev. Lett.* **79**, 2827 (1997).
25 C. Donati, J.F. Douglas, W. Kob, S.J. Plimpton, P.H. Poole and S.C. Glotzer *Phys. Rev. Lett.* **80**, 2338 (1998).
26 C. Donati, S.C. Glotzer, P.H. Poole, W. Kob and S.J. Plimpton, *Spatial Correlations of Mobility*
and Immobility in a Glassforming Lennard-Jones Liquid, cond-mat/9810060.

27 J.-L. Barrat and W. Kob, Fluctuation dissipation ratio in an aging Lennard-Jones glass, cond-mat/9806027.

28 L.F. Cugliandolo and J. Kurchan, Thermal properties of slow dynamics, Invited talk at STAT-PHYS20, Paris (1998), cond-mat/9807226.

29 L.F. Cugliandolo and J. Kurchan, J. Phys. A: Math. Gen. 27, 5749 (1994).

30 U. Müssel and H. Rieger, Phys. Rev. Lett. 81, 930 (1998).

31 G. Zerah and J.P. Hansen, J. Chem. Phys. 84 (4), 2336 (1986).

32 R. Monasson, Phys. Rev. Lett. 75, 2847 (1995).

33 S. Franz, M. Mézard, G. Parisi and L. Peliti, Phys. Rev. Lett. 81, 1758 (1998); The response of glassy systems to random perturbations: a bridge between equilibrium and off-equilibrium, cond-mat/9903370.

34 E. Marinari, G. Parisi, F. Ricci-Tersenghi and J.J. Ruiz-Lorenzo, J. Phys. A: Math and Gen. 31, L481 (1998).

35 T. Keyes, J. Phys. Chem. A 101, 2921 (1997), and reference therein.

36 Y. Rosenfeld and P. Tarazona, Mol. Phys. 95, 141 (1998).