

## LETTER TO THE EDITOR

## Diffusivity and configurational entropy maxima in short range attractive colloids

Luca Angelani<sup>1</sup>, Giuseppe Foffi<sup>2,3</sup>, Francesco Sciortino<sup>4</sup> and Piero Tartaglia<sup>1</sup>

<sup>1</sup> Dipartimento di Fisica and INFM CRS-SMC, Università di Roma *La Sapienza*, Piazzale Aldo Moro 2, 00185 Roma, Italy

<sup>2</sup> Dipartimento di Fisica and INFM, Università di Roma *La Sapienza*, Piazzale Aldo Moro 2, 00185 Roma, Italy

<sup>3</sup> Institut Romand de Recherche Numérique en Physique des Matériaux IRRMA, PPH-Ecublens, CH-105 Lausanne, Switzerland

<sup>4</sup> Dipartimento di Fisica and INFM CRS-SOFT, Università di Roma *La Sapienza*, Piazzale Aldo Moro 2, 00185 Roma, Italy

Received 7 February 2005

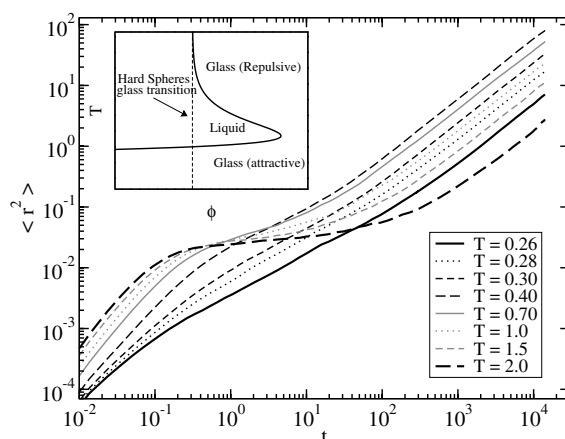
Published 11 March 2005

Online at [stacks.iop.org/JPhysCM/17/L113](http://stacks.iop.org/JPhysCM/17/L113)

### Abstract

We study tagged particle diffusion at large packing fractions, for a model of particles interacting with a generalized Lennard-Jones  $2n-n$  potential, with large  $n$ . The resulting short range potential mimics interactions in colloidal systems. In agreement with previous calculations for short range potentials, we observe a diffusivity maximum as a function of temperature at constant density. By studying the temperature dependence of the configurational entropy—which we evaluate with two different methods—we show that a configurational entropy maximum is observed at a temperature close to that of the diffusivity maximum. Our findings suggest a relation between the dynamics and number of distinct states for short range potentials.

Advances in colloidal science have been extremely useful in the development of the physics of liquids, in linking thermodynamic and dynamic properties of systems to the interparticle interaction potential (for recent reviews see for example references [1, 2]). Almost 20 years ago it was experimentally shown that hard sphere (HS) particles crystallize [3], a result that confirmed previous numerical predictions [4]. More recently, experiments showed that when the packing fraction of the system is higher than  $\approx 0.58$  the system is so packed that the HS particles are arrested in a glass structure, i.e. a glass transition is encountered [3]. Other important phenomenology emerges when the HS interaction is complemented by a short range attraction. Colloidal dispersions, with particles interacting with a range of attraction short compared to the nearest neighbour distances, present new physical phenomena that are not encountered in atomic and molecular liquids where the attraction is generally long ranged.



**Figure 1.** Mean square displacements for different  $T$  (from  $T = 0.26$  to  $2.0$ ). The inset shows a sketch of the glass transition lines for short range attractive potentials [14].

For example, the liquid–liquid coexistence becomes metastable with respect to the fluid–crystal one [5, 6]. One of the most puzzling discoveries is that, if the attraction range is short enough, the increase of the strength of the attraction (as compared to the thermal energy  $k_B T$ ) destabilizes the hard sphere glass, transforming it into a liquid. Further increase of the attraction over  $k_B T$  ratio, however, generates an additional glass transition. Thus, colloidal dispersions with short range attractions are characterized by a non-monotonic dependence on  $T$  of the diffusivity: dynamics slows down not only upon cooling (as is commonly observed in molecular systems), but also upon heating. In experiments [7–10] and in numerical simulations [11, 12] two different glasses have been identified [13]: one at low  $T$ , called *attractive glass*, and one at high  $T$ , called *repulsive glass* (analogous to the HS glass). The situation is sketched in the inset of figure 1.

The existence of a fluid phase between two glasses suggests that the diffusion coefficient  $D$  exhibits a maximum when the strength of the attraction (or the temperature) is varied along a path of constant density. According to mode coupling theory, the non-monotonic behaviour of  $D$  results from the competition of two different localization lengths, one associated with the ‘hard core’ and one with the short range attractive bond [14]. In this letter we calculate the  $T$  dependence of the configurational entropy  $S_{\text{conf}}$ —a measure of the number of distinct states of the system—with the aim of providing insights into the physical origin of the  $D$  maximum. A diffusivity maximum emerges also in water on isothermal compression, due to the non-spherical feature of the potential. In the case of water [15] the locations of the  $S_{\text{conf}}$  extrema correlate with those of  $D$  extrema. However for colloidal particles the potential is symmetric and the nature of the maximum in diffusivity must be related to a different mechanism. It is then natural to ask whether, in a model which is so different from water, this correlation is still present.

We use two different routes to determine  $S_{\text{conf}}$ : the first one, based on a potential energy landscape (PEL) investigation, requires an estimate of the vibrational free energy of the system close to the local minima of the PEL explored (the so-called inherent structures (IS) [16]); the second one uses a perturbed Hamiltonian [17, 18] and requires a thermodynamic integration from a known reference state. In both cases, the configurational entropy is calculated as a difference between total entropy (estimated via thermodynamic integration from the ideal gas state) and the vibrational entropy. The main results of the present work are:

- (i) the presence of a diffusivity maximum on varying  $T$ , confirming that the origin of this phenomenon does not depend on the specific shape of the short range attractive potential [11, 12];
- (ii) the existence of a maximum in the  $T$  dependence of  $S_{\text{conf}}$ ;
- (iii) the equivalence of the temperatures at which  $D$  and  $S_{\text{conf}}$  have a maximum.

In the PEL formalism, it is crucial that the interaction potential of the system is continuous, so that IS can be properly located via a steepest descent minimization of the potential energy and so that vibrational frequencies can be properly calculated. For this reason we focus on a continuous model that possesses a steep repulsion and a short ranged attraction, and that has been proved to reproduce features of the short ranged attractive colloidal system discussed above [19]. The model of attractive colloid that we study is based on a generalization of the Lennard-Jones pair potential (LJ  $2n-n$ ) proposed by Vliegthart *et al* [19]:  $V_{\text{LJ}n}(r) = 4\epsilon [(\sigma/r)^{2n} - (\sigma/r)^n]$ . Unlike [19] we choose an extremely large value of the exponents, i.e.  $n = 100$ . For this value of  $n$ , the range of attraction is less than a few per cent of  $\sigma$ .

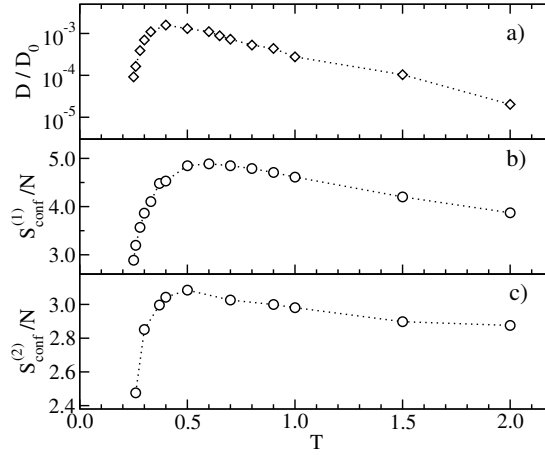
We perform standard isothermal molecular dynamics using the Nosé–Hoover thermostat. The simulated system is composed of 256 particles confined in a cubic box with periodic boundary conditions. In order to prevent crystallization we study a 50:50 binary mixture with the following parameters:  $\sigma_{AA}/\sigma_{BB} = 1.2$ ,  $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$ ,  $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB}$ . We use Lennard-Jones units ( $\sigma_{AA}$  for length,  $\epsilon_{AA}$  for energy,  $\tau = (m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$  for time). We chose the Boltzmann constant  $k_B = 1$ ; consequently  $T$  is measured in units of  $\epsilon_{AA}$ . A cut and shift in the pair potential are used ( $r_{\text{cut}} = 1.4$ ). The integration time step is  $t_0 = 7 \times 10^{-5}$ . The number density investigated is  $\rho \simeq 1.43$ , corresponding to  $\phi \equiv \pi\rho(\sigma_{AA}^3 + \sigma_{BB}^3)/12 = 0.59$ .

Figure 1 shows the time dependence of the mean square displacement,  $r^2(t) = N^{-1} \langle \sum_{i=1}^N [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$ , where  $\mathbf{r}_i(t)$  is the position of particle  $i$  at time  $t$ , for  $T$  ranging from  $T = 0.26$  to  $2.0$ . The results are in agreement with previous findings based on the square-well model [12]: at high  $T$  there is a well defined plateau at about  $r^2 = 2 \times 10^{-2}$ , while at low  $T$  the plateau disappears and one observes a transient sub-diffusive regime before the diffusive one. It is worth noting that at low  $T$ , the transient regime starts around  $r^2 \sim 10^{-3}$ , a value corresponding to the length (squared) of the attractive range of the pair potential. Figure 2(a) shows  $D$  (evaluated from the long time limit behaviour of  $r^2$  and rescaled by the quantity  $D_0 = \sqrt{\sigma_{AA}^2 T/m}$ ) as a function of  $T$ . One observes a maximum located at about  $T_{\text{max}} = 0.4$ . On lowering  $T$ , for  $T < T_{\text{max}}$ ,  $D$  decreases quickly, as the system approaches the attractive glass line (almost horizontal in the  $\phi$ – $T$  plane as shown in the inset of figure 1). On increasing  $T$ , for  $T > T_{\text{max}}$ ,  $D$  decreases smoothly, consistent with the observation that the repulsive glass line is almost vertical in the  $\phi$ – $T$  phase diagram.

In analogy with recent studies for atomic and molecular liquids, one can ask whether the  $T$  dependence of  $D$  close to arrested states is correlated with the  $T$  dependence of  $S_{\text{conf}}$ . In the case of short range models, a test of the correlation between  $D$  and  $S_{\text{conf}}$  can be exploited in a more direct way, capitalizing on the presence of the  $D$  extremum at  $T = T_{\text{max}}$ . We try to answer this question, calculating  $S_{\text{conf}}$ . We write the total entropy  $S$  as a sum of two contributions: a local vibration entropy  $S_{\text{vib}}$  and a configurational entropy  $S_{\text{conf}}$  that takes into account the number of distinct local states:

$$S(T, \rho) = S_{\text{conf}}(T, \rho) + S_{\text{vib}}(T, \rho). \quad (1)$$

This expression, which can be formally derived within the PEL framework [16] and within the mean field for models of disordered p-spin systems [20], is consistent with the idea that dynamics is described by two well separated timescales: a fast dynamics describing local



**Figure 2.** (a) Diffusivity  $D$  as a function of  $T$ . The value of  $D$  is plotted rescaled by  $D_0 = \sqrt{\sigma_{AA}^2 T/m}$ . (b) Configurational entropy  $S_{\text{conf}}^{(1)}$  per particle obtained using equation (2) to estimate  $S_{\text{vib}}$  (*PEL approach*). (c)  $S_{\text{conf}}^{(2)}$  per particle obtained using equation (5) for  $S_{\text{vib}}$  (*perturbed Hamiltonian approach*).

rearrangements of particles within a state and a slow dynamics which accounts for the slow exploration of different states.

Equation (1) shows that  $S_{\text{conf}}$  can be calculated from the knowledge of  $S$  and  $S_{\text{vib}}$ . The total entropy  $S$  can be calculated using thermodynamic integration along paths in the  $T$ - $\rho$  plane. Without going into details, we can write (measuring entropy in units of  $k_B$ ):  $S(T, \rho) = S(T_0, \rho) + \int_{T_0}^T dT (\frac{3}{2}N + \partial U/\partial T)/T$ , where  $U$  is the potential energy,  $T_0$  is a reference temperature ( $T_0 = 0.4$  in our case).  $S(T_0, \rho)$  describes the path at constant  $T_0$  connecting the ideal gas to the reference state ( $T_0, \rho$ ):  $S(T_0, \rho) = S^{\text{id}}(T_0, \rho) + U(T_0)/T_0 - T_0^{-1} \int_0^\rho d\rho P_{\text{ex}}/\rho^2$ , where  $S^{\text{id}}$  is the ideal gas contribution (which includes the entropy of mixing, since we are dealing with a binary mixture), and  $P_{\text{ex}}$  is the excess pressure. Performing numerical simulations at 15 different  $\rho$  values from 0.036 up to 1.43, we estimated  $P_{\text{ex}}(T_0, \rho)$  and  $U(T_0, \rho)$ , which, taken together with  $U(T, \rho)$ , allow us to calculate with sufficiently high precision the  $T$  dependence of  $S$ .

In the *PEL approach*, the vibrational entropy can be calculated from the local curvature of the PEL around the inherent structures explored [16]. In the harmonic approximation, the vibrational entropy can be written as

$$S_{\text{vib}}^{(1)}(T) = \sum_{i=1}^{3N-3} [1 - \ln(\beta \hbar \omega_i)], \quad (2)$$

where  $\hbar$  is Planck's constant,  $\beta = 1/k_B T$  and  $\omega_i$  are the eigenfrequencies of the Hessian matrix evaluated at the inherent structure. The  $T$  dependence, besides the factor  $\beta$ , is contained in  $\omega_i$  [21].

Figure 2(b) shows the configurational entropy per particle  $S_{\text{conf}}^{(1)}/N$ , calculated as the difference between the total entropy in equation (1) and the vibrational entropy  $S_{\text{vib}}^{(1)}$  given by equation (2). The  $T$  dependence shows a maximum at temperature  $T_{\text{max}}^{(1)} \simeq 0.6$ , slightly higher than that of the diffusivity ( $T_{\text{max}} = 0.4$ ). The presence of the maximum is a remarkable result, indicating a close relationship between  $D$  and  $S_{\text{conf}}$ , even if a quantitative coincidence of the peaks seems not to be achieved. The use of the harmonic approximation deserves a

few remarks: first of all, the steepness of the  $2n-n$  potential reduces the range of  $T$  where the harmonic approximation is valid and, due to the strong  $T$  dependence of the anharmonic energy, prevents us from applying anharmonic corrections; moreover, at high  $T$  the confining cage is controlled not by the short range attractive interaction but by the excluded volume. Caging emerges from an averaging over many different IS, each with its own distinct environment. At high  $T$ , a state is made of particles moving inside the cage created by the nearest neighbours and during the exploration of the state the system will traverse many IS that are all connected together.

To strengthen the observation of the correlation between  $D$  and  $S_{\text{conf}}$  maxima, we also calculate  $S_{\text{vib}}$  using an alternative method, based on a *perturbed Hamiltonian approach* [17, 18]<sup>5</sup>. This method offers the possibility of a direct calculation of the free energy. One considers a perturbed Hamiltonian:

$$\beta H' = \beta H + \alpha \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{0,i})^2, \quad (3)$$

where  $H$  is the original Hamiltonian,  $\alpha$  is the strength of the perturbation and  $\mathbf{r}_0 \equiv \{\mathbf{r}_{0,i}\}$  is an equilibrium configuration of the unperturbed system. The free energies  $F(\alpha)$  of two systems with different  $\alpha$  values ( $\alpha_\infty$  and  $\alpha_0$ ) are related by

$$\beta F(\alpha_\infty) = \beta F(\alpha_0) + \int_{\alpha_0}^{\alpha_\infty} d\alpha' \left\langle \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{0,i})^2 \right\rangle_{\alpha'}, \quad (4)$$

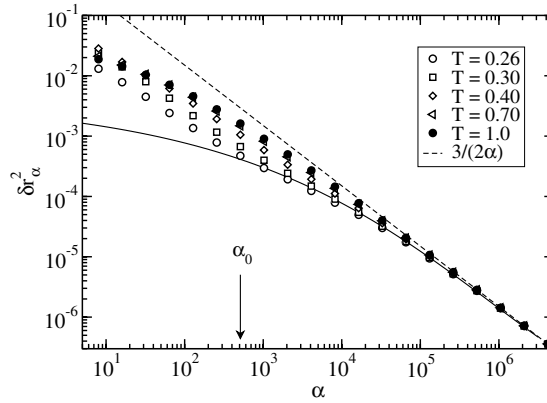
where  $\langle \dots \rangle_{\alpha'}$  is the canonical average for a specified  $\alpha'$ . In the large  $\alpha_\infty \rightarrow \infty$  limit,  $\beta F(\alpha_\infty) = 3N \ln \lambda + \beta E_0 + \frac{3N}{2} \ln(\alpha_\infty/\pi)$ , where  $E_0$  is the potential energy of the reference configuration  $\mathbf{r}_0$  and  $\lambda$  is the thermal de Broglie wavelength  $\lambda = (2\pi\beta\hbar^2/m)^{1/2}$ . If a small  $\alpha_0$  value can be chosen in such a way that the perturbed system is equivalent to the original system, but constrained to explore only the phase space of one state,  $\int_{\alpha_0}^{\alpha_\infty} d\alpha' \langle \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{0,i})^2 \rangle_{\alpha'}$  allows us to evaluate the vibrational free energy. Indeed, writing the free energy as a sum of a potential energy term and of an entropic term,  $\beta F(\alpha_0) = \beta E_0 + 3N/2 - S_{\text{vib}}$ , the following expression for the vibrational entropy is derived:

$$S_{\text{vib}}^{(2)}(T) = \int_{\alpha_0}^{\alpha_\infty} d\alpha' \left\langle \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{0,i})^2 \right\rangle_{\alpha'} - \frac{3N}{2} \ln \left( \frac{\alpha_\infty \lambda^2}{\pi e} \right), \quad (5)$$

where  $e$  is the Neper number. We use isothermal molecular dynamics with Hamiltonian  $H'$  to calculate  $\langle (\mathbf{r} - \mathbf{r}_0)^2 \rangle_\alpha$  at different  $\alpha$  and  $T$ . We perform averages over 20 different  $\mathbf{r}_0$ , chosen from equilibrated configurations with an unperturbed Hamiltonian  $H$  at temperature  $T$ . Figure 3 shows  $\delta r_\alpha^2 = N^{-1} \langle \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{0,i})^2 \rangle_\alpha$  as a function of  $\alpha$  for different  $T$ . The dashed line is the ( $T$  independent) high  $\alpha$  limit,  $3/(2\alpha)$ . As discussed above, one has to choose an  $\alpha_0$  value in equation (5) in such a way that the system remains trapped in a given local state. While at high temperature the data are smooth and the values of  $\delta r_\alpha^2$  remain well below the mean square displacement plateau value (about  $2 \times 10^{-2}$ ), at low  $T$  the behaviour is quite different: starting from high  $\alpha$ , we observe first an approach to a small value  $2 \times 10^{-3}$  (corresponding to more or less the same behaviour in the mean square displacement, even if less pronounced—see figure 1) and then a departure from it at smaller values of  $\alpha$ . We interpret the former value as indicative of the vibrational motion inside the state. The full curve in figure 3 is a fitting function for the large  $\alpha$  values for the  $T = 0.26$  case<sup>6</sup>, used to

<sup>5</sup> We note that, due to the presence of some misprints in [18], our formulae do not match those reported in that paper.

<sup>6</sup> The fitting function is  $\ln \delta r_\alpha^2 = A \exp[-(\alpha/\alpha^*)^\beta]$ , where  $A$ ,  $\alpha^*$  and  $\beta$  are free parameters and the fit is performed in the range  $10^3 < \alpha < 10^6$ .



**Figure 3.** The quantity  $\delta r_\alpha^2 = N^{-1} \langle \sum_{i=1}^N (\mathbf{r}_i - \mathbf{r}_{0,i})^2 \rangle_\alpha$  at different  $T$  as a function of  $\alpha$ . The dashed line is the high  $\alpha$  limit  $3/(2\alpha)$ . The full curve is a fit of the  $T = 0.26$  data (see the footnote in the text). The arrow indicates the chosen value  $\alpha_0 = 5 \times 10^2$ .

define the phase space of a state. We have chosen  $\alpha_0 = 5 \times 10^2$  in equation (5) (see the arrow in figure 3), since this is the smallest  $\alpha$  value for which the mean square displacement of the system lies on the fitting line. Although this is a feature only of the low  $T$  data, we have chosen the same  $\alpha_0$  for the estimation of  $S_{\text{vib}}^{(2)}$  for all  $T$ , in order to obtain a coherent definition of it. The  $\alpha_\infty$  has been fixed at  $2 \times 10^6$ , where  $\delta r_\alpha^2$  has reached the asymptotic behaviour (dashed line in figure 3). Figure 2(c) shows the  $T$  dependence of the configurational entropy per particle  $S_{\text{conf}}^{(2)}/N$ , calculated as the difference between the total entropy and  $S_{\text{vib}}^{(2)}$ .<sup>7</sup> Again one observes a peak, located at about  $T_{\text{max}}^{(2)} \simeq 0.5$ , close to that of the diffusivity. Note that using the same value of  $\alpha_0$  for all the  $T$  introduces an underestimation of  $S_{\text{vib}}^{(2)}$ , more pronounced for the high  $T$  data. This could have the effect of moving the peak to a lower  $T$  value, approaching the peak value of the diffusivity.

We note that there is a quantitative difference between the values of  $S_{\text{conf}}$  obtained by the two approaches. Underestimation and/or overestimation of  $S_{\text{conf}}$  are indeed present in both methods. Looking at the details, one recognizes that in the PEL method, these can be ascribed to the harmonic approximation (which worsens on increasing  $T$ ); for the perturbed Hamiltonian method, these can arise from the choice of  $\alpha_0$  and/or the choice of the function for extrapolating to low  $\alpha$  values. However, the qualitative agreement between the  $T$  behaviours is a strong argument as regards the robustness of the result: the configurational entropy and diffusivity show a maximum at the same temperature. Our work strongly supports the possibility that in short range colloidal systems the diffusivity maximum is related to a maximum in the number of states explored by the system.

We thank G Parisi for useful discussions and for suggesting the use of the perturbed Hamiltonian method to calculate the vibrational entropy.

<sup>7</sup> A constant  $c = 0.4$  has been added to the  $S_{\text{vib}}^{(2)}$ , to estimate the error arising from the finite value of  $\alpha_0$  used. The value of  $c$  has been calculated as the integral of the extrapolated line for  $\langle (r - r_0)^2 \rangle$  at  $T = 0.26$  (see the full curve in figure 3) from 0 to  $\alpha_0$ . This gives a correct estimation of  $S_{\text{vib}}^{(2)}$  for  $T = 0.26$ , and represents a lower bound for the  $S_{\text{vib}}^{(2)}$  at higher  $T$ .

## References

- [1] Frenkel D 2002 *Science* **296** 65
- [2] Anderson V and Lekkerkerker H 2002 *Nature* **416** 811
- [3] Pusey P N and van Megen W 1986 *Nature* **320** 340
- [4] Alder B J and Wainwright T E 1957 *J. Chem. Phys.* **27** 1208
- [5] Gast A P, Russel W and Hall C 1983 *J. Colloid Interface Sci.* **96** 1977
- [6] Meijer E and Frenkel D 1991 *Phys. Rev. Lett.* **67** 1110
- [7] Mallamace F, Gambadauro P, Micali N, Tartaglia P, Liao C and Chen S H 2000 *Phys. Rev. Lett.* **84** 5431
- [8] Pham K N, Puertas A M, Bergholtz J, Egelhaaf S U, Moussaïd A, Pusey P N, Schofield A B, Cates M E, Fuchs M and Poon W C K 2002 *Science* **296** 104  
Pham K N, Egelhaaf S U, Pusey P N and Poon W C K 2004 *Phys. Rev. E* **69** 011503
- [9] Chen S H, Chen W R and Mallamace F 2003 *Science* **300** 619  
Chen S H, Chen W R and Mallamace F 2003 *Phys. Rev. E* **68** 041402
- [10] Eckert T and Bartsch E 2002 *Phys. Rev. Lett.* **89** 125701  
Eckert T and Bartsch E 2003 *Faraday Discuss.* **123** 51
- [11] Puertas A M, Fuchs M and Cates M E 2002 *Phys. Rev. Lett.* **88** 098301  
Puertas A M, Fuchs M and Cates M E 2002 *Phys. Rev. E* **67** 031406
- [12] Zaccarelli E, Foffi G, Dawson K A, Buldyrev S V, Sciortino F and Tartaglia P 2002 *Phys. Rev. E* **66** 041402
- [13] Sciortino F 2002 *Nat. Mater.* **1** 145
- [14] Dawson K, Foffi G, Fuchs M, Götze W, Sciortino F, Sperl M, Tartaglia P, Voigtmann T and Zaccarelli E 2001 *Phys. Rev. E* **63** 011401
- [15] Scala A, Starr F W, La Nave E, Sciortino F and Stanley H E 2000 *Nature* **406** 166
- [16] Stillinger F H and Weber T A 1982 *Phys. Rev. A* **25** 978  
Stillinger F and Weber T A 1984 *Science* **225** 983
- [17] Frenkel D and Smit B 2001 *Understanding Molecular Simulation* 2nd edn (London: Academic)
- [18] Coluzzi B, Mézard M, Parisi G and Verrocchio P 1999 *J. Chem. Phys.* **111** 9039
- [19] Vliegthart G A, Lodge J and Lekkerkerker H N W 1999 *Physica A* **263** 378
- [20] Cavagna A, Giardina I and Parisi G 1998 *Phys. Rev. B* **57** 11251
- [21] La Nave E, Sciortino F, Tartaglia P, De Michele C and Mossa S 2003 *J. Phys.: Condens. Matter* **15** S1085