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LETTER TO THE EDITOR

Dynamics of supercooled liquids interacting with a repulsive Yukawa potential

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Abstract. We report molecular dynamics results for the single-particle diffusion in liquids where the interparticle interaction is a repulsive Yukawa potential $U(r) \propto \exp(-\kappa r)/r$. In supercooled liquids, atypical subdiffusive behaviour is observed in a range of times intermediate between the early-time ballistic and late-time diffusive regimes. This subdiffusive regime is evidence for strongly correlated motion and increases in size as the glass transition is approached. Introduction of a viscous damping term to the equations of motion does not destroy this effect.

The study of the dynamic properties of correlated liquids is one of the classical problems of statistical mechanics. Although there exists a large amount of literature on the subject, there are still many unanswered questions. One such question is whether one should visualise a correlated liquid via Kirkwood's picture of an atom in a cage formed by its nearest neighbours [1]. This concept is often used in describing reaction rate kinetics [2] and the liquid-glass transition [3]. Simulations studying the motion of individual particles or pairs of particles without configuration averaging [4]§, provide some evidence in support for Kirkwood's picture of a cage structure. However, previous results for the single-particle diffusion in the liquid phase show no evidence of a correlated cage. The diffusion changes directly from ballistic, $r \propto t$, for very short times t to diffusive, $r^2 \propto t$, for long times. Here we present results of simulations on supercooled liquids interacting with a repulsive Yukawa potential which show a clear subdiffusive regime between the ballistic and diffusive regimes (subdiffusive means that r^2 varies weaker than t with time t). This is evidence for strongly correlated motion. The subdiffusive regime increases in size as the glass transition is approached.

In this letter, we present the first analysis of the dynamical properties of strongly correlated particles interacting with a purely repulsive Yukawa potential. This potential is known [5] to describe the interactions in dilute charge-stabilised colloids, such as sulphonated Latex spheres in water [6]. The sulphonate ions dissociate in water and

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§ Jacucci and Rahman found that F^- ions diffuse by jumps between cages formed by Ca^{2+} ions in the superionic conductor CaF_2 . The F^- ions were fluid whereas the Ca^{2+} formed an FCC lattice. Jacucci (unpublished) studied the motion of pairs of atoms in a Lennard-Jones fluid. No sign of the microscopic jump diffusion was observed in $\langle r^2(t) \rangle$ in either case.

the charged spheres then repel one another. Calculations [5] based on a spherical Wigner-Seitz cell show that the interaction is described very well by a Yukawa potential with a renormalised charge Q^* . The potential is

$$U(r) = U_0 \exp(-\kappa r)/r \quad (1)$$

where

$$U_0 = \frac{Q^{*2}}{\epsilon} \exp(2\kappa r_a)/(1 + \kappa r_a)^{-2}. \quad (2)$$

Here κ is the inverse screening length, ϵ is the dielectric constant of the medium and r_a is the radius of the spheres. In the simulation, the value of κ is fixed, independent of temperature[†]. ϵ is chosen to equal its value in water at 300 K, $\epsilon = 78$. The remaining parameters are chosen to agree with experiments on Latex spheres. The typical concentration n for such spheres is quite low, only 1–3% volume density. We chose $n = 2.3 \times 10^{13} \text{ cm}^{-3}$, which gives a lattice spacing of $a_s = n^{-1/3} = 3516 \text{ \AA}$. The mass of each sphere is $m = 3.95 \times 10^{-16} \text{ g}$ and $r_a = 455 \text{ \AA}$.

The phase diagram of the Yukawa system as a function of T/U_0 and $\lambda = \kappa a_s$ was calculated recently using molecular dynamics simulations [7]. Although the relevant dynamics of such spheres are purely Brownian, because they are immersed in water, we will first analyse the case in which the dynamics are non-dissipative (undamped). As it turns out, for this case the supercooled liquid exhibits very interesting time dependence. We used standard microcanonical molecular dynamics simulations at constant volume for $N = 500$ particles. The time step was $4 \times 10^{-8} \text{ s}$, which corresponds to about $\frac{1}{50}$ of the period of the highest frequency vibrational mode. The calculations were performed with a fifth-order predictor–corrector loop and the interaction was truncated at $3a_s$. The run times (100 000 steps) were long enough to ensure relaxation to a representative configuration and (except in one case) to allow determination of the diffusion constant [8]: the particles diffused at least several nearest-neighbour spacings during the runs. Results for the mean square displacement $r^2(t) \equiv \sum_i \langle (r_i(t) - r_i(0))^2 \rangle / N$ were averaged over at least 75 starting configurations, 200 steps apart. No systematic variation in the results with starting time was observed.

Our results for the mean square displacement $\langle r^2(t) \rangle$ against time are shown in figure 1 for $Q^* = 400e$, $\lambda = 3.2$ and $T = 550$ and 320 K. Here e is the electron charge. Comparing these parameters with the phase diagram of [7], we find that $T = 550 \text{ K}$ is above the BCC to liquid melting temperature, while $T = 320 \text{ K}$ is slightly supercooled. Results for the pair correlation function $g(r)$ and static structure factor $S(q)$ confirm this. For $T = 320 \text{ K}$, the height of the first peak in $S(q)$ is slightly above 2.8. According to the Hansen–Verlet [9] rule, melting occurs when the peak is below 2.8. The lower curves, which correspond to the right-hand scale, give the diffusion constant $D_0(t) = r^2(t)/6t$. Comparing the two sets of data, one sees a dramatic decrease in D_0 as T decreases from 550 K to 320 K. Also, the mean square displacement clearly shows a *subdiffusive* regime in figure 1 for $T = 320 \text{ K}$. To our knowledge, such behaviour has not been discussed in the literature before. Near the melting temperature this effect is weak, while at higher T it vanishes completely. At high T , we find the expected

[†] Though $\kappa^2 = 4\pi n e Q^* / \epsilon k_B T$ in the screened Coulomb potential, κ can also be changed by varying the salt concentration of the water. We have fixed κ so that the potential is independent of temperature to facilitate comparison of our results with those from simulations on systems with short-range potentials.

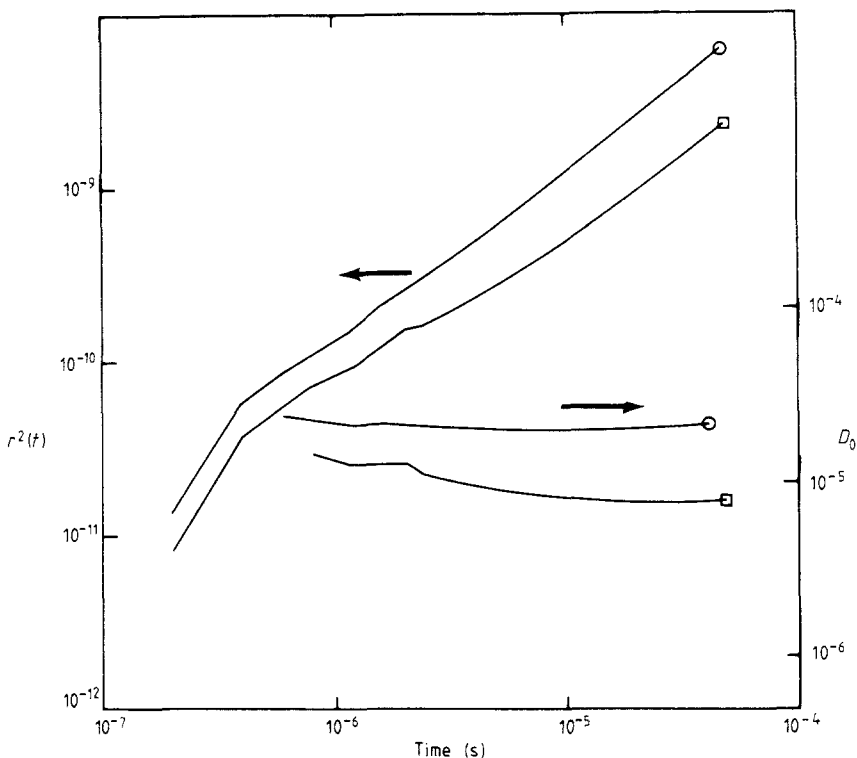


Figure 1. Mean square displacement $r^2(t)$ (in cm^2) and diffusion constant $D_0(t)$ for a monatomic system with $Q^* = 400$ and $\lambda = 3.2$ at 550 K (\circ) and 320 K (\square).

direct crossover from the ballistic $r^2(t) \propto t^2$ regime to the diffusive regime $r^2(t) \propto t$ without an intermediate subdiffusive regime. Since this intermediate regime clearly requires a more detailed investigation, we tried to measure $r^2(t)$ for lower T , but the system crystallised for this value of λ . To overcome this difficulty, we studied a binary mixture of particles, with two different charges Q^* , since the nucleation rate for alloy crystallisation is much slower than for monatomic systems.

We studied a binary mixture of particles of equal size, but of different charge. The system we chose was a 1:2 mixture of charge $Q_1^* = 350e$ and $Q_2^* = 500e$ and $\lambda = 3.4$. In figure 2, results for $g(r)$ are shown for three temperatures, $T = 550, 450$ and 360 K. For $T = 550$ K the system is a liquid. The heights of the first peak in $g(r)$ and $S(q)$ indicate that $T = 450$ K is very near the melting temperature and that for $T = 360$ K the system is supercooled. Only for the lowest T does any structure begin to develop in the second peak of $g(r)$. None of our runs for the binary alloy crystallised. In figure 3, we present our results for $r^2(t)$ and $D_0(t)$. For $T = 550$ K, the crossover from ballistic to diffusive motion was very rapid: $r^2(t) \propto t$ and D_0 is constant for more than two decades. In contrast, the results for $T = 450$ K, figure 3(b), show a clear subdiffusive regime, which is much more pronounced than in the monodisperse case, figure 1. This subdiffusive regime extends over almost two decades of time before the diffusive regime sets in. The value of $r^2(t)$ above which D_0 is constant is of approximately the same magnitude as in the monodisperse case. For $T = 360$ K, only the subdiffusive regime was seen within our averaging time. However, the particles moved several nearest-neighbour distances over the entire run. This indicates that the system is still a

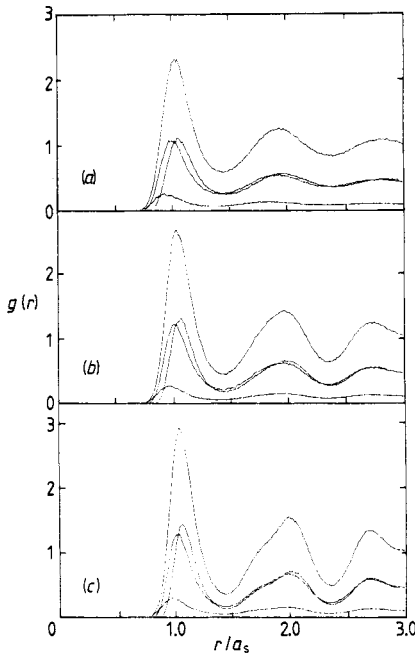


Figure 2. Pair correlation function $g(r)$ for the alloy (a) $T = 550$ K, (b) 450 K and (c) 360 K. The upper curve is the total $g(r)$ for all particles. The other curves, in decreasing order, are $g_{22}(r)$, $g_{12}(r)$ and $g_{11}(r)$, where $Q_1^* = 350$ and $Q_2^* = 500$. The partial pair correlation functions are normalised so that their sum equals $g(r)$.

supercooled liquid rather than a glass. Our statistics at long times are not sufficient to give an accurate diffusion constant for this case.

These observations are a clear indication of strongly correlated motion in a liquid. There are two distinct timescales in the problem. The first is the time for the velocity autocorrelation function to cross zero. Roughly speaking, this is the Einstein frequency, which describes the local motion of individual particles in a static environment. From our simulations, we find that there is a second timescale that describes the collective motion of the particles, which can become very much larger than the first as the glass transition is approached. This is the time for the particle to escape its local environment. As seen in figure 3(b), these two times can be well separated. The concept of a cage has also been invoked to explain why the velocity autocorrelation function (VAC) becomes negative. We observe oscillations in the VAC at more than twice the melting temperature where there is no evidence of subdiffusive behaviour. These oscillations require only that correlations exist on a timescale comparable to the inverse Einstein frequency. Our results indicate correlations over times which are orders of magnitude larger. As is well known from polymer theory [10] and from studies of anomalous diffusion in the one-dimensional lattice gas [11], the existence of two timescales can produce an intermediate subdiffusive regime for the mean square displacement of a single particle. For the Rouse model of an ideal polymer (bead spring in a viscous solvent) this results in an intermediate power law regime $r^2(t) \propto t^{1/2}$. Similar behaviour occurs for the 1D lattice gas [10]. In both these cases the subdiffusive intermediate time regime is a consequence of strong correlations. The situation in liquids is not as simple as in the Rouse case for polymers where the nearest neighbours are connected

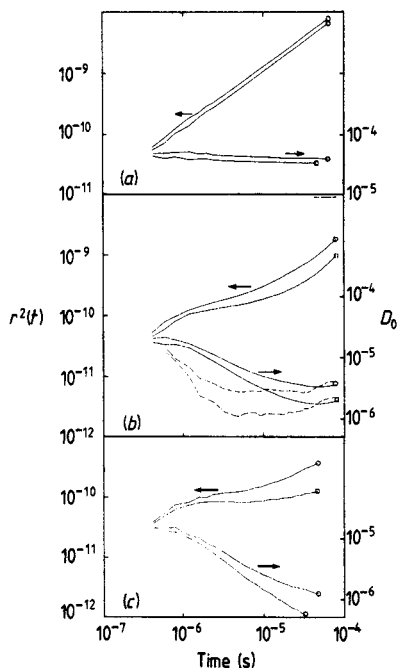


Figure 3. $r^2(t)$ (in cm^2) and $D_0(t)$ for the alloys shown in figure 2. (a) $T = 550$ K, (b) 450 K and (c) 360 K. Circles are for $Q_1^* = 350$ and squares for $Q_2^* = 500$. The broken curve in (b) is the differential diffusion constant $D_{0,d}(t)$.

to the same chain. At present we do not know whether a single universal power law should describe the intermediate regime in the Yukawa systems as it does in the other two examples.

We have also measured the differential diffusion constant

$$D_{0,d} = \frac{1}{6} \frac{\partial}{\partial t} r^2(t) \quad (3)$$

which is included in figure 3(b) for $T = 450$ K. As expected, this quantity approaches its asymptotic value more rapidly than $D_0(t)$. However, the apparent minimum is unusual and cannot be explained by the analogy to the Rouse model for polymers.

So far, we have only discussed the motion of undamped particles. However, to properly describe the experimental situation, we must include viscous damping since the colloidal suspensions are in water. In order to check the influence of stochastic noise on our results, we included a viscous damping term and white noise term in the equation of motion:

$$m \frac{d^2 \mathbf{r}}{dt^2} = -\nabla U - \Gamma \frac{d\mathbf{r}}{dt} + \mathbf{W}_i(t) \quad (4)$$

where Γ is a bead friction and $\mathbf{W}_i(t)$ a Gaussian white noise term which describes the random force acting on the particles from the heat bath. Results for $T = 320$ K for a monodisperse system are shown in figure 4 for $\Gamma/m = 0, 5 \times 10^5$ and $1.5 \times 10^6 \text{ s}^{-1}$. For these values of the friction Γ , the intermediate subdiffusive regime is still visible. Non-zero Γ seems to actually enhance the subdiffusive regime for the values of Γ

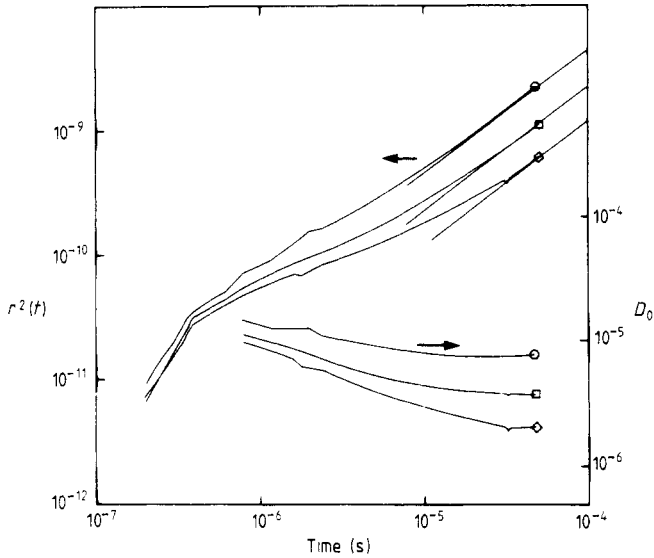


Figure 4. $\langle r^2(t) \rangle$ and $D_0(t)$ for a monatomic system for $Q^* = 400$, $T = 320$ K and three values of the bead friction $\Gamma/m = 0$ (\circ), 5×10^5 (\square) and 1.5×10^6 s $^{-1}$ (\diamond). Straight lines represent asymptotic diffusion.

studied. From these results, we think that it may be possible to observe this intermediate subdiffusive region experimentally by light scattering or tracer diffusion experiments of colloidal alloys.

To conclude, we have presented evidence of an intermediate subdiffusive regime in the motion of individual particles in supercooled liquids, which increases in size as the glass transition is approached. This regime is the result of strongly correlated motion. The Yukawa system differs from other systems which have been studied previously in that the range of interaction is long and the melting occurs for quite low density. We believe that, while this subdiffusive regime should be observable in other supercooled liquids, the long-range repulsive nature of the Yukawa interaction enhances the size of the effect. Preliminary results [8] indicate that as λ increases the size of the subdiffusive regime decreases. Simulations are underway to determine which of these factors is important in producing this novel time dependence in $\langle r^2(t) \rangle$.

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Note added. After this letter was finished we learned of some work by Y Hiwatari, B Bernu and J P Hansen (poster at *StatPhys 16*) who observe a similar effect in repulsive Lennard-Jones systems. The size of the effect they observed is comparable to our figure 1.

References

- [1] Kirkwood J G 1950 *J. Chem. Phys.* **18** 380
- [2] Franck J and Rabinowitch E 1924 *Trans. Faraday Soc.* **30** 120
Kapral R 1981 *Adv. Chem. Phys.* **48** 71
- [3] Grest G S and Cohen M H 1981 *Adv. Chem. Phys.* **48** 455

- [4] Jacucci G and Rahman A 1976 *J. Chem. Phys.* **69** 4117
- [5] Alexander S, Chaikin P M, Grant P, Morales G J, Pincus P and Hone D 1984 *J. Chem. Phys.* **80** 5776
- [6] Pieranski P 1983 *Contemp. Phys.* **24** 25
van Meegen W and Snook I 1984 *Adv. Colloid Interface Sci.* **21** 119
Chaikin P M, diMeglio J M, Dozier W D, Lindsay H M and Weitz D A to be published
- [7] Kremer K, Robbins M O and Grest G S 1986 *Phys. Rev. Lett.* **57** 2694
- [8] Angell C A *et al* 1981 *Adv. Chem. Phys.* **48** 397
- [9] Hansen J P and Verlet L 1969 *Phys. Rev.* **184** 150
- [10] Rouse P E 1953 *J. Chem. Phys.* **21** 1273
de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
- [11] Alexander S and Pincus P 1978 *Phys. Rev. B* **18** 2011