



ELSEVIER

Journal of Non-Crystalline Solids 307–310 (2002) 215–224

JOURNAL OF
NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrysol

Theory of non-linear susceptibility and correlation length in glasses and liquids

Claudio Donati ^a, Silvio Franz ^{b,*}, Sharon C. Glotzer ^{a,c,*},¹, Giorgio Parisi ^d^a Center for Theoretical and Computational Material Science, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA^b The Abdus Salam ICTP, Strada Costiera 11, P.O. Box 563, 34100 Trieste, Italy^c Departments of Chemical Engineering and Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA^d Università di Roma 'La Sapienza' P.le A. Moro 2, 00185 Rome, Italy

Abstract

Within the framework of the effective potential theory of the structural glass transition, we calculate for the p -spin model and for a hard sphere liquid in the hypernetted chain approximation a static non-linear susceptibility related to a four-point density correlation function, and show that it diverges in mean field with exponent $\gamma = 1/2$ as the critical temperature T_c is approached from below. When T_c is approached from above, we calculate for the p -spin model a time dependent non-linear susceptibility and show that there is a characteristic time where this susceptibility has a maximum, and that this time grows with decreasing T . This susceptibility diverges as T_c is approached from above, and has key features in common with a generalized susceptibility related to particle displacements, previously introduced to measure correlated particle motion in simulations of glass-forming liquids.

© 2002 Elsevier Science B.V. All rights reserved.

PACS: 64.70.Pf; 05.20.-y

1. Introduction

Tempted by the possibility of treating the glass transition within the framework of conventional critical phenomena, researchers have long searched for evidence of a static correlation length that becomes large as the glass transition is ap-

proached. Scattering experiments have failed to find a growing length associated with density fluctuations [1], although experiments on the vanishing of the isotope effect in metallic glasses and undercooled liquids suggest the presence of a large correlation length [2–4]. Numerical studies of liquids above and below the glass transition have identified a dynamical length associated with the range over which particle motions are correlated [5–13]. By introducing a ‘displacement–displacement’ correlation function $g_u(r, t)$ and generalized susceptibility $\chi_u(t)$, Refs. [7,8] showed in two different model liquids that this length – which depends on the time window of observation – grows

* Corresponding authors.

E-mail addresses: franz@ictp.trieste.it (S. Franz), sglotzer@umich.edu (S.C. Glotzer).

¹ Present address: Departments of Chemical Engineering and Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA.

with decreasing temperature T as the mode coupling temperature T_c is approached from above, despite the fact that density and composition correlations remain short-ranged [14]. Calculations of the average size of clusters of particles that move together within locally dynamically homogeneous regions give another measure of a characteristic length [10,11]. Recent work has shown that this length – like the length scale associated with the displacement-displacement correlation function – is time dependent, and maximal at a time that scales with $T - T_c^+$ like the β -relaxation time [11]. Experiments on colloidal liquids and glasses in two [15] and three [16] dimensions have provided confirmation of key aspects of the dynamical heterogeneity observed in simulations [17–20].

The aim of this paper is to provide an interpretation of simulation and experimental findings of dynamical heterogeneity within a suitable theoretical framework. We calculate within the *effective potential theory* a susceptibility χ_4 associated with a four-point density correlation function. A time-dependent, four-point density correlation function was first studied in a supercooled liquid in Ref. [21]. In that paper, no growing correlations were found, possibly because some of the data analyzed were in the aging regime where more complex analysis should be done. Within the approximations we use, we show that below T_c , χ_4 diverges with exponent $1/2$ as $T \rightarrow T_c^-$. We show that above T_c , χ_4 is time-dependent and in certain ways resembles the susceptibility calculated in [7,8], and that $\chi_4(t)$ has a maximum which diverges in mean field as $T \rightarrow T_c^+$. We argue that (1) the diverging correlation length implied by the diverging susceptibility is associated with incipient ergodicity breaking at T_c , and (2) this length underlies the growing range of dynamical heterogeneity measured in Refs. [7,8,16]. Finally, we test our theoretical predictions above T_c using data from molecular dynamics simulations of a model glass-forming liquid.

We use two different theoretical approaches depending on T . In the low T regime ($T < T_c$), we calculate a static, non-linear susceptibility using the effective potential theory [22], and in the high T regime ($T > T_c$), we calculate a dynamic, non-linear susceptibility in a dynamical approach. The

low- T calculations are performed both for a hard-sphere liquid in the hypernetted chain (HNC) approximation [23] and for the spherical p -spin model [24]; the dynamical calculations are performed only for the spherical p -spin model. This is the simplest model that (i) allows both static and dynamic quantities to be calculated exactly, and (ii) exhibits several key features common to liquids in and close to their glassy regime [23,25,26]. For example, the high- T dynamics of the p -spin model are described exactly by the ideal mode coupling equations [27,28], which capture qualitatively, and for some quantities quantitatively, the separation of time scales between local ‘rattling’ and long-time structural relaxation.

An unrealistic feature of the model (and of ideal mode coupling theory) is the presence of a sharp dynamical transition temperature T_c . Below T_c , large-scale structural rearrangements are arrested, and phase space splits into individual ergodic components that remain stable at all temperatures. This stability is a consequence of the mean field nature of the theory, which in p -spin and similar models is due to the long-range interactions between the various degrees of freedom.

An assumption made in mode coupling theory, and often taken in mean field theories of glasses, is that in real systems the temperature T_c corresponds to a change of the dominant relaxation mechanisms [29]. According to this interpretation, what are seen as ergodic components in mean field would actually be metastable states, or *dynamical quasi-states* with a long but finite escape time of the order of the α -relaxation time τ_α . Our basic observation is that within the described theoretical framework, the quasi-states correspond to highly correlated regions of configuration space; that is, configurations belonging to the same quasi-state would appear to be highly correlated. On the other hand, configurations belonging to distant quasi-states, that is, separated by large times $t \gg \tau_\alpha$, are largely uncorrelated.

We argue, then, that a dynamical correlation length and susceptibility characterizing dynamical heterogeneity can be estimated by the corresponding quantities within a quasi-state. On the other hand, the static limit of the same quantities, i.e., the value reached for times much larger than the

lifetime of the quasi-states, correspond to maximally distant quasi-states. This would predict maximal fluctuations and heterogeneity on a time scale of the order of τ_α .

In this interpretative framework we can use a static approach to compute the properties of these metastable states below T_c . We can also obtain information above T_c directly in a dynamical approach, where mean field theory predicts a finite escape time from the metastable states, which diverges on approaching T_c . The divergence of a *static* susceptibility inside the metastable state when we approach T_c from below is directly related to the divergence of the corresponding *dynamical* susceptibility when we approach T_c from above. As is typical for mean field theories, which neglect spatial fluctuations, a diverging correlation length is deduced from the diverging susceptibility. A slowly growing correlation length has been directly measured in simulations from the time dependent four-point density correlation function described below [31].

2. Dynamical quasi-states and effective potential theory

A basic fact of glassy phenomenology is the existence of two widely separated time scales. In supercooled liquids, time-dependent correlation functions display a characteristic two-step shape corresponding to local atomic motion on short time scales, and structural relaxation on long time scales. These two processes, and thus time scales, become more and more separated as the temperature is lowered. Under these conditions it is possible to decompose the dynamical variables defining the microstate of the system into a fast and a slow part. The fast variable can equilibrate almost completely before the slow variable changes appreciably. This feature was used in Ref. [32] to define dynamical quasi-states as regions of configuration space where a glassy system almost equilibrates before moving away.

We begin by defining the microscopic state X of a supercooled liquid or a glass in terms of the local time-dependent density field $\rho_X(x, t)$. The correlator $\langle \rho(x, t) \rho(y, s) \rangle$ displays a plateau whose char-

acteristic scale \bar{t} can be used to define a slow variable,

$$\rho_{\text{slow}}(x, t) = \frac{1}{\bar{t}} \int_t^{t+\bar{t}} ds \rho(x, s) \quad (1)$$

and a fast variable,

$$\delta\rho(x, t) = \rho(x, t) - \rho_{\text{slow}}(x, t). \quad (2)$$

If the fast degrees of freedom thermalize before the slow ones can significantly vary, the configurations inside a quasi-state are sampled with a constrained Boltzmann–Gibbs weight,

$$\mu_t[\delta\rho] = \exp\left(-\beta H[X] + \int dx h_t(x) \rho_X(x)\right), \quad (3)$$

where the ‘external field’ $h_t(x)$ is chosen in such a way that the consistency relation $\langle \rho(x) \rangle_{\mu_t} = \rho_{\text{slow}}(x, t)$ is verified. In supercooled liquids and glasses, since the configurational entropy is extensive, the single quasi-states have vanishing weight in the full equilibrium probability. We stress that the description in terms of quasi-states is valid both above (and close to) T_c and below. We will argue that the dynamical correlations observed in the simulations and the experiments are directly related to the growth of correlations *inside* quasi-states at the mode coupling temperature T_c , while the static correlations, which are dominated by configurations belonging to different quasi-states, remain short ranged.

Given any local observable $A(x)$, its Boltzmann average can be decomposed as

$$\langle A(x) \rangle_{\text{Boltzmann}} = \sum_{\alpha} w_{\alpha} \langle A(x) \rangle_{\alpha}, \quad (4)$$

where the index α runs over all the $e^{N\Sigma}$ quasi-states. The weights w_{α} of the different states will all be of the same order $w_{\alpha} \approx \exp(-N \Sigma(T))$. In the following we will be interested to compute spatial averages (correlation functions) among local observables, $\int dx \langle A(x) \rangle \langle B(x+y) \rangle$. If by $\langle \cdot \rangle$ we mean Boltzmann average, we can expand each of the two averages according to (4), and find that

$$\begin{aligned} & \int dx \langle A(x) \rangle \langle B(x+y) \rangle \\ &= \int dx \sum_{\alpha, \beta} w_{\alpha} w_{\beta} \langle A(x) \rangle_{\alpha} \langle B(x+y) \rangle_{\beta}, \end{aligned} \quad (5)$$

which, due to the fact that the number of ergodic components is exponentially large, is dominated by the terms in the double sum with $\alpha \neq \beta$. Instead, our main interest will be to compute averages of the kind $\int dx \sum_{\alpha} w_{\alpha} \langle A(x) \rangle_{\alpha} \langle B(x+y) \rangle_{\alpha}$; i.e., to compute correlation functions within the same quasi-state.

The effective potential theory provides a static prescription to compute averages in quasi-states. Here we describe the essential elements of the theory (a complete description can be found in [25]). The theory is formulated using a measure of the similarity or ‘overlap’ q between two configurations X and Y as an order parameter to detect vitrification. Different definitions of q can be used in different systems and the main results of the theory do not depend on the definition adopted. In the case of simple liquids with N particles at fixed density [25,33], one can define

$$\begin{aligned} q(X, Y) &= \frac{1}{N} \sum_{i=1}^N w(x_i - y_i) \\ &= \frac{1}{N} \int dx dy w(x-y) \rho_X(x) \rho_Y(y), \end{aligned} \quad (6)$$

where $X = \{x_1, \dots, x_N\}$, $Y = \{y_1, \dots, y_N\}$, and $\rho_Z(x) = \sum_{i=1}^N \delta(x - z_i)$ is the microscopic density corresponding to the configuration $Z = X, Y$. Here $w(r)$ is chosen to be a smooth, continuous, short-range function close to one for $r < ar_0$ and close to zero otherwise (r_0 is the radius of a particle). The value of $a < 1$ is arbitrary, and $a = 0.3$ is a good compromise for an overlap insensitive to small thermal fluctuations [25,31,33].

The effective potential $V(q)$, which is a constrained free energy, is constructed by choosing a fixed reference equilibrium configuration Y at temperature T , and calculating the free energy of a configuration X that has an overlap q with Y :

$$\begin{aligned} V(q) &= -\frac{T}{N} \log \int dX \\ &\quad \exp(-\beta H(X)) \delta(q(X, Y) - q). \end{aligned} \quad (7)$$

This free energy corresponds to weighting the configurations with a constrained canonical probability,

$$\mu(X|Y) = \frac{1}{Z_q(Y)} \exp(-\beta H(X)) \delta(q(X, Y) - q), \quad (8)$$

where the constrained partition function is

$$Z_q(Y) = \int dX \exp(-\beta H(X)) \delta(q(X, Y) - q). \quad (9)$$

Since Y is, by hypothesis, an equilibrium configuration, it will belong to some quasi-state α . Therefore, if we choose q as the typical overlap between configurations in this quasi-state (i.e., the Edwards–Anderson order parameter q_{EA}), such that with probability one almost all configurations have the same overlap, we will be able to compute the quasi-state averages as follows. Given two observables $A(X)$ and $B(X)$, we can write

$$\begin{aligned} \sum_{\alpha} w_{\alpha} \langle A \rangle_{\alpha} \langle B \rangle_{\alpha} &= \int dY \frac{e^{\beta H(Y)}}{Z} A(Y) \\ &\quad \times \int dX \frac{e^{-\beta H(X)} \delta(q(X, Y) - q)}{Z_q(Y)} B(X). \end{aligned} \quad (10)$$

Notice that if, on the other hand, in Eq. (8) we would choose q as the typical overlap among different quasi-states, the constraint would be irrelevant and we would obtain the Boltzmann average (5).

The typical mean-field shape of $V(q)$ for a system undergoing vitrification is shown in Fig. 1 for several values of T . The shape of $V(q)$ allows one to distinguish the liquid from the glassy phase since the presence of a single or multiple minima indicates either ergodicity or broken ergodicity, respectively. At high T , the system is ergodic and $V(q)$ is convex, with a single minimum at a small value of the overlap q between any two configurations chosen with the Boltzmann weight. Upon lowering T , the curvature changes sign, and at T_c , $V(q)$ develops a secondary minimum at a higher value of q . This signals breaking of ergodicity: at T_c the configuration space become disconnected into an exponentially large number of ‘ergodic components’ $\mathcal{N} \sim \exp(N \sum)$, each carrying vanishing weight in the Boltzmann distribution [25]. As discussed in detail in [22], physical quantities calculated in the primary minimum represent

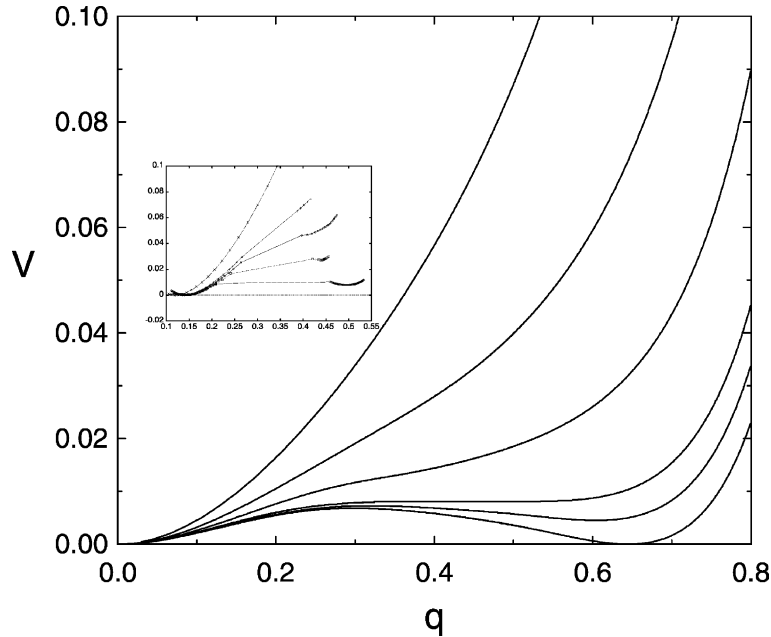


Fig. 1. The effective potential $V(q)$ for the p -spin model, for several values of T . At high T the potential is everywhere convex, and at low T , $V(q)$ exhibits two minima. In the inset we show the effective potential for a hard sphere fluid in the HNC approximation for several values of the density ($\rho = 1.0, 1.14, 1.17, 1.19, 1.20$). Here the potential is calculated around the high- and in the low- q minima, and the lines joining the two minima are guides to the eye [25].

averages computed with the full Boltzmann weight, while the same quantities calculated in the secondary minimum represent averages computed only within a single ergodic component. The overlap in the secondary minimum is the typical overlap between configurations in the same ergodic components.

Notice that the shape of the effective potential resembles that of a free energy as a function of the order parameter for a conventional mean-field system undergoing a first-order phase transition, with the temperature T_c corresponding to the spinodal temperature. In conventional theories, the secondary minimum describes metastable phases that are unstable against nucleation of the dominating phase while the spinodal point describes the limit of stability of the phase.

Here the situation is analogous, except that there is not a unique metastable phase, but instead exponentially many equally likely quasi-states that are visited during the dynamical evolution of the system. These states are mechanically stable below T_c where activated jumps of local energy barriers

are responsible for the relaxation, while they are mechanically unstable above T_c . For that reason, as seen in the correlation function, the equilibrium dynamics of a supercooled liquid bear some resemblance to the decay of a metastable state, or to spinodal decomposition in systems with first order phase transitions. We show here that, as it happens for metastable states in ordinary systems, the loss or gain of correlation on approaching T_c from below or above corresponds to increasing correlations within the quasi-states.

To calculate physical quantities in the effective potential formalism, it is useful to introduce the Legendre transform of $V(q)$: $\Gamma(\epsilon) = \min_q V(q) - \epsilon q$, where ϵ is a ‘field’ conjugate to q , and corresponds to a coupling between configurations. For example, the average overlap $\langle q \rangle$ can be computed as $\langle q \rangle = \frac{\partial \Gamma}{\partial \epsilon} \Big|_{\epsilon \rightarrow 0}$, where $\langle \cdot \rangle$ represents either of the two types of averages. The overlap susceptibility is

$$\chi_4 = \frac{\partial \langle q \rangle}{\partial \epsilon} \Big|_{\epsilon \rightarrow 0} = \beta N (\langle q^2 \rangle - \langle q \rangle^2), \quad (11)$$

where $q \equiv q(X, Y)$. Inserting Eq. (6) in Eq. (11) allows us to rewrite χ_4 as

$$\chi_4 = N^{-1} \beta \int dx_1 dy_1 dx_2 dy_2 w(x_1 - y_1) w(x_2 - y_2) \times G_4(x_1, y_1, x_2, y_2), \quad (12)$$

where the four-point density correlation function is [21]

$$G_4(x_1, y_1, x_2, y_2) = [\langle \rho_X(x_1) \rho_Y(y_1) \rho_X(x_2) \rho_Y(y_2) \rangle - \langle \rho_X(x_1) \rho_Y(y_1) \rangle \langle \rho_X(x_2) \rho_Y(y_2) \rangle]. \quad (13)$$

The two types of averages for χ_4 are easily calculated. We find that when calculated with respect to the Boltzmann average, χ_4 is regular (and small) at all T . However, when calculated within the secondary minimum (i.e. averaged within a single ergodic component) χ_4 grows for increasing T , and diverges at T_c as a power law $\chi_4 \sim (T_c - T)^{-\gamma}$, as shown in Fig. 2 for the 3-spin model. This demonstrates that equilibrium configurations within a single ergodic component are highly correlated, while configurations in different compo-

nents are not. In both the p -spin model and hard sphere model in the HNC approximation, the form of $V(q)$ is cubic around the second minimum, and thus the value of the exponent γ is equal to 1/2 (i.e., the coefficient of the quadratic term resulting when $V(q)$ is expanded around the second minimum vanishes as $(T_c - T)^{1/2}$). This value is universal within mean field and coincides with the value of γ for mean-field spinodal transitions. The correlation function is bounded in position space and an increase of the susceptibility signals a corresponding increase in the range of the correlations. If we assume usual scaling with this value of γ then the correlation length exponent ν is related to the anomalous dimension η by $\nu = 1/2(2 - \eta)$. The mean field level at which we are describing the system is the same as that of the ideal mode coupling theory [34]. The success of MCT in predicting relations between exponents of various dynamical quantities [35] leads us to speculate that the mean-field value of γ , or a close value, could be observed in real systems, and we test this using MD simulations at $T > T_c$ later in this paper.

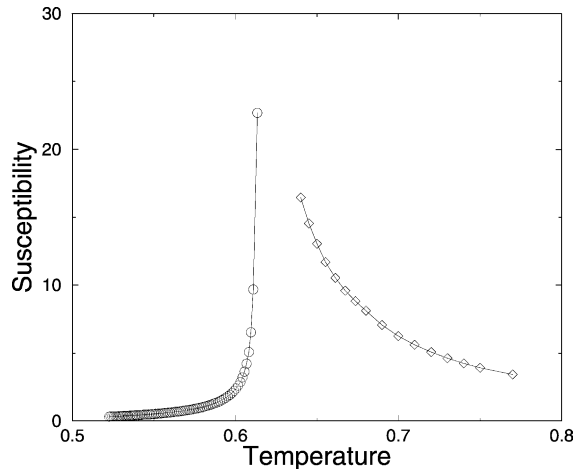


Fig. 2. The static susceptibility χ_4 (circles) calculated at low temperature ($T < T_c$), plotted vs. T , together with the maximum of the time dependent susceptibility $\chi_4(t)$ (diamonds) at high temperature ($T > T_c$). The solid line through the low- T data is included as a guide to the eye. The dashed line through the high- T data indicates a power law fit: $\chi_4(T) = a/(T - T_c)^{1/2} + b$. In the 3-spin model, $T_c = 0.612$ [24] and the fit gives $a = 3.67$, $b = -6.28$.

3. Dynamical approach above T_c

We now turn to the high temperature region $T > T_c$ where the quasi-states are mechanically unstable and the system is ergodic even in the mean field approximation. In this region there is no secondary minimum in $V(q)$, and the static susceptibility does not exhibit any singular behavior. However, in this temperature regime particles of a supercooled liquid ‘oscillate’ within cages formed by their neighbors, and the system is effectively ‘frozen’ for a characteristic time that grows and would appear to diverge as a power law as T_c is approached. This transient localization corresponds to highly correlated regions of phase space that have finite lifetime and represent the high temperature precursors of the low temperature ergodic components.

The idea of considering a system coupled with a reference configuration can also be used in dynamics to compute a time dependent susceptibility. We study the dynamics of such a system starting in an equilibrium initial condition $Y = X(0)$ and

evolving in time with potential energy $\mathcal{H} = H[X] - \epsilon q(X, Y)$, and we calculate a dynamic response

$$\tilde{\chi}_4(t) = \frac{\delta \langle q(X(t), X(0)) \rangle}{\delta \epsilon}. \quad (14)$$

Although the presence of the initial configuration does not, strictly speaking, allow us to relate this susceptibility to an overlap–overlap correlation function via the fluctuation dissipation theorem, this quantity has the same physical dimensions of χ_4 (Eq. (12)), so we can expect it to have the same singular behavior close to T_c .

We calculate $\chi_4(t)$ above T_c in the p -spin model, which is the simplest model displaying an ideal mode-coupling transition. The p -spin model [24] describes N interacting variables S_1, \dots, S_N (spins) on the sphere $\sum_i S_i^2 = N$, with Hamiltonian $H = \sum_{i_1 < \dots < i_p} J_{i_1 \dots i_p} S_{i_1} \dots S_{i_p}$, where the couplings are random independent Gaussian variables with zero mean and variance $J^2 = p!/(2N^{p-1})$. The appropriate notion of overlap for this system is $q(S, S') = 1/N \sum_i S_i S'_i$. For this model it is customary to consider Langevin dynamics, which in our case will be performed with Hamiltonian $H_{\text{tot}}(S) = H(S) - \epsilon q(S, S_0)$, where $S_0 = S(t=0)$ is an equilibrium initial condition. The equation of motion for $S_i(t)$ is then

$$\frac{dS_i(t)}{dt} = -\frac{\partial H(S(t))}{\partial S_i} + \epsilon S_i(0) + \eta_i(t), \quad (15)$$

where $\eta_i(t)$ is a white noise with amplitude $2T$, and $\mu(t)$ is a Lagrange multiplier fixed to impose the spherical constraint at all times. One can easily check from linear response theory that $\tilde{\chi}_4$ can be written in the form

$$\tilde{\chi}_4(t) = \sum_{i,j}^{1,N} \int_0^t du \left\langle \frac{\delta S_i(t)}{\delta \eta_j(u)} S_i(0) S_j(0) \right\rangle. \quad (16)$$

Through standard functional methods, discussed, e.g., in [28], we can write a self consistent equation for a single spin which, using the notation $f(q) = 1/2q^p$, reads

$$\frac{dS(t)}{dt} = -\mu(t)S(t) + \int_0^t ds f''(C(t,s))R(t,s)S(s) + \beta f'(C(t,0))S(0) + \epsilon S(0) + \xi_i(t), \quad (17)$$

where $\xi(t)$ is a colored Gaussian noise variable with variance

$$\langle \xi(t)\xi(s) \rangle = f'(C(t,s)) + 2T\delta(t-s), \quad (18)$$

where C and R are the correlation and response functions of the system, to be determined self-consistently by $C(t,s) = \langle S(t)S(s) \rangle$ and $R(t,s) = \frac{\delta S(t)}{\delta \xi(s)}$.

Taking the correlations with $S(s)$ and $\xi(s)$ in Eq. (17), one can derive equations for C and R which read, for $t > s$,

$$\begin{aligned} \frac{\partial C(t,s)}{\partial s} &= -\mu(t)C(t,s) \\ &+ \int_0^t du f''(C(t,u))R(t,u)C(u,s) \\ &\times \int_0^s f'(C(t,u))R(s,u) \\ &+ \beta f'(C(t,0))C(s,0) + \epsilon C(s,0) \end{aligned} \quad (19)$$

$$\begin{aligned} \frac{\partial R(t,s)}{\partial s} &= -\mu(t)R(t,s) \\ &+ \int_s^t du f''(C(t,u))R(t,u)R(u,s). \end{aligned} \quad (20)$$

The equation specifying the time dependence of $\mu(t)$ is

$$\begin{aligned} \mu(t) &= \int_0^t du f''(C(t,u))R(t,u)C(u,t) \\ &+ \int_0^t f'(C(t,u))R(t,u) + \beta f'(C(t,0))C(t,0) \\ &+ \epsilon C(t,0) + T. \end{aligned} \quad (21)$$

Although an analytic evaluation of the susceptibility $\chi_4(t)$ might be possible close to T_c , we did not attempt this. Instead, we studied $\chi_4(t)$ by integrating the equation of motion numerically for various values of T with the method developed in [36]. As shown in Fig. 3(a), we find that $\chi_4(t)$ displays a maximum as a function of time, which increases and shifts to larger t as $T \rightarrow T_c^+$.

The temperature dependence of the maximum of $\chi_4(t)$ is shown in Fig. 2 (diamonds); we find that the maximum behaves as a negative power of $T - T_c$ on approaching T_c . Although we did not attempt to compute the value of γ above T_c

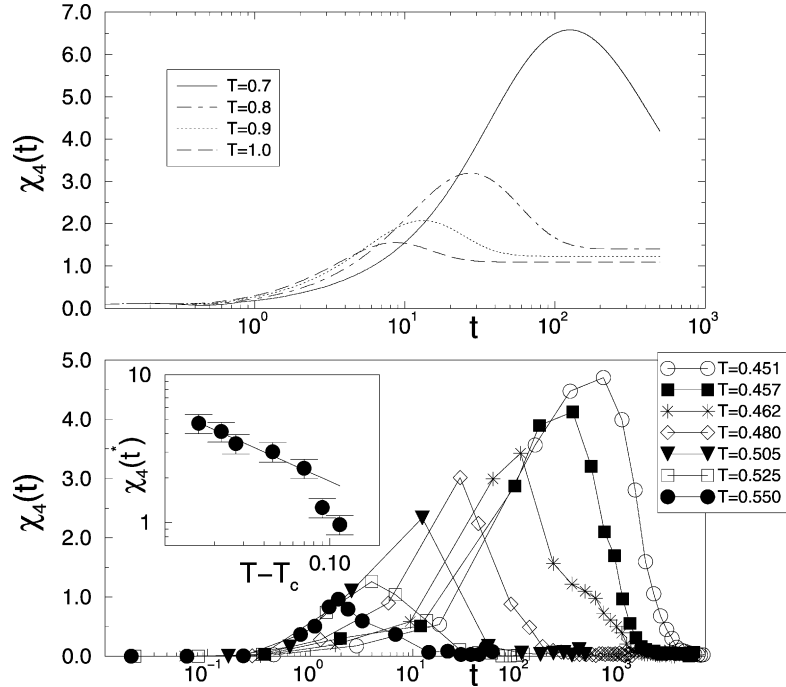


Fig. 3. (a) The non-linear susceptibility $\chi_4(t)$ computed from the theory in the p -spin model with $p = 3$, for temperatures $T = 0.7, 0.8, 0.9, 1.0$ ($T_c = 0.612$). The long time limit corresponds to the static susceptibility, which, for this model above T_c , is equal to $\chi_4(\infty) = 1/kT$. (b) The non-linear, time-dependent susceptibility $\chi_4(t)$ calculated for the LJ binary mixture above T_c . The long time limit for the liquid is negligible due to the normalization. Inset: the maximum $\chi_4(t_4^*)$ plotted as a function of $T - T_c$, with $T_c = 0.435$ [9,10,37]. Here t_4^* is the value of t at the maximum of $\chi_4(t)$. The solid line indicates a power law fit to $\chi_4(t_4^*) \sim (T - T_c)^{1/2}$, and is included to compare the simulation data with the analytical mean-field prediction.

analytically, we expect in analogy with spinodal points that the values of the exponents on the two sides of the transition would be the same. Indeed, we find that the data are compatible with the mean-field value of $1/2$ calculated below T_c (a power-law fit to the high- T data with T_c fixed and γ as a free parameter gives $\gamma = 0.52$). Thus we find that MCT predicts a diverging dynamic, non-linear susceptibility, (and thus a diverging dynamical correlation length), associated with a four-point, time-dependent density correlation function. In real systems, we expect that the transition at T_c will be smeared by the existence of dynamical processes that restore ergodicity, and which are not taken into account in the mean field approach. This has two important ramifications. The first is that even below T_c , $\chi_4(t)$ should display a maximum at finite time. The second is that the divergence of χ_4 as a function of T should be smoothed.

4. Numerical simulations

To test our predictions, we calculate $\chi_4(t)$ for an 80:20 Lennard-Jones liquid containing 8000 particles, the same system as that studied in Ref. [7,9,10]. This model displays many of the canonical features of glass-forming liquids, and has been shown to follow key predictions of mode-coupling theory [37]. Complete details of the simulation may be found in [10]. We evaluate $\chi_4(t)$ by calculating the fluctuations in the time-dependent overlap $q(t)$ measured between two equilibrium configurations of the system separated by a time t . In Fig. 3(b) we show $\chi_4(t)$ for seven different values of T approaching $T_c = 0.435$ from high T . In qualitative agreement with our theoretical predictions, we find that for the binary Lennard-Jones liquid, $\chi_4(t)$ has a maximum $\chi_4(t_4^*)$ at an intermediate time t_4^* . The amplitude of the peak grows and

its position shifts to longer times with decreasing T . As shown in the inset, the T -dependence of $\chi_4(t_4^*)$ is compatible with the mean field prediction. We caution that a rigorous test of the theory would require additional simulations closer to T_c and of a larger system size to minimize finite size effects resulting from the growing correlations. Calculations of $\chi_4(t)$ in a different binary LJ mixture reported in Refs. [30,31] show qualitatively similar results. In Ref. [31], it is shown that the dynamical correlation length characterizing the growing range of the four-point correlation function corresponding to $\chi_4(t)$, grows slowly but steadily with decreasing T while the static correlation length characterizing the range of the static pair correlation function $g(r)$ remains essentially constant.

5. Summary

We have calculated both within the effective potential theory and in a dynamical approach, a diverging susceptibility below and above the mode coupling dynamical critical temperature, respectively. This susceptibility is related to the growing range of a four-point, time-dependent density correlation function. Although in real systems, the ‘divergence’ may be ‘smeared out’ or shifted to lower T , we believe that this growth of dynamical correlations may be intrinsic to, or underly, the change of the dominant relaxation mechanism at T_c , where the quasi-states acquire mechanical stability. Our findings suggest [38–40] an interpretation of the dynamical heterogeneity underlying the behavior of the displacement-displacement correlation function calculated in Refs. [7,8] in terms of a time-dependent, four-point density correlation function. The correlation function calculated in Refs. [7,8] measures the extent to which the (scalar) displacements of a pair of particles separated by a distance r are spatially correlated. Specifically, this function is similar to the static, two-point pair correlation function $g(r)$, but with each particle’s contribution to $g(r)$ weighted by its subsequent displacement over a time interval $[0, t]$. In contrast, the four-point function G_4 studied in the present work measures the extent to which ‘overlapping’ particles within a time interval $[0, t]$ are correlated.

Although these two correlation functions are different (and thus their time- and T -dependence are different [19,20,30,31]), we believe that the length scale associated with G_4 is related to the growing range of correlated particle displacements measured in Ref. [7,8,15,16]. A further critical test of our theoretical predictions would be provided by a simulation or experimental measurement of $\chi_4(t)$ or its related correlation length below T_c . Additional simulation studies of the quantities introduced in this paper are presented in Ref. [31].

Acknowledgements

S.F. would like to acknowledge the kind hospitality of the NIST Center for Theoretical and Computational Materials Science where part of this work was accomplished.

References

- [1] R.L. Leheny, N. Menon, S.R. Nagel, D.L. Price, K. Suzuya, P. Thiyagarajan, *J. Chem. Phys.* 105 (1996) 7783; A. van Blaaderen, P. Wiltzius, *Science* 270 (1995) 1177.
- [2] Ehmler et al., *Phys. Rev. Lett.* 80 (1998) 4919, and references therein.
- [3] M. Kluge, H.R. Schober, *Phys. Rev. E* 62 (2000) 597.
- [4] H.R. Schober, *Solid State Commun.* 119 (2001) 73.
- [5] Y. Hiwatari, T. Muranaka, *J. Non-Cryst. Solids* 235–237 (1998) 19; D. Perera, P. Harrowell, *J. Non-Cryst. Solids* 235–237 (1998) 314; A. Onuki, Y. Yamamoto, *J. Non-Cryst. Solids* 235–237 (1998) 34.
- [6] B. Doliwa, A. Heuer, *Phys. Rev. Lett.* 80 (1998) 4915.
- [7] C. Donati, S.C. Glotzer, P.H. Poole, *Phys. Rev. Lett.* 82 (1999) 5064.
- [8] C. Benneman, C. Donati, J. Baschnagel, S.C. Glotzer, *Nature* 399 (1999) 246, See also p. 207.
- [9] W. Kob, C. Donati, S.J. Plimpton, P.H. Poole, S.C. Glotzer, *Phys. Rev. Lett.* 79 (1997) 2827.
- [10] C. Donati, S.C. Glotzer, P.H. Poole, W. Kob, S.J. Plimpton, *Phys. Rev. E* 60 (1999) 3170.
- [11] Y. Gebremichael, T.B. Schröder, F.W. Starr, S.C. Glotzer, *Phys. Rev. E* 64 (2001) 051503.
- [12] H.R. Schober, C. Gaukel, C. Oligschleger, *Prog. Theor. Phys. Suppl.* 126 (1997) 67; H.R. Schober, C. Oligschleger, B.B. Laird, *J. Non-Cryst. Solids* 156–158 (1993) 965.

- [13] G. Parisi, J. Phys. Chem. 103 (20) (1999) 4128.
- [14] The time dependence of dynamical heterogeneity was also studied in D. Caprion, J. Matsui, H.R. Schober, Phys. Rev. Lett. 85 (2000) 4293, and in Refs. [5,6].
- [15] A.H. Marcus, J. Schofield, S.A. Rice, Phys. Rev. E. 60 (1999) 5725.
- [16] W. Kegel, A. van Blaaderen, Science 287 (2000) 5451; E. Weeks, J.C. Crocker, A.C. Levitt, A. Schofield, D.A. Weitz, Science 287 (2000) 627.
- [17] S.C. Glotzer, Phys. World 13 (2000) 22.
- [18] S.C. Glotzer, J. Non-Cryst. Solids 274 (2000) 342.
- [19] S.C. Glotzer, Y. Gebremichael, N. Lacevic, T.B. Schröder, F.W. Starr, in: ACS Symposium Proceedings of Dynamics of Liquids, in press.
- [20] S.C. Glotzer, Y. Gebremichael, N. Lacevic, T.B. Schröder, F.W. Starr, Comp. Phys. Comm., in press.
- [21] C. Dasgupta, A.V. Indrani, S. Ramaswami, M.K. Phani, Europhys. Lett. 15 (1991) 307, Addendum: Europhys. Lett. 15 (1991) 467.
- [22] S. Franz, G. Parisi, J. Phys. I 5 (1995) 1401; Phys. Rev. Lett. 79 (1997) 2486; Physica A 261 (1998) 317.
- [23] M. Mezard, G. Parisi, J. Phys. A 29 (1996) 65155.
- [24] A review of the p -spin model can be found in A. Barrat, cond-mat/9701031, unpublished.
- [25] M. Cardenas, S. Franz, G. Parisi, J. Phys. A 31 (1998) L163; J. Chem. Phys. 110 (1999) 1726.
- [26] M. Mezard, G. Parisi, cond-mat/9812180.
- [27] T.R. Kirkpatrick, P.G. Wolynes, Phys. Rev. A 35 (1987) 3072; T.R. Kirkpatrick, D. Thirumalai, Phys. Rev. B 36 (1987) 5388.
- [28] A. Crisanti, H. Horner, H.J. Sommers, Z. Phys. B 92 (1993) 257.
- [29] T.B. Schröder, S. Sastry, J.C. Dyre, S.C. Glotzer, J. Chem. Phys. 112 (2000) 9834.
- [30] S.C. Glotzer, V.N. Novikov, T.B. Schröder, J. Chem. Phys. 112 (2000) 509.
- [31] N. Lacevic, F.W. Starr, T.B. Schröder, V.N. Novikov, S.C. Glotzer, preprint.
- [32] S. Franz, M.A. Virasoro, J. Phys. A 33 (2000) 891.
- [33] G. Parisi, J. Phys. A: Math. Gen. 30 (1997) L765.
- [34] J.-P. Bouchaud, L. Cugliandolo, J. Kurchan, M. Mezard, Physica A 226 (1996) 243; S. Franz, G. Parisi, in: Proceedings of the workshop Non-equilibrium Phenomena in Supercooled Fluids Glasses and Amorphous Materials, September 1995, Pisa, World Scientific, Singapore, 1996.
- [35] W. Götze, in: J.P. Hansen, D. Levesque, J. Zinn-Justin (Eds.), Liquids Freezing and the Glass Transition, North Holland, 1990.
- [36] S. Franz, M. Mezard, Physica A 210 (1994) 48.
- [37] W. Kob, H.C. Andersen, Transport Theor. Stat. Phys. 24 (6–8) (1995) 1179.
- [38] S.C. Glotzer, C. Donati, P.H. Poole, in: Computer Simulation Studies in Condensed Matter Physics, Springer, Heidelberg, 1999.
- [39] S. Franz, G. Parisi, unpublished comment, cond-mat/9804084.
- [40] S. Franz, C. Donati, G. Parisi, S.C. Glotzer, Philos. Mag. B 79 (1999) 1827.