THEORY OF NON-LINEAR SUSCEPTIBILITY 
AND CORRELATION LENGTH IN GLASSES AND LIQUIDS

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Abstract

Within the framework of the effective potential theory of the structural glass transition, we calculate for the $p$-spin model and a hard sphere liquid in the hypernetted chain approximation a static nonlinear susceptibility related to a four-point density correlation function, and show that it grows and 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 nonlinear susceptibility and show that there is a characteristic time where this susceptibility has a maximum, and that this time grows with decreasing $T$. We find that this susceptibility diverges as $T_c$ is approached from above, and has key features in common with the “displacement-displacement susceptibility” recently introduced to measure correlated particle motion in simulations of glass-forming liquids.
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 approached. However, no clear evidence for such a length has been reported [1]. Recent numerical studies of glass-forming liquids have identified a dynamical length associated with the range over which particle motions are correlated [2-7]. By introducing a “displacement-displacement” correlation function and generalized “displacement susceptibility” \( \chi_a(t) \), Refs. [4,5] showed in two different model liquids that this length grows 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. Evidence for a growing length associated with correlated particle motion at fixed \( T \) in simulations below \( T_c \) has also been reported [8].

In this Letter we calculate within the effective potential theory a new susceptibility \( \chi_4 \) associated with a four-point density correlation function [9]. We show that below \( T_c \), \( \chi_4 \) diverges with exponent 1/2 as \( T \to T_c^- \). We show that above \( T_c \), \( \chi_4 \) is time-dependent and resembles the susceptibility calculated in [4,5]. In particular, we show that \( \chi_4(t) \) has a maximum which diverges in mean field as \( T \to T_c^+ \). 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 correlated particle displacements measured in Refs. [4,5]. 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 approaches depending on \( T \). In the low \( T \) regime (\( T < T_c \)), we calculate a static, nonlinear susceptibility using the effective potential theory [10], and in the high \( T \) regime (\( T > T_c \)), we calculate a dynamic, nonlinear susceptibility in a dynamical approach. The low \( T \) calculations are performed both for a hard-sphere liquid in the hypernetted chain (HNC) approximation [12] and for the spherical \( p \)-spin model [11]; 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 [12-14]. For example, the high-\( T \) dynamics of the \( p \)-spin model is described exactly by the ideal mode coupling equations [15,16] and displays a sharp transition at \( T_c \).

In the effective potential theory, below \( T_c \) phase space is split into separate ergodic components which remain stable at all temperatures (this stability is due to the mean field nature of the theory). A key hypothesis of our approach is that in real systems the ergodic components are metastable states with a long but finite escape time. In this framework we can use a static approach to compute the properties of these metastable states below \( T_c \). We can also obtain information on the dynamical properties above \( T_c \), where mean field theory predicts that the time to escape from a metastable state 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.

We first describe the essential elements of the effective potential theory (a complete description can be found in [13]). 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 particular definition adopted. In the case of simple liquids with $N$ particles at fixed density [13,17], one can define

$$q(X,Y) = \frac{1}{N} \sum_{i=1}^{N} w(x_i - y_j) = \frac{1}{N} \int dx \, dy \, w(x-y) \rho_X(x) \rho_Y(y),$$

where $X = \{x_1, ..., x_N\}$, $Y = \{y_1, ..., y_N\}$, 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 $r < a r_0$ 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 [13,17].

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 $Y$:

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

Here $\beta \equiv 1/k_B T$ and $H(X)$ is the potential energy of $X$. $V(q)$ is self-averaging with respect to the choice of $Y$.

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” $\mathcal{N} \sim \exp(N \Sigma)$, each carrying vanishing weight in the Boltzmann distribution [13]. A fundamental result of the theory, central in the following discussion, is that physical quantities calculated in the primary minimum represent averages computed with the Boltzmann weight, while the same quantities calculated in the secondary minimum represent averages computed only within a single ergodic component.
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 [13].

To calculate physical quantities in the effective potential theory, we introduce the Legendre transform of $V(q)$: $\Gamma(\epsilon) = \min_q V(q) - \epsilon q$, where $\epsilon$ 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 $\langle q \rangle = \langle \epsilon \rangle_{\epsilon \rightarrow 0}$, where $\langle \cdot \rangle$ represents either of the two types of averages. The overlap susceptibility is defined as

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

where $q \equiv q(X,Y)$. Inserting Eq. 1 in Eq. 3 allows us to rewrite $\chi_4$ as

$$\chi_4 = N\beta \int dx_1 dy_1 dx_2 dy_2 w(x_1 - y_1)w(x_2 - y_2)G_4(x_1, y_1, x_2, y_2),$$

where we have defined the four-point density correlation function [9].
The two types of averages for $\chi_4$ are easily calculated. We find that when calculated with respect to the Boltzmann average, $\chi_4$ is regular (and small) at all $T$. However, when calculated within the secondary minimum (i.e. averaged within a single ergodic component) $\chi_4$ 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.

This demonstrates that equilibrium configurations within a single ergodic component are highly correlated, while configurations in different components 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 $\gamma$ 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 $\gamma$ for mean-field spinodal transitions. If we assume usual scaling with this value of $\gamma$ then the correlation length exponent $\nu$ is related to the anomalous dimension $\eta$ by $\nu = 1/2(2 - \eta)$. We emphasize that the mean field level at which we are describing the system should be the same as that of the ideal mode coupling theory. The success of MCT in predicting relations between exponents of various dynamical quantities [18] leads us to speculate that the mean-field value of $\gamma$, 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.

We now turn to the high temperature region $T > T_c$ where the system is ergodic. 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 which grows and diverges 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.

We study the dynamics of such a system starting in an equilibrium initial condition $Y = X(0)$ and evolving in time with potential energy $H = H[X] - \epsilon q(X, Y)$, and we calculate the dynamic susceptibility $\chi_4(t)$ associated with the time dependent overlap $q(t) \equiv q(X(t), X(0))$ from Eqs. 4 and 5, with $q \equiv q(t)$. To calculate $\chi_4(t)$ above $T_c$ we use the mode coupling approximation (again the calculations are performed for the spherical $p$-spin model, where MCT is exact).

This gives rise to closed equations for the time-dependent overlap correlation and response functions $C(t, t') = \langle q(X(t), X(t')) \rangle$ and $R(t, t') = \frac{\delta C(t, t')}{\delta \epsilon(t)}$ which are a slight generalization of the equations discussed in Ref. [10] (the details of the calculation will be given elsewhere). We solve for $\chi_4(t) = \frac{\delta C(t, 0)}{\delta \epsilon}$ by integrating these equations numerically as in [10] for different values of $T$. As shown in Fig. 3a, we find that $\chi_4(t)$ displays a maximum as a function of time, which increases and shifts to larger $t$ as $T \to T_c^+$.
FIG. 2. The static susceptibility $\chi_4$ (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 $p$-spin model, $T_c = 0.612$ [11] and the fit gives $a = 3.67$, $b = -6.28$. In real systems one can expect a rounding of the divergence at $T_c$. 
FIG. 3. (a) The nonlinear 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 nonlinear, 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 $T_c = 0.435$ [6,7,20]. The solid line indicates a power law fit to $\chi_4(t_4^*) \sim (T - T_c)^{1/2}$, and is included in order to compare the simulation data with the analytical mean-field prediction.

The temperature dependence of the maximum of $\chi_4(t)$ is shown in Fig. 2 (circles); 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 $\gamma$ above $T_c$ analytically, in analogy with spinodal points we expect 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 $\gamma$ as a free parameter gives $\gamma = 0.52$). Thus we find that the dynamic theory of the $p$-spin model predicts a diverging dynamic, nonlinear susceptibility, (and thus by standard arguments a diverging dynamical correlation length), associated with a four-point 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 $\chi_4$ as a function of $T$ should be smoothed.

To test our predictions, we calculate $\chi_4(t)$ for the same 80:20 Lennard-Jones liquid (containing 8000 particles) studied in Ref. [4,6,7]. Complete details of the simulation may be found in [7]. We evaluate $\chi_4(t)$ using the time-dependent generalization of Eq. 3, by calculating the fluctuations in the overlap $q$ measured between two configurations of the system separated by a time $t$. In Fig. 3 we show $\chi_4(t)$ as a function of the time interval $t$ between the two equilibrium configurations, for seven different values of $T$ approaching $T_c = 0.435$ from above. 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 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. However, we caution that a rigorous test of the theory would require additional simulations closer to $T_c$ and improved statistics. In 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. As seen clearly from Eq. 4, this susceptibility is related to the growing range of a four-point, time-dependent density correlation function. Our findings suggest [19,21] an interpretation of the physics underlying the displacement-displacement correlation function calculated in Refs. [4,5] in terms of a four-point density correlation function. The correlation function calculated in Refs. [4,5] 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 by definition (and thus, e.g. the exponents describing the $T$-dependence of the generalized susceptibilities $\chi_4$ and $\chi_U$ will be different), we believe that the length scale associated with $G_4$ underlies the growing range of correlated particle displacements measured in Ref. [4,5]. A further critical test of our theoretical predictions would consist in the simulation or experimental measurement of $\chi_4(t)$ or the related correlation length below $T_c$. The quantities studied here should be measurable experimentally in colloidal liquids using confocal video microscopy [22].

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References


[9] This four-point correlation function was first studied in a supercooled liquid in C. Dasgupta, A.V. Indrani, S. Ramaswami, and M.K. Phani, Europhys. Lett. 15 (1991) 307 [Addendum: Europhys. Lett. 15 (1991) 467]. In that paper, a negative result was found, possibly because some of the data analyzed were in the aging regime, where more complex analysis should be done.


Susceptibility