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Correlation functions for glass-forming systems

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We present a simple, linear, partial-differential equation for the density-density correlation function in a glass-forming system. The equation is written down on the basis of fundamental and general considerations of linearity, symmetry, stability, thermodynamic irreversibility and consistency with the equation of continuity (i.e., conservation of matter). The dynamical properties of the solutions show a change in behavior characteristic of the liquid–glass transition as a function of one of the parameters (temperature). The equation can be shown to lead to the simplest mode-coupling theory of glasses and provides a partial justification of this simplest theory. It provides also a method for calculating the space dependence of the correlation functions not available otherwise. The results suggest certain differences in behavior between glassy solids and glass-forming liquids which may be accessible to experiment. A brief discussion is presented of how the method can be applied to other systems such as sandpiles and vortex glasses in type II superconductors.

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The glass transition is a continuous transition between a disordered solid and a viscoelastic liquid. Both systems can be described in terms of linear partial-differential equations (in the limit of small strains and low flow velocities) [1,2]. This suggests that a similar linear differential equation can be written down for the density-density correlation function $\Phi(\mathbf{r},t)=\langle \delta\rho(\mathbf{r},t)|\delta\rho(\mathbf{0},0)\rangle$ which describes the system on both sides of the transition where $\delta\rho(\mathbf{r},t)$ is the excess density at the point $\mathbf{r}$ and time t. The simplest, low-order, linear, partial-differential equation which contains enough information to describe the transition is

$$\frac{\partial^2\Phi}{\partial t^2}+\gamma\frac{\partial\Phi}{\partial t}=\alpha\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\Phi)+\beta\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Phi}{\partial r}\right). \quad (1)$$

The interpretation is as follows: The equation is a damped wave equation with an extra term. The coefficient of the first term on the left is a mass density and is therefore positive and is normalized to unity. The coefficient of the last term on the right is a compressibility and is therefore positive for stability. The coefficient of the second term on the left is a damping and the thermodynamic arrow of time implies that it is positive also. The first term on the right, the extra term, arises from the fact that the object we are calculating is a correlation function and the average we are calculating is an average conditional on the fact that the excess density at the origin is nonzero at time zero. Thus rotational symmetry remains but translational symmetry with respect to the origin is broken and a term of this kind is therefore allowed. It would of course be forbidden if we were calculating the density not subject to the condition because then the symmetry would not be broken. There is no basic principle which helps us to decide the sign of the coefficient and we shall see that it is reasonable to assume that it depends on the temperature, being positive at low T and negative at high T. A further point is that the equation may be split into two equations thus

$$\frac{\partial\Phi}{\partial t}+\frac{1}{r^2}\frac{\partial}{\partial r}(r^2J)=0$$

and

$$\frac{\partial J}{\partial t}+\gamma J+\alpha\Phi+\beta\frac{\partial\Phi}{\partial r}=0 \quad (2)$$

or equivalently in vectorial form

$$\frac{\partial\Phi}{\partial t}+\operatorname{div}\mathbf{J}=0$$

and

$$\frac{\partial\mathbf{J}}{\partial t}+\gamma\mathbf{J}+\alpha\Phi\hat{\mathbf{r}}+\beta\,\operatorname{grad}\boldsymbol{\Phi}=\mathbf{0}, \quad (3)$$

which displays the equation of continuity explicitly and establishes that the equation preserves conservation of matter.

The one-dimensional version of these equations is as follows:

$$\frac{\partial\Phi}{\partial t}+\frac{\partial J}{\partial x}=0, \quad (4)$$

$$\frac{\partial J}{\partial t}+\gamma J+(\lambda-1)\Omega^2a\Phi+\frac{1}{2}(\lambda+1)\Omega^2a^2\frac{\partial\Phi}{\partial x}=0. \quad (5)$$

It is slightly easier to relate this version to the mode-coupling [3–7] theories and its solutions are closely related to the solutions of the full three-dimensional equation (1). We will present solutions of the one-dimensional equation only but comment on the relation of these to the solutions of the three-dimensional equation (1). We have written the coefficients in a slightly different form to make the relation to the mode-coupling theories a little more obvious later. We only note here that a is a length scale, Ω is a frequency, and $\lambda\equiv T_0/T$ is an inverse temperature and that the coefficient of Φ changes sign at $T=T_0$.

A simple way of solving the equations is to discretize the length scale and solve the resulting coupled ordinary-differential equations by a simple Runge-Kutta method. The discretization procedure gives the following equations:

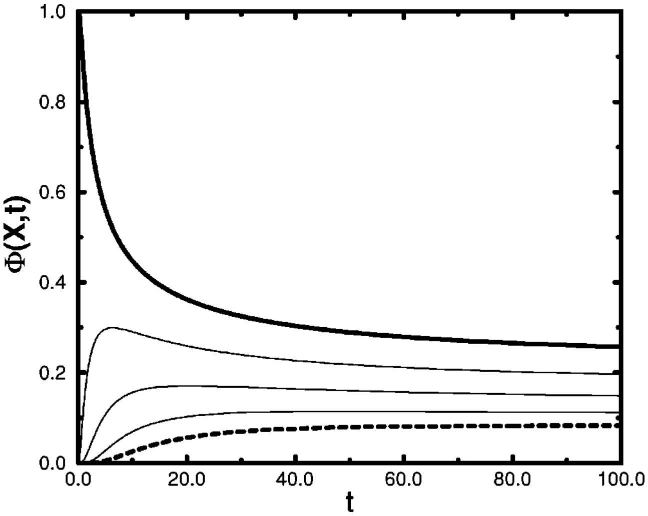

FIG. 1. Φ vs t for $\lambda=1.3$ (i.e., low T) at $x=1$ (heavy curve), 2, 3, 4, 5 (dashed curve). The remaining parameters are $\Omega=1$, $\gamma=5$, and $a=1$. Note that the curves approach finite limits as $t\to\infty$ characteristic of a solid.

$$\frac{d\Phi_n(t)}{dt}+\frac{1}{a}(J_{n+\frac{1}{2}}(t)-J_{n-\frac{1}{2}}(t))=0, \tag{6}$$

$$\frac{dJ_{n+\frac{1}{2}}(t)}{dt}+\gamma(J_{n+\frac{1}{2}}(t)-\Omega^2a\,\Phi_n(t)+\lambda\Omega^2a\,\Phi_{n+1}(t))=0 \tag{7}$$

where $\Phi_n(t)=\Phi(na,t)$ and $J_{n+1/2}(t)=J((n+1/2)a,t)$. The initial condition used is $\Phi_n(0)=0$ for $n\neq0$ and $\Phi_0(0)=1$ and $J_{n+1/2}(0)=0$ for all n, which corresponds in the continuum case to $\Phi(x,0)=2\delta(x)$ and $J(x,0)=0$. The condition at $n=0$ is $J_{-1/2}(t)=0$ for all t.

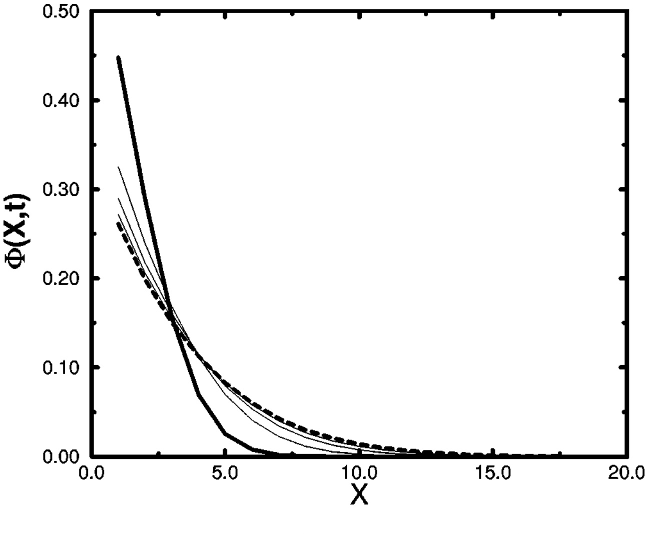

FIG. 2. Φ vs x for $\lambda=1.3$ (i.e., low T) at $t=10$ (heavy curve), 30, 50, 70, 90 (dashed curve). The remaining parameters are $\Omega=1$, $\gamma=5$, and $a=1$. Note that the curves approach an envelope as $t\to\infty$ indicating a freezing phenomenon.

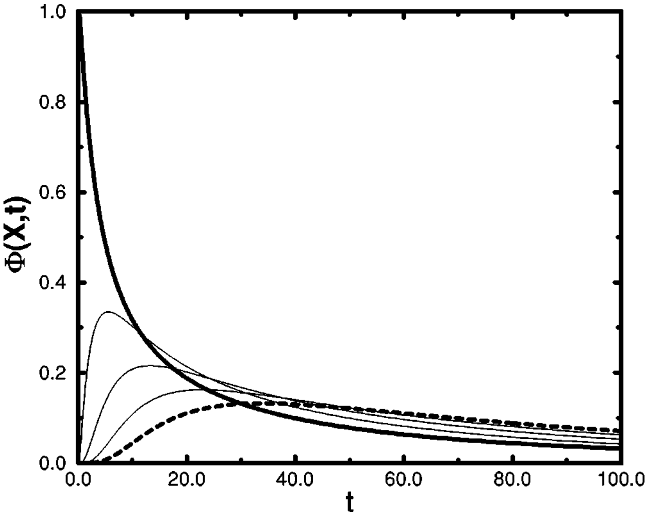

FIG. 3. Φ vs t for $\lambda=0.7$ (i.e., high T) at $x=1$ (heavy curve), 2, 3, 4, 5 (dashed curve). The remaining parameters are $\Omega=1$, $\gamma=5$, and $a=1$. Note that the curves approach zero as $t\to\infty$ characteristic of a liquid.

We present graphs of the results for $\lambda>1$ i.e., for $T<T_0$ in Figs. 1 and 2 and for $\lambda<1$, i.e., for $T>T_0$ in Figs. 3 and 4. Note that for $\lambda<1$

$$\Phi_n(t)\to0$$

and

$$\Phi(x,t)\to0 \quad \text{as } t\to\infty$$

but that for $\lambda>1$

$$\Phi_n(t)\to\frac{\lambda-1}{\lambda^n}$$

and

$$\Phi(x,t)\to\frac{2(\lambda-1)}{\lambda+1}\exp\left(-\frac{2(\lambda-1)x}{(\lambda+1)a}\right) \quad \text{as } t\to\infty.$$

This demonstrates that the correlation function has at high temperature the characteristic behavior of a liquid where an

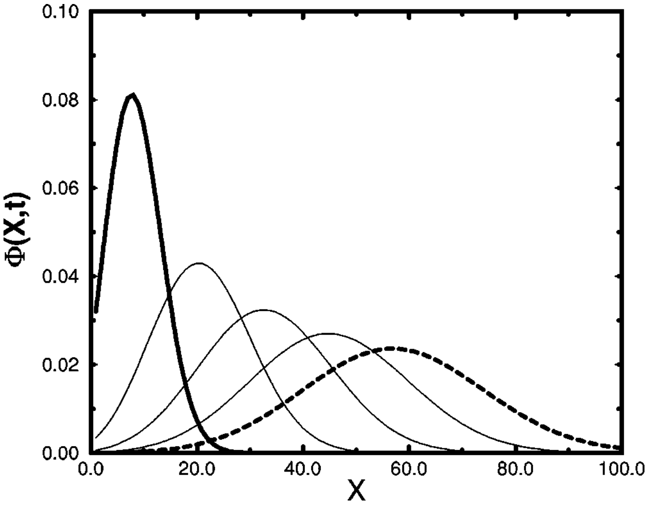

FIG. 4. Φ vs x for $\lambda=0.7$ (i.e., high T) at $t=100$ (heavy curve), 300, 500, 700, 900 (dashed curve). The remaining parameters are $\Omega=1$, $\gamma=5$, and $a=1$. Note the outgoing wave pulse.

imposed strain produces a stress that decays to zero as t increases and that it has at low temperature the characteristic behavior of a solid where an imposed strain produces a stress that does not decay to zero as t increases. These results remain true in three dimensions. Internal stresses of this kind are indeed characteristic of glasses.

Furthermore at high temperatures the imposed strain at the origin decays via an almost dispersionless outward traveling wave pulse as is shown in Fig. 4. The speed of propagation of the pulse is $|\lambda-1|\Omega^2 a/\gamma$, which goes to 0 as $T \rightarrow T_0$. In three dimensions the pulse decays proportional to $1/r^2$ as it travels outward. These outward-traveling waves appear only above T_0 and this indicates that there are strong differences in the properties of the dynamical correlation functions between solid and liquid near T_0, which may be accessible experimentally. These results are sensitive to the assumed form of the damping term which may be oversimplified here. Obviously more research is needed on this point. At low temperatures the imposed strain settles down to an exponentially decreasing profile (in x) which is very much what one would expect on physical grounds. These results seem related to some recently reported experiments [8].

At the transition temperature $T=T_0$ the asymptotic form of Eq. (1) can be solved exactly because the first term on the left becomes negligible and the equation becomes the diffusion equation and this gives the three-dimensional result

$$\Phi(\mathbf{r},t)=\left(\frac{1}{4\pi Dt}\right)^{3/2}\exp(-r^2/4Dt) \qquad (8)$$

with $D=\beta/\gamma$ and a corresponding result in one dimension.

If we take Laplace transforms of the discrete equations (6) and (7) we get algebraic equations for $\tilde{\Phi}_n(p) \equiv \int_0^\infty \Phi_n(t)\exp(-pt)dt$ which can be solved for $\tilde{\phi}(p) \equiv \tilde{\Phi}_0(p)$ by elementary matrix manipulations. The result can be inverse transformed to give the following integrodifferential equation for $\phi(t)$:

$$\ddot{\phi}(t)+\gamma\dot{\phi}(t)+\Omega^2\phi(t)+\lambda\Omega^2\int_0^t \phi(t-\tau)\dot{\phi}(\tau)d\tau=0. \qquad (9)$$

This equation is well known as the simplest mode-coupling equation for the glass transition [5,6]. This shows that this simplest theory is a consequence of the one-dimensional phenomenological theory outlined above.

More complicated versions of this equation exist which have the kernel $\phi(t-\tau)$ replaced by a low-order polynomial in $\phi(t-\tau)$ [3,4,7,9]. Some kind of microscopic many-body theory is usually presented in justification of these versions. It is clearly impossible to relate these versions to a linear partial-differential equation which interpolates smoothly between the corresponding equations for a liquid and a solid. Furthermore a reasonably simple heuristic argument can be mounted in favor of the simplest mode-coupling theory with linear kernel [5]. We consider our phenomenological and heuristic arguments as strong evidence for the essential correctness of the simplest version of the mode-coupling theory.

Numerical calculations of $\phi(t)$ from Eq. (9) and $\Phi(\mathbf{0},t)$ from Eqs. (4) and (5) compare very well thus confirming the correctness of the numerical analysis and the algebra. The phenomenological partial-differential equation however is superior because it enables us to calculate the space dependence of the correlation functions (impossible in the mode-coupling theories [7]) and to generalize from one to three dimensions.

In order to see the range of validity of our phenomenology it is worthwhile examining analogies with other systems. There are two systems that provide two-dimensional analogues of glasses; the first is the vortex system in extreme type II superconductors, the second is a sandpile i.e., a pile of strongly interacting but not cohesive objects on a flat surface. In some experiments [10] on the vortex system long-lived pulses of increased vortex density are observed to travel across the sample under the influence of an external force. These pulses may be similar to the almost dispersionless pulses seen in our calculations at high T. A crucial experiment would be to measure the velocity of the pulses in the experimental system as a function of T and check whether the velocity disappears at some finite low temperature as our results indicate. Sandpiles bear a certain operational similarity to low-T glasses as the following experiment suggests. Insert a pencil vertically into a sandpile and displace it laterally. Observe the resulting lateral force on the pencil as a function of time. The force will decay from its initial value to a lower value and then remain steady. The force displays the same remnant behavior as the stress in a similar experiment on a glassy system at low T. Investigations of the transport of matter up and down the slope of shaken and unshaken sandpiles are obviously relevant here. Some simple models of sandpiles [11] have the same one-sided character as our basic equations (1), (2), (3), and (5).

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