Disorder-Assisted Melting and the Glass Transition in Amorphous Solids

Alessio Zaccone and Eugene M. Terentjev

Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom
(Received 10 October 2012; published 26 April 2013)

The mechanical response of solids depends on temperature, because the way atoms and molecules respond collectively to deformation is affected at various levels by thermal motion. This is a fundamental problem of solid state science and plays a crucial role in materials science. In glasses, the vanishing of shear rigidity upon increasing temperature is the reverse process of the glass transition. It remains poorly understood due to the disorder leading to nontrivial (nonaffine) components in the atomic displacements. Our theory explains the basic mechanism of the melting transition of amorphous (disordered) solids in terms of the lattice energy lost to this nonaffine motion, compared to which thermal vibrations turn out to play only a negligible role. The theory is in good agreement with classic data on melting of amorphous polymers (for which no alternative theory can be found in the literature) and offers new opportunities in materials science.

The problem of describing the melting transition into a fluid state [1–9] is complicated in amorphous solids by the difficulties inherent in describing the elasticity down to the atomistic level (where the thermal fluctuations take place). It is well known that the standard (Born-Huang) lattice-dynamic theory of elastic constants, and also its later developments [10], breaks down on the microscopic scale. The reason is that its basic assumption, that the macroscopic deformation is *affine* and thus can be downscaled to the atomistic level, does not hold [11]. Atomic displacements in amorphous solids are in fact strongly *nonaffine* [11–14], a phenomenon illustrated in Fig. 1.

Recently, it has been shown [15] that nonaffinity could play a role in the melting of model amorphous solids, although the basic interplay between nonaffinity, thermal expansion, and thermal vibrations is still not fully understood. Previous models of the glass transition, such as mode-coupling theories [16], have indicated that the transition from a liquid into a glass is a consequence of nonlocal slowing down of the dynamics. Theories which build on this framework predict that the shear modulus G of athermal hard-sphere colloids remains finite at the glass transition [17] and that it jumps discontinuously to zero upon decreasing the packing fraction ϕ. Other analytical [15] and numerical [18] works, instead, indicate that the vanishing of G is continuous with T. This issue is not resolved even now, with a new important experimental study probably supporting the discontinuous transition scenario [19], in contrast to the simulations of Wittmer *et al.* [20], where a continuous critical law $G \sim \sqrt{T_c - T}$ is reported. Here we should note that all these approaches, however, are limited to central-force interactions and therefore not strictly applicable to real amorphous materials with covalent bonds.

Here we introduce a compact analytically tractable model describing the melting of amorphous solids.

The model shows that the melting is driven by nonaffinity of deformations and relies on counting the effective bond connectivity, which in turn is affected by T via thermal expansion. In contrast, we find that the contribution of thermal vibrations to the shear modulus G is very low. The model accounts for both central contact forces and covalent bonds that have a bond-bending constraint. The results offer a closed expression for $G(T)$ and the glass transition temperature, which are both in quantitative agreement with classical experiment [21] on amorphous polymer glasses. Also, our theory appears to reproduce the continuous square-root criticality first found in the simulations of Wittmer *et al.* [20].

Let us start from the basic assumptions of Born-Huang lattice dynamics [2]. The free energy density of affine
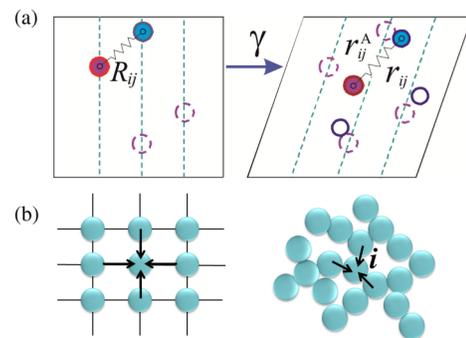

FIG. 1 (color online).   (a) If the deformation was affine, the particles labeled with darker color would lie on the dashed lines also in the deformed (right) frame. Because of nonaffinity, they do not. (b) In a monatomic crystal lattice (left), the forces (arrows) transmitted to any particle i by its nearest neighbors cancel each other and $\underline{f}_i = 0$. In a disordered lattice (right), the forces do not balance, and $\underline{f}_i \neq 0$ has to be balanced by a nonaffine motion, in order to preserve the local mechanical equilibrium.

deformation is given by the following harmonic lattice sum: $F_A = (1/2V)\sum_{ij}(\partial^2 U/\partial \underline{r}_{ij}^2)_{R_0}(\underline{u}_{ij}^A)^2$, which runs over all bonded atom pairs ij. Here $U(\underline{r}_{ij})$ is the pair-interaction potential, and the vector $\underline{u}_{ij}^A = \underline{r}_{ij}^A - \underline{R}_{ij} = \underline{\underline{\eta}} \cdot \underline{R}_{ij}$ denotes the affine displacement, with $\underline{\underline{\eta}}$ the macroscopic strain tensor and $\underline{R}_{ij}$ the bond vector in the undeformed frame. R_0 is the equilibrium lattice constant in the undeformed frame, at which one evaluates the lattice spring constant $\kappa = (\partial^2 U/\partial \underline{r}_{ij}^2)_{R_0}$. Since our interest is in the solid state, we focus on a *shear* strain $\eta_{xy} \equiv \gamma$. The lattice sum can be evaluated upon introducing the average number of bonds per atom z, and in the affine approximation [22]: $F_A = (2/10\pi)(\kappa/R_0)\phi z\gamma^2$, where $\phi = \upsilon N/V$ is the packing fraction occupied by the atoms in the solid.

In general, the (negative) contribution to F due to thermal lattice fluctuations (phonons) is given by $F_T = -kT \ln \sum_n^\infty \exp[-\hbar\omega_n(n + 1/2)/kT]$, where n labels the eigenmodes. If $kT \gg \hbar\omega_{max}$, one can use the mean frequency $\bar{\omega}$ so that $F_T = -(3N/V)kT \ln(kT/\hbar\bar{\omega})$ [9]. The contribution of the elastic energy can be written as $F_T \approx -(3N/V)kT\theta\gamma^2$, where the nondimensional factor $\theta = -(\partial^2/\partial\gamma^2)_{\gamma\to 0} \ln\hbar\bar{\omega}/kT$ has been demonstrated to be of order unity when the harmonic potential dominates the pair-interaction potential [9]. This gives a good estimate: $F_T \approx -3(kT/\upsilon)\phi\gamma^2$.

The number of bonds per atom z requires a careful definition in amorphous systems. If there were only covalent bonds, then z is obviously just equal to the number of covalent bonds per atom, z_{co}. However, in addition to covalent bonds, weaker interactions can be present between pairs of monomers in contact. Such interactions are of van der Waals nature and could be modeled by the Lennard-Jones (LJ) potential [23]. It is important to distinguish quantitatively between these contributions to the total $z = z_{co} + z_{LJ}$, where we shall count a contribution to z_{LJ} when the two monomers are separated by $r \leq r_{min}$ of the LJ potential well; see Fig. 2. Later in the text, we shall derive the explicit values for the two components contributing to z, from which we derive a quantitative form of
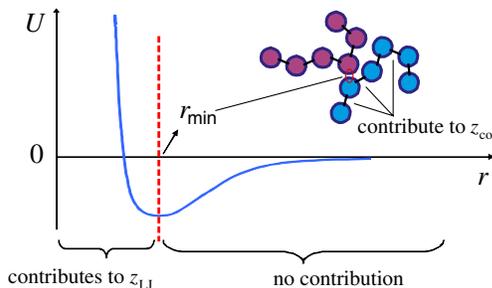

FIG. 2 (color online). Schematic of the criterion used to define the contribution of the contact LJ interactions and covalent bonds to the total number of mechanical bonds z. Only pairs of particles that lie within the soft repulsive part of the LJ potential contribute to the z_{LJ} counting.

glass transition temperature and compare the model predictions with experiment [21].

Having defined the total z, we now need to relate it to T. Upon introducing the thermal expansion coefficient $\alpha_T = \frac{1}{V}(\partial V/\partial T)$ and replacing the volume V via $\phi = \upsilon N/V$, after integration we obtain $\ln(1/\phi) = \alpha_T T + const$ (later we shall need to estimate this constant, obtaining $C \sim 0.48$). Now z can be estimated as a function of ϕ by introducing the radial distribution function (rdf) $g(r)$. Since the average connectivity due to covalent bonds remains fixed, only the weaker contact bonds contributing to z_{LJ} are changing upon increasing the packing fraction ϕ by $\delta\phi$. The increment δz can be calculated in full analogy with soft-sphere systems, where only the repulsive part of the potential is active. This increment is given by [24] $\delta z \sim \int_1^{1+\delta\phi} \xi^2 g(\xi)d\xi$, where ξ is the normalized center-to-center distance. The rdf in the repulsive part is dominated by $g(\xi) \sim \sqrt{\xi - 1}$, as shown in theory [24] and simulations [25]. To keep things analytical, here we neglect the thermal broadening of the rdf, which could be calculated only by using involved replica techniques [26]. This particular simplification should still work for relatively low-T_c polymer glassy systems, as we are going to verify below, but certainly has to be adjusted when dealing with inorganic glasses which have an order of magnitude higher T_c. The increment δz has to be measured from the point where the system is marginally stable, i.e., $z = z_c$ at $\phi = \phi_c$, and from the integral we obtain $z - z_c \sim \sqrt{\phi - \phi_c}$.

In the affine approximation, the solid becomes marginally stable only in the limit $z_c \to 0$ and $\phi_c \to 0$, and hence we have $z \sim \phi^{1/2}$. Using the earlier relation between ϕ and α_T we obtain $z \sim e^{-\alpha_T T/2}$. Substituting z and ϕ in $F_A + F_T$ we now can write the full expression for the shear modulus in the affine approximation, $G_A = \partial^2(F_A + F_T)/\partial\gamma^2$, yielding

$$G_A(T) = \frac{2}{5\pi}\frac{1}{R_0^3}(\kappa R_0^2 e^{-(3/2)\alpha_T T} - kTe^{-\alpha_T T}). \quad (1)$$

The Born criterion of melting [2] is given by Eq. (1) set to zero: $\kappa R_0^2 = kTe^{\alpha_T T/2}$. We shall see later that $\alpha_T T \ll 1$ and, remarkably, this relation reproduces the Lindemann criterion [27], which uses equipartition to state that melting occurs when the average vibrational energy of a bond equals kT. It is also known that the Lindemann criterion grossly overestimates melting temperatures for amorphous solids [11]; in the same way, Eq. (1) cannot capture the vanishing of rigidity as seen in the melting of glassy polymers [21]. It turns out that to describe the melting of amorphous solids one has to account for nonaffine deformations in the lattice dynamics.

The shear modulus accounting for nonaffine deformations is derived in Ref. [28] as a lattice sum: $G = G_A - G_{NA} = G_A - \sum_i \underline{f}_i \sum_j \underline{\underline{H}}_{ij}^{-1} \underline{f}_j$, where $\underline{\underline{H}}_{ij}$ is the dynamical matrix of the solid (Hessian) [29]. The vector $\underline{f}_i$ measures

the increment of force acting on an atom in response to the deformation of its environment. It can be shown that for harmonic pair potential and the xy-shear deformation [28] $\underline{f}_i = -R_0 \kappa \sum_j \underline{e}_{ij} e_{ij}^x e_{ij}^y$, where $\underline{e}_{ij}$ is the unit vector along the bond connecting two atoms i and j. Since the sum runs over bonds to the nearest neighbors j of the atom i, it is evident that in many crystal lattices one finds a mirror image for each bond [Fig. 1(b), left panel], causing cancellation in the sum and $\underline{f}_i = 0$, $\forall i$. As a result, $\underline{f}_i$ is nonzero only in crystals with a lack of reflection symmetry in unit cells—but most importantly in the presence of disorder; see Fig. 1(b), right panel. The nonaffine correction to the elastic free energy then arises to ensure that local mechanical equilibrium, which disorder tends to compromise, is preserved upon deformation. In fully disordered lattices the angular averaging of bond-orientation vectors between harmonically bonded particles in the summation leads to a simple result [30,31]:

$$G = G_A - G_{NA} = \frac{2}{5\pi} \frac{\kappa}{R_0} \phi(z - z_c). \quad (2)$$

The nonaffine contribution is encoded in Eq. (2) in the term proportional to z_c which expresses the internal energy required to fuel the nonaffine motions necessary for the preservation of mechanical equilibrium against the effect of disorder. With purely central interparticle interactions in d dimensions, the shear modulus vanishes at $z_c = 2d$ ($z_c = 6$ in 3D), because the nonaffine term is proportional to the number of degrees of freedom that can be involved in the nonaffine energy relaxation. This is consistent with the classical Maxwell criterion for marginal stability with purely central forces: $G \sim (z - 6)$. In general, z_c defines the critical coordination at which the lattice is no longer rigid, because all the lattice potential energy is "spent" on sustaining the nonaffine motions and no energy is left to support the elastic response to deformation. Using again $\ln(1/\phi) = \alpha_T T + C$, we arrive at $\ln(\phi_c/\phi) = \alpha_T(T - T_c)$. The corresponding relation $z - z_c \sim \sqrt{\phi - \phi_c}$ can be manipulated into

$$\ln(\phi_c/\phi) = -\ln[1 + (z - z_c)^2/\phi_c]. \quad (3)$$

Combining this with the relation for $\phi(\alpha_T)$, we obtain $\ln[1 + (z - z_c)^2/\phi_c] = \alpha_T(T - T_c)$ and finally arrive at the condition $z - z_c = \sqrt{\phi_c[e^{\alpha_T(T_c - T)} - 1]}$. Substituting it in Eq. (2), we obtain

$$G_A - G_{NA} = \frac{2}{5\pi} \frac{\kappa}{R_0} \phi_c e^{\alpha_T(T_c - T)} \sqrt{\phi_c[e^{\alpha_T(T_c - T)} - 1]}. \quad (4)$$

According to this equation for the shear modulus $G(T)$, nonaffinity alone (induced by disorder) causes the melting at a critical point T_c with the scaling $\sim \sqrt{T_c - T}$, even without the effects of thermal vibrations on the rigidity. By including the effect of thermal phonons in the same way as was done in Eq. (1), the full expression for $G(T)$ becomes

$$G = \frac{2}{5\pi} \left(\frac{\kappa}{R_0} \phi_c e^{\alpha_T(T_c - T)} \sqrt{\phi_c[e^{\alpha_T(T_c - T)} - 1]} - \frac{kT}{R_0^3} e^{-\alpha_T T} \right). \quad (5)$$

To assess the interplay and relative magnitude of nonaffinity and thermal phonons, it is important to have an expression for the critical point T_c in terms of parameters used in this analysis. Since T_c is, in effect, the glass transition temperature, the task of finding it explicitly for a general system remains challenging. However, since our comparison will be with a particular experimental system of polymeric glass, we can in fact offer an expression in such a case.

For polymer chains of n units, the average connectivity due to covalent bonds is close to 2: $z_{co} = 2(1 - 1/n)$, while the total coordination number is $z = z_{co} + z_{LJ}$. Unlike the LJ, which are central forces, the covalent bonds put a constraint on the bond angle [32]. The classical Phillips-Thorpe analysis of marginal stability [33,34] gives the fraction of floppy modes $f = N_{floppy}/3N$ in a purely covalent network: $f = 1 - 1/3[(1/2)z_{co} + (2z_{co} - 3)]$, where every z_{co}-coordinated monomer contributes $2z_{co} - 3$ bending constraints, in addition to $(1/2)z_{co}$ stretching constraints. We also need to add the LJ contact bonds into the counting. However, for these only the stretching constraints apply. As a result, the fraction of floppy modes becomes

$$f = 1 - \frac{1}{3} \left(\frac{1}{2} z_{co} + [2z_{co} - 3] + \frac{1}{2} z_{LJ} \right). \quad (6)$$

Keeping z_{co} fixed, since it is T independent and fixed by the polymer chemistry, we set $f = 0$ in the above equation and solve for the critical value of z_{LJ} at the rigidity transition, obtaining $z_{LJ}^* = 12 - 5z_{co}$. Upon applying $z_c = z_{co} + z_{LJ}^*$, we obtain the critical value of the total connectivity z at which the rigidity is lost: $z_c = 12 - 4z_{co} = 12 - 8(1 - 1/n)$. In other words, in order for the amorphous polymer assembly to become a solid glass, there need to be at least $z_{LJ}^* = z_c - z_{co} = 12 - 5z_{co}$ LJ bonds established per monomer, in addition to the ordinary chain connectivity. For very long chains, the glass solidifies when $z_c = 4$, i.e., when each monomer acquires additional $z_{LJ}^* = 2$ physical bonds.

Now we convert z_c into the critical volume fraction ϕ_c, via $\phi_c = \phi_c^* - \Lambda z_{co}$, where ϕ_c^* is the packing fraction in the limit $z_{co} = 0$. If the attraction is weak or absent, as in a system of hard spheres, then $\phi_c^* \simeq 0.64$ as for the random packing. Finally, using the expression for $z_{co}(n)$ and $\phi_c = \exp(-\alpha_T T_c - C)$, and expanding the exponential to the linear order since in all cases one expects ϕ_c close to 1, we obtain an estimate for the glass transition temperature for chains with degree of polymerization n:

$$T_c \approx \frac{1}{\alpha_T}(1 - C - \phi_c^* + 2\Lambda) - \frac{2\Lambda}{\alpha_T n} \quad (7)$$
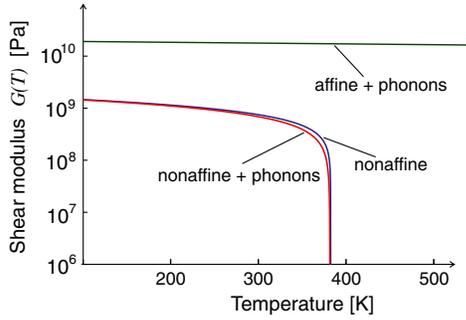
FIG. 3 (color online). Comparison of theoretical predictions from Eq. (5) (nonaffine + phonons), Eq. (4) (nonaffine athermal), and Eq. (1) (affine + phonons). We take $T_c = 383$ K, $R_0 = 0.3$ nm, $\alpha_T = 2 \times 10^{-4}$ K^{-1}, as for polystyrene, $\phi_c = \phi_c^* - \Lambda z_{co} = 0.44$, and the spring constant $\kappa = 50$ N/m.

(the full expression will involve the logarithm, but we find the linear-order expansion adequate). The first term is what remains for very long chains ($n \gg 2\Lambda/\alpha_T$). The expression (7) provides a theoretical foundation for the empirical dependence of the glass transition on n, first discussed by Flory [35,36]. For common polymers, the experimental values of the factor $2\Lambda/\alpha_T$ [35,36] are of the order of 10^3 K, and hence $\Lambda \simeq 0.1$. If we take $T_c \simeq 383$ K, as for polystyrene glass used in the experimental comparison below, this gives a reasonable value of $C \simeq 0.48$. This value implies that $\phi \simeq 0.61 e^{-\alpha_T T}$, in dense amorphous polystyrene, justifying the expansion above.

In Fig. 3, we have plotted predictions of different theories for the shear modulus $G(T)$ using the parameters of amorphous polystyrene, taking $n = 200$ [21]. It is evident that nonaffinity is the main effect driving the melting transition, whereas thermal phonons have practically no effect on the qualitative behavior of the melting curve. If nonaffinity is neglected, the transition would be shifted to unrealistic, enormously high temperatures. Accordingly, the main prediction of our theory, Eq. (5), has an interesting behavior on approaching the glass transition from the solid side: There is a square-root cusp singularity $G \sim \sqrt{T_c - T}$ that is added to a small contribution due to phonons. The origin of this scaling lies in the relationship $\delta z \sim \sqrt{\delta \phi}$ arising from the integral of the rdf [24,25]. Exactly this singularity has been recently reported in numerical simulations of the melting of colloidal glasses [20].

Finally, Fig. 4 shows the comparison of our theory prediction for the melting of amorphous polystyrene with the classical experimental data of Schmieder and Wolf [21], reported also in Ferry's monograph as representative of the quasistatic, low-frequency $G(T)$ in the glassy solid state [37]. As discussed by Ferry, the catastrophic drop of G at the critical point is the hallmark of the low-frequency (static) response, whereas at higher frequency the drop becomes more gradual.

The value of the fitting parameter, the spring constant $\kappa \approx 52$ N/m, is very sensible: It corresponds to the C-C
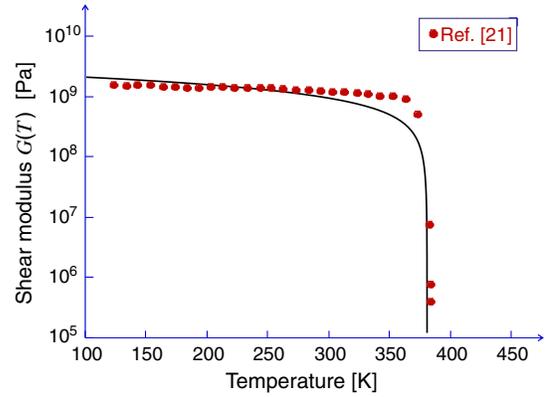

FIG. 4 (color online). Theoretical fit of the experimental data for amorphous polystyrene using Eq. (5) and the same values for parameters as in Fig. 3, including $T_c = 383$ K, and fitting for the single parameter the spring constant $\kappa = 52$ N/m. The experimental data were taken at a frequency of 0.9 Hz.

covalent bond enthalpy 350 kJ/mol over a distance of 0.15 nm, which is almost exactly the C-C bond length (0.146 nm). More importantly, the theory can reproduce the qualitative behavior of the experimental curve and the criticality (that are found also with many other polymers [21,37]) very well indeed. No alternative theory is available in the literature for the mechanical response of amorphous polymers at $T < T_g$ (in contrast, at $T > T_g$, the reptation theory of de Gennes, Doi, and Edwards [38] provides a good understanding of viscoelasticity of polymer melts).

Plastic rearrangements may play an important role across the transition when the local mechanical rigidity is lost. These effects deserve more detailed investigation in future studies, although they seem not to affect the comparison with the data in this case. A further caveat is about our use of the harmonic interaction potential to estimate the nonaffine contribution [39] which appears to define the melting transition. It is a typical approximation used in the theory of solids where the binding energy is strong; however, one expects anharmonic corrections to contribute to the central LJ potentials near the glass transition point. Accordingly, the accuracy of our theory at $T \simeq T_c$ could be questioned, even though the agreement with simulations and experiment is encouraging.

In practice, our theory can be used to reconstruct the thermoelastic behavior of glassy polymers at $T < T_g$, something which has not been possible so far, in the same way as the Williams-Landel-Ferry theory [37] is used for the viscosity at $T > T_g$. The theory may be extended in the future to model the melting curves of inorganic materials, such as amorphous oxides, semiconductors, and metallic glasses, where the thermal phonons play a more important role in view of the much higher T_c.

P H Y S I C A L   R E V I E W   L E T T E R S

week ending
26 APRIL 2013

[1] G. Adam and J. H. Gibbs, J. Chem. Phys. **43,** 139 (1965); E. A. DiMarzio and J. H. Gibbs, J. Polym. Sci. **40,** 121 (1959); J. Polym. Sci. A **1,** 1417 (1963).
[2] M. Born, J. Chem. Phys. **7,** 591 (1939).
[3] S. F. Edwards and M. Warner, Philos. Mag. A **40,** 257 (1979).
[4] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, England, 1995).
[5] B. J. Siwick, J. R. Dwyer, R. E. Jordan, and R. J. D. Miller, Science **302,** 1382 (2003).
[6] S. Angioletti-Uberti, B. Mognetti, and D. Frenkel, Nat. Mater. **11,** 518 (2012).
[7] S. Rastogi, D. R. Lippits, G. W. M. Peters, R. Graf, Y. F. Yao, and H. W. Spiess, Nat. Mater. **4,** 635 (2005).
[8] L. Brillouin, Phys. Rev. **54,** 916 (1938).
[9] J. Frenkel, *Kinetic Theory of Liquids* (Clarendon, Oxford, 1946).
[10] P. C. Martin, O. Parodi, and P. S. Pershan, Phys. Rev. A **6,** 2401 (1972).
[11] S. Alexander, Phys. Rep. **296,** 65 (1998).
[12] B. A. DiDonna and T. C. Lubensky, Phys. Rev. E **72,** 066619 (2005).
[13] A. Tanguy, J. P. Wittmer, F. Leonforte, and J.-L. Barrat, Phys. Rev. B **66,** 174205 (2002).
[14] D. A. Head, A. J. Levine, and F. C. MacKintosh, Phys. Rev. Lett. **91,** 108102 (2003).
[15] H. Yoshino and M. Mezard, Phys. Rev. Lett. **105,** 015504 (2010); H. Yoshino, J. Chem. Phys. **136,** 214108 (2012).
[16] W. Goetze, *Complex Dynamics of Glass-Forming Liquids: A Mode-Coupling Theory* (Oxford University, Oxford, 2009).
[17] M. Siebenburger, M. Fuchs, H. Winter, and M. Ballauff, J. Rheol. **53,** 707 (2009); G. Szamel and E. Flenner, Phys. Rev. Lett. **107,** 105505 (2011).
[18] J. L. Barrat, J. N. Roux, J. P. Hansen, and M. L. Klein, Europhys. Lett. **7,** 707 (1988).
[19] C. L. Klix, F. Ebert, F. Weysser, M. Fuchs, G. Maret, and P. Keim, Phys. Rev. Lett. **109,** 178301 (2012).
[20] J. P. Wittmer, H. Xu, P. Polińska, F. Weysser, and J. Baschnagel, J. Chem. Phys. **138,** 12A533 (2013).
[21] K. Schmieder and K. Wolf, Kolloid Z. **134,** 149 (1953).
[22] A. Zaccone, J. Phys. Condens. Matter **21,** 285103 (2009).
[23] F. Puosi and D. Leporini, J. Chem. Phys. **136,** 041104 (2012).
[24] M. Wyart, Ann. Phys. (Paris) **30,** 1 (2005).
[25] C. S. O'Hern, L. E. Silbert, A. J. Liu, and S. R. Nagel, Phys. Rev. E **68,** 011306 (2003).
[26] L. Berthier, H. Jacquin, and F. Zamponi, Phys. Rev. E **84,** 051103 (2011).
[27] F. A. Lindemann, Phys. Z. **11,** 609 (1910).
[28] A. Lemaitre and C. Maloney, J. Stat. Phys. **123,** 415 (2006).
[29] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, Oxford, 1976).
[30] A. Zaccone and E. Scossa-Romano, Phys. Rev. B **83,** 184205 (2011).
[31] A. Zaccone, J. R. Blundell, and E. M. Terentjev, Phys. Rev. B **84,** 174119 (2011).
[32] A. Zaccone, Mod. Phys. Lett. B **27,** 1330002 (2013).
[33] J. C. Phillips, J. Non-Cryst. Solids **34,** 153 (1979).
[34] H. He and M. F. Thorpe, Phys. Rev. Lett. **54,** 2107 (1985).
[35] L. H. Sperling, *Introduction to Physical Polymer Science* (Wiley, New York, 2006).
[36] T. G. Fox and P. J. Flory, J. Appl. Phys. **21,** 581 (1950).
[37] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980), 3rd ed.
[38] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
[39] J. F. Lutsko, J. Appl. Phys. **65,** 2991 (1989).

178002-5