

Resolving vibrational and structural contributions to isothermal compressibility

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The well-known and general “compressibility theorem” for pure substances relates $\kappa_T = -(\partial \ln V/\partial p)_{N,T}$ to a spatial integral involving the pair correlation function $g^{(2)}$. The isochoric inherent structure formalism for condensed phases separates $g^{(2)}$ into two fundamentally distinct contributions: a generally anharmonic vibrational part, and a structural relaxation part. Only the former determines κ_T for low-temperature crystals, but both operate in the liquid phase. As a supercooled liquid passes downward in temperature through a glass transition, the structural contribution to κ_T switches off to produce the experimentally familiar drop in this quantity. The Kirkwood–Buff solution theory forms the starting point for extension to mixtures, with electroneutrality conditions creating simplifications in the case of ionic systems. © 1998 American Institute of Physics. [S0021-9606(98)50634-4]

I. INTRODUCTION

The fundamental task of statistical mechanics is to relate macroscopic observables to molecular-level properties. One of the notable connections of this sort, usually derived in the grand canonical ensemble context, expresses the isothermal compressibility κ_T in terms of number (or density) fluctuations,¹

$$k_B T \kappa_T / V = \langle (N - \langle N \rangle)^2 \rangle / \langle N \rangle^2. \quad (1.1)$$

Here N , V , k_B , and T have their usual meanings as numbers of molecules, system volume, Boltzmann’s constant, and absolute temperature; and

$$\kappa_T = -(1/V)(\partial V/\partial p)_{N,T}. \quad (1.2)$$

Apparently Ornstein and Zernike² were the first to recast the right member of Eq. (1.1) as a spatial integral involving the two-point density–density correlation function. In modern terminology^{3,4} this transforms Eq. (1.1) into

$$\rho k_B T \kappa_T = 1 + \rho \int [g^{(2)}(r) - 1] d\mathbf{r}, \quad (1.3)$$

where $\rho = \langle N \rangle / V$ is the mean number density, and $g^{(2)}$ is the molecular pair correlation function. The integral in this last expression covers all space, and $g^{(2)}$ is to be interpreted as the infinite-system limit function. The compressibility relation (1.3) is noteworthy in that it contains no explicit appearance of molecular interactions.

Most applications that use relation (1.3) involve liquids under conditions of thermal equilibrium. Deviations of $g^{(2)}(r)$ from its asymptote unity denote short-range order in the arrangement of molecules comprised in the liquid, as well as long-ranged density fluctuations if the fluid system exists near a critical point. The relation is equally true for quantum fluids as it is for classical fluids, provided for the

former that $g^{(2)}$ is obtained from the diagonal elements of the pair density matrix.⁵ Although certain delicacies of interpretation are involved, we point out below that the compressibility relation (1.3) also applies to the crystalline solid phase.

Measured κ_T values for common liquids vary considerably, but normally increase with temperature at constant pressure.⁶ Water is exceptional, with κ_T declining with increasing temperature below 46 °C at atmospheric pressure.^{6,7} No doubt such a distinction enjoyed by water arises from its peculiar intermolecular interactions and the characteristic open structures they produce at low enough temperatures and pressures. That situation highlights the desirability of isolating specific structural contributions to κ_T for water, and indeed for all liquids regardless of whether they are conventional or unusual. This paper provides a theoretical strategy for effecting that separation.

The following Sec. II shows that by casting the problem in the language of inherent structures, there emerge naturally two contributions to κ_T , one structural and one “vibrational.” Section III applies this separation to the low-temperature crystal, for which inherent structure is substantially unique, and the vibrational effects are described in terms of noninteracting harmonic normal modes (phonons). Section IV considers the extension of compressibility relation (1.3) to supercooled liquids and to the glasses they form below a glass transition temperature. Finally, Sec. V offers some discussion of related problems, and some conclusions. An Appendix contains technical details for a simple Debye-spectrum analysis of the vibrational contribution to compressibility.

II. ROLE OF INHERENT STRUCTURES

Although generalization to more complex materials presents no basic problems, for simplicity we will restrict atten-

tion to the case of structureless (spherically symmetric) particles. Let $\Phi_N(\mathbf{r}_1 \cdots \mathbf{r}_N)$ be the potential energy function for interaction among the N particles when they are located at positions $\mathbf{r}_1 \cdots \mathbf{r}_N$. By constructing a steepest-descent path for the Φ_N hypersurface, any system configuration $\mathbf{r}_1 \cdots \mathbf{r}_N$ (with only zero-measure exceptions) can be mapped uniquely onto the corresponding “quenched” configuration $\mathbf{r}_{1q} \cdots \mathbf{r}_{Nq}$ of an inherent structure.^{8–11} More specifically, the constant-volume steepest descent equations

$$d\mathbf{r}_i(s)/ds = \nabla_i \Phi_N[\mathbf{r}_1(s) \cdots \mathbf{r}_N(s)] \quad (1 \leq i \leq N) \quad (2.1)$$

for $s \geq 0$, with $\mathbf{r}_1 \cdots \mathbf{r}_N$ as initial conditions, converge to the quenched configuration $\mathbf{r}_{1q} \cdots \mathbf{r}_{Nq}$ as s approaches infinity. The set of all system configurations that map to the same Φ_N minimum constitutes the basin of attraction for that minimum. The mapping itself serves to remove intrabasin “vibrational” displacements that have taken the particles away from positions of mechanical equilibrium, and that may indeed be quite anharmonic in some cases.

We can imagine subjecting each representative configuration from the ensemble that produced $g^{(2)}(r)$ to the steepest descent mapping. The resulting collection of quenched configurations offers a representative sampling of inherent structures for the initial thermodynamic state, and possesses its own quenched pair correlation function $g_q^{(2)}(r)$. By construction, this process removes the influence of vibrational deformation from the pattern of short-range order. Past experience^{12–17} has revealed that $g_q^{(2)}(r)$ tends to exhibit a strongly enhanced vision of short-range order in comparison with $g^{(2)}(r)$.

Equation (1.3) trivially transforms into the following:

$$\rho k_B T \kappa_T = 1 + \rho \int [g_q^{(2)}(r) - 1] d\mathbf{r} + \rho \int \Delta g^{(2)}(r) d\mathbf{r}, \quad (2.2)$$

where

$$\Delta g^{(2)}(r) = g^{(2)}(r) - g_q^{(2)}(r) \quad (2.3)$$

represents the effect of purely vibrational “smoothing” of short-range molecular order, and for fluids at least is likely to diminish to near zero beyond third or fourth neighbor shells. The first term, unity, in the right member, is a pure kinetic contribution to κ_T ; the following integral captures the entirety of the structural component; and the last, integral term provides the vibrational part of κ_T .

III. CRYSTAL COMPRESSIBILITY

Although the compressibility relation, (1.1) or (1.2), is usually invoked in connection with fluid state studies, it is valid for all equilibrium phases. In particular it describes the crystal phase (or phases) that obtains for any pure substance (exclusive of He at low pressure) at sufficiently low temperature. For crystals, κ_T is but one of several isothermal elastic constants, the number of which depends on the symmetry of the crystalline phase (3 for cubic symmetry, up to 18 for triclinic symmetry¹⁸).

If absolute temperature T is sufficiently low, the inherent structure of the crystal will be substantially unique (particle permutations are irrelevant in the present context), and will

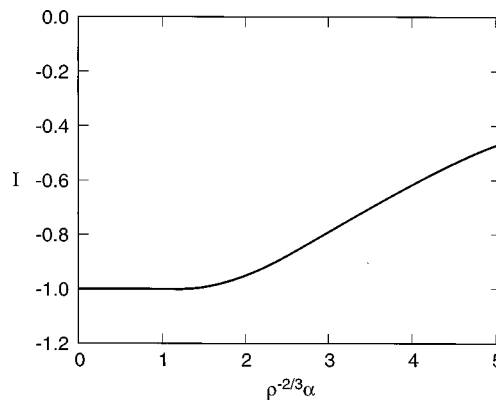


FIG. 1. Plot of the quantity $I(\rho^{-2/3}\alpha)$ defined in Eq. (3.3), for the specific case of the face-centered cubic lattice.

correspond to the absolute minimum of the potential energy function. Vibrations are the familiar phonons of solid state physics,¹⁹ and can be viewed accurately as independent harmonic normal modes of motion.

The geometric structure of the perfect crystal may be characterized by distances r_ν and coordination numbers Z_ν for the successive shells of neighbors ($\nu = 1, 2, \dots$) around any particle. Assuming that only one crystallographic particle type occurs in the lattice, $g_q^{(2)}$ will then have the following form:

$$g_q^{(2)}(r) = (4\pi\rho)^{-1} \sum_{\nu=1}^{\infty} Z_\nu r_\nu^{-2} \delta(r - r_\nu), \quad (3.1)$$

in other words a suitably weighted radial Dirac delta function for each coordination shell. The presence of such singular terms in Eq. (3.1) nominally seems problematic for convergence of the integrals in Eq. (2.2) that contain $g_q^{(2)}$. However, we can properly assure convergence by reinterpreting Eq. (2.2) in the following manner:

$$\rho k_B T \kappa_T = 1 + \rho \lim_{\alpha \rightarrow 0^+} \int \exp(-\alpha r^2) [g_q^{(2)}(r) - 1] d\mathbf{r} + \rho \lim_{\alpha \rightarrow 0^+} \int \exp(-\alpha r^2) \Delta g^{(2)}(r) d\mathbf{r}. \quad (3.2)$$

The first integral in the right member of the last equation can readily be evaluated numerically, as a function of convergence parameter α , for any simple lattice. Using expression (3.1), this integral reduces as follows:

$$\begin{aligned} I(\rho^{-2/3}\alpha) &\equiv \rho \int \exp(-\alpha r^2) [g_q^{(2)}(r) - 1] d\mathbf{r} \\ &= \sum_{\nu} Z_\nu \exp(-\alpha r_\nu^2) - \rho(\pi/\alpha)^{3/2}. \end{aligned} \quad (3.3)$$

Figure 1 displays I for the face-centered cubic lattice, showing how this quantity converges rapidly to -1 as $\alpha > 0$ declines toward 0. The same behavior has been observed for other lattices with other symmetries, and merely illustrates the “missing particle phenomenon.” The function $g_q^{(2)}$ includes a contribution from every particle in the periodic lattice except for the one at the origin; consequently,

$$\lim_{\alpha \rightarrow 0^+} I(\rho^{-2/3}\alpha) = -1. \quad (3.4)$$

Owing to the last result, Eq. (3.4), we expect cancellation of the first two terms in the right member of Eq. (3.2), when T is sufficiently low that the perfect crystal obtains. Equilibrium concentrations of point defects (specifically vacancies and interstitials) appear in crystals, but even just below the melting point their concentrations are typically very low on a per-lattice-site basis.²⁰ Furthermore, point defects have a positive creation energy ε , so their concentrations should be dominated by Boltzmann factors $\exp(-\varepsilon/k_B T)$, vanishing more strongly as $T \rightarrow 0$ than any positive power of T . The consequence of these considerations is that in the low-temperature limit, the isothermal compressibility of the crystal must emerge strictly from the vibrational contribution integral in Eq. (3.2),

$$\kappa_T = \lim_{\alpha \rightarrow 0^+} (k_B T)^{-1} \int \exp(-\alpha r^2) \Delta g^{(2)}(r) dr. \quad (3.5)$$

It is easy to see that the integral in Eq. (3.5) must be proportional to $k_B T$, thereby cancelling the inverse of this factor which multiplies it, and leaving a finite κ_T for the crystal in the low-temperature limit. The integral measures the local accumulation (or reduction) in matter about a central particle due to the action of independent normal modes. Consequently, we must be able to write (compare results in the Appendix),

$$\int \exp(-\alpha r^2) \Delta g^{(2)}(r) dr = \sum_{\mu} C_{\mu}(\alpha) \langle a_{\mu}^2 \rangle, \quad (3.6)$$

where μ indexes the normal modes, whose amplitudes are given by the a_{μ} , respectively. The weights $C_{\mu}(\alpha)$ depend on the mode wave vectors and polarizations, and in particular will vanish for pure transverse waves. Equation (3.6) recognizes that the local density fluctuation effect sought must depend on amplitude squared. The thermal averages involved have the form

$$\langle a_{\mu}^2 \rangle = \frac{\int a_{\mu}^2 \exp(-K_{\mu} a_{\mu}^2 / 2k_B T) da_{\mu}}{\int \exp(-K_{\mu} a_{\mu}^2 / 2k_B T) da_{\mu}} = k_B T / K_{\mu}, \quad (3.7)$$

where K_{μ} is a restoring-force constant for mode μ . Substituting from Eqs. (3.7) and (3.6), one sees that the factor $(k_B T)^{-1}$ is cancelled in Eq. (3.5) to leave the formal expression for low-temperature crystal compressibility,

$$\kappa_T = \sum_{\mu} C_{\mu}(0) / K_{\mu}. \quad (3.8)$$

IV. SUPERCOOLED LIQUIDS AND GLASSES

In contrast to the perfect crystal case examined in the preceding Sec. III, application of steepest-descent quenching to the liquid phase generates a diverse collection of amorphous inherent structures.^{13-15,21} This is true whether the liquid is in a strict equilibrium state (i.e., above its melting temperature T_m), or is supercooled ($T < T_m$). The irregularity of the inherent structures as well as their diversity causes the corresponding $g_q^{(2)}(r)$ to be smooth and continuous as a

function of r , just as is its precursor $g^{(2)}(r)$. In particular this means that both $g_q^{(2)}$ and $g^{(2)}(r)$ smoothly approach unity with increasing r , so that the convergence-assuring limit operation invoked earlier in Eq. (3.2) is no longer necessary. Hence we can revert to Eq. (2.2) for separation of vibrational and inherent structural contributions to isothermal compressibility in liquids.

Under conventional circumstances, metastable supercooled liquids have finite (but often very long) lifetimes before they succumb to phase-changing nucleation events. This permits experiment to characterize supercooled liquids by a substantial variety of reproducible measurements.²² The theory for the quasiequilibrium states of liquid supercooling is considerably simplified by introducing constraints that force the many-particle system to remain permanently in that portion of the multidimensional configuration space that corresponds to non-nucleated (crystallite-free) inherent structures.^{9,11} Application of these mathematical constraints converts the quasiequilibrium status to true equilibrium status, while causing virtually no effect on reproducibly measurable properties of the liquid. We shall assume that such constraints are present for the remainder of this section.

The virial equation of state for the pressure is affected by the presence of constraints. Specifically, constraints designed to stabilize supercooled liquids generate an extra term in the equation of state beyond those conventionally occurring.²³ If κ_T were to be obtained via this route, performing the necessary partial derivative required by its definition Eq. (1.2), the constraint would continue to make an explicit appearance in the result. Equations (1.3) and (2.2), however, stand in refreshing contrast; provided the correct pair correlation function for the constrained ensemble is used, no such explicit constraint contributions are needed to evaluate κ_T .

The fundamental diversity of inherent structures quenched from the liquid phase carries with it a corresponding fluctuation in number density. Put simply, amorphous packings incorporate distinct regions that deviate substantially above as well as below the overall number density, owing to the vast number of ways that mechanically stable arrangements of particles can be achieved.^{23,24} This contrasts with the single, uniform density, inherent structure characterizing the low-temperature crystal described in the preceding section. As a result of this density fluctuation we now expect to find

$$1 + \rho \int [g_q^{(2)}(r) - 1] dr > 0 \quad (4.1)$$

for the liquid, as opposed to 0 for the perfect crystal implied by Eq. (3.4).

As the temperature of a supercooled liquid declines through its glass transition at T_g , the isothermal compressibility suddenly drops. The change can involve a factor of 2 or more.²⁵ The generally accepted explanation of the glass transition and associated phenomena is that the many-particle system becomes kinetically trapped in a small portion of the available configuration space.²² In the present inherent structure representation, this means that the $T > T_g$ quasiergodic sampling of the amorphous, constrained, region of configuration space ceases below T_g . At most, the low-

temperature glass can explore only a tiny subset of all steepest-descent basins. In particular, this subset would be connected across low potential energy barriers that are associated with the localized switching of small groups of particles, the so-called two-level systems.^{26,27}

The capacity of the many-particle system to experience structure-related density fluctuations thus is “frozen out” for $T < T_g$. This leaves only the vibrational contribution to κ_T operative in the glass state, analogous to the situation found in the preceding section for the low-temperature crystal [cf. Eq. (3.5)]. Consequently, the sudden drop in κ_T at T_g can be identified,

$$\Delta\kappa_T = \kappa_T^{(c)} - \kappa_T^{(g)} = (k_B T_g)^{-1} \left\{ 1 + \int [g_q^{(2)}(r) - 1] d\mathbf{r} \right\}. \quad (4.2)$$

Therefore, in the glass we have

$$\kappa_T^{(g)} = (k_B T)^{-1} \int \Delta g^{(2)}(r) d\mathbf{r} \quad (T < T_g). \quad (4.3)$$

An Appendix supplies a simple Debye-spectrum estimate for this remaining contribution, the vibrational compressibility.

V. CONCLUDING REMARKS

The analysis presented above concerns isothermal compressibility in a single-component system, for which basic relation (1.3) is appropriate. The generalization of that relation to multicomponent solutions of nonelectrolytes appears in the Kirkwood–Buff solution theory,²⁸

$$k_B T \kappa_T = |B| / \sum_{\lambda, \mu} \rho_\lambda \rho_\mu |B|_{\lambda\mu}. \quad (5.1)$$

Here λ and μ index species whose number densities are ρ_λ and ρ_μ , respectively. The determinant $|B|$ is composed of elements

$$B_{\lambda\mu} = \rho_\lambda \delta_{\lambda\mu} + \rho_\lambda \rho_\mu \int [g_{\lambda\mu}^{(2)}(r) - 1] d\mathbf{r}, \quad (5.2)$$

and $|B|_{\lambda\mu}$ is the cofactor of element $B_{\lambda\mu}$. The component-specific pair correlation functions have been denoted in obvious fashion by $g_{\lambda\mu}^{(2)}$. Equation (5.1) clearly reduces to Eq. (1.3) in the one-component case.

Vibrational and inherent-structural contributions to the multicomponent κ_T can be distinguished in analogy to the same separation for the single-component analysis. Replacing the $g_{\lambda\mu}^{(2)}$ in Eq. (5.2) with corresponding “quenched” pair correlation functions $g_{\lambda\mu q}^{(2)}$ produces determinant elements $B_{\lambda\mu q}$, and so the inherent-structural part of the solution compressibility has the form,

$$k_B T \kappa_{Tq} = |B_q| / \sum_{\lambda, \mu} \rho_\lambda \rho_\mu |B_q|_{\lambda\mu}. \quad (5.3)$$

The vibrational contribution is the difference in values given by Eqs. (5.1) and (5.3) which, however, does not have a simple expression in terms of the $\Delta g_{\lambda\mu}^{(2)}$.

Ionic systems present a significant exception. Formally they are mixtures, but the long-range Coulomb interactions they possess profoundly influence density fluctuations. In

particular, ionic systems are subject to local electroneutrality conditions, and to a “second moment” or “perfect shielding” condition, on the pair correlation functions.²⁹ The first of these leads to the result

$$\rho_+^{-1} + \int [g_{++}^{(2)}(r) - 1] d\mathbf{r} = \rho_-^{-1} + \int [g_{--}^{(2)}(r) - 1] d\mathbf{r}. \quad (5.4)$$

Because the anions (–) and cations (+) are forced to fluctuate together, either species can be used separately to calculate κ_T . Consequently, $k_B T \kappa_T$ can be expressed either as the left or the right member of Eq. (5.5). This reduction to single-component format means that the analysis of the preceding Secs. I and IV is directly applicable to the single-salt systems.

The constant-volume heat capacity C_v can be viewed as the energy fluctuation analog of κ_T . In the canonical ensemble,³⁰

$$N k_B T^2 c_v = \langle (E - \langle E \rangle)^2 \rangle, \quad (5.5)$$

a relation similar to Eq. (1.1) for κ_T . Not surprisingly, then, c_v can also be separated into vibrational and inherent-structural contributions. This is obvious given that the Helmholtz free energy F has the same kind of separation in its inherent structure representation,^{8,9}

$$F/Nk_B T = (F_q + F_v)/Nk_B T. \quad (5.6)$$

The inherent-structural portion F_q is a linear combination of a mean “quenched” potential energy ϕ_q , and a basin enumeration function σ defined so that $\exp(N\sigma)$ gives their distribution versus depth,¹¹

$$F_q/Nk_B T = \phi_q/k_B T - \sigma(\phi_q), \quad (5.7)$$

$$\phi_q = \langle \Phi_q \rangle / N.$$

The vibrational part, F_v , is just the conventional intrabasin vibrational free energy for those inherent structures whose potential energy per particle lies at depth ϕ_q . Consequently, we have

$$\begin{aligned} c_v/k_B &= -(T/Nk_B) [\partial^2 (F_q + F_v) / \partial T^2]_v \\ &\equiv (c_{vq} + c_{vv}) / k_B. \end{aligned} \quad (5.8)$$

Upon passing downward in temperature through a glass transition, the inherent-structural contribution suffers a dynamical switching off, thus producing a drop in c_v .

Other thermodynamic quantities of interest in connection with glass transitions are the thermal expansion coefficient α_p and the isobaric heat capacity c_p . Both of these change abruptly as the material is cooled across its glass transition.^{22,31} These properties are also amenable to resolution into vibrational and inherent-structural contributions. However, this resolution proceeds most naturally in a constant-pressure quenching scenario that falls outside the scope of the present paper. We reserve this extension for subsequent study.

APPENDIX

Inherent structures prepared from the liquid phase by steepest-descent mapping are homogeneous, isotropic, amor-

phous solids, at least when viewed at the macroscopic length scale. Their elastic properties are specified by two constants, which can be chosen to be Young's modulus (E) and Poisson's ratio (σ). The present application requires isothermal versions of these elastic constants, E_T and σ_T . The isothermal compressibility for the isotropic amorphous medium is the combination,³²

$$\kappa_T = 3(1 - 2\sigma_T)/E_T. \quad (A1)$$

Finding exact vibrational normal modes and frequencies for an amorphous solid is difficult due to local disorder. However, the Debye continuum approximation^{33,34} affords a conveniently simple estimate for present purposes. In this approach all modes are treated as spatially extended sinusoidal waves with either pure longitudinal or pure transverse character. Only the former type can contribute to density fluctuations.

A typical longitudinal mode, with wave vector \mathbf{k} and amplitude $A(\mathbf{k})$, possesses a displacement field

$$\mathbf{u}(\mathbf{r}) = A(\mathbf{k}) \sin(\mathbf{k} \cdot \mathbf{r}) \mathbf{u}_k, \quad (A2)$$

$$\mathbf{u}_k = \mathbf{k}/|\mathbf{k}|$$

The corresponding density variation is

$$\delta\rho(\mathbf{r}) = -\rho k A(\mathbf{k}) \cos(\mathbf{k} \cdot \mathbf{r}), \quad (A3)$$

and the energy increment required to produce this disturbance is³⁵

$$\delta E(\mathbf{k}) = \frac{E_T(1 - \sigma_T) V k^2 A^2(\mathbf{k})}{4(1 + \sigma_T)(1 - 2\sigma_T)}, \quad (A4)$$

where V is the system volume. It is necessary to impose an upper limit k_{\max} on wave vector magnitude that is inversely proportional to the mean nearest-neighbor spacing in the amorphous medium.

Next, calculate the spatial correlation of density fluctuations due to the linear superposition of independent longitudinal modes, and perform a thermal average,

$$\begin{aligned} \langle \delta\rho(0) \delta\rho(\mathbf{r}) \rangle &= \rho^2 \sum' k^2 \cos(\mathbf{k} \cdot \mathbf{r}) \langle A^2(\mathbf{k}) \rangle \\ &= \frac{2(1 + \sigma_T)(1 - 2\sigma_T) k_B T \rho^2}{E_T(1 - \sigma_T) V} \sum' \cos(\mathbf{k} \cdot \mathbf{r}). \end{aligned} \quad (A5)$$

Here the primed sum covers all contributing independent \mathbf{k} 's. Replacing the \mathbf{k} sum by an integral is appropriate for the large-system limit of interest, so Eq. (A5) becomes

$$\begin{aligned} \langle \delta\rho(0) \delta\rho(\mathbf{r}) \rangle &= \frac{(1 + \sigma_T)(1 - 2\sigma_T) k_B T \rho^2}{8\pi^3 E_T(1 - \sigma_T)} \\ &\quad \times \int_{k < k_{\max}} \cos(\mathbf{k} \cdot \mathbf{r}) d\mathbf{k} \\ &= \left[\frac{(1 + \sigma_T)(1 - 2\sigma_T) k_{\max}^3 \rho^2 k_B T}{2\pi^2 E_T(1 - \sigma_T)} \right] F(k_{\max} r). \end{aligned} \quad (A6)$$

Here the distance dependence is controlled by the function

$$F(u) = (\sin u - u \cos u)/u^3, \quad (A7)$$

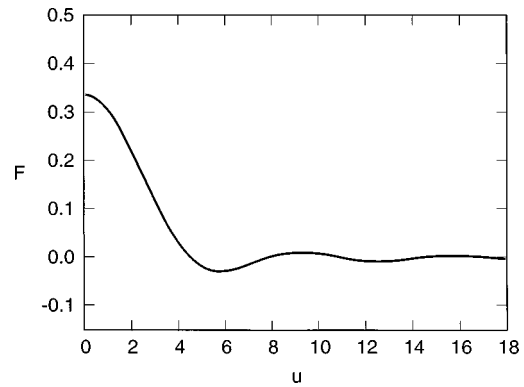


FIG. 2. Spatial dependence of local density enhancement estimated with longitudinal Debye-spectrum normal modes. The function F is defined in Eq. (A7).

which is plotted in Fig. 2. Notice that it implies substantial density enhancement at small separation, followed by algebraically damped oscillations at larger distances.

Connection with the main text of the paper, specifically with the separated form (2.2) of the compressibility relation, rests on the identification

$$\rho^{-1} \langle \delta\rho(0) \delta\rho(\mathbf{r}) \rangle \cong \rho \Delta g^{(2)}(r). \quad (A8)$$

Therefore the estimate of $\Delta n(R)$, the incremental average number of neighbors out to radius R due to vibrational deformations, is given by

$$\begin{aligned} \Delta n(R) &= \rho \int_{r < R} \Delta g^{(2)}(r) dr \\ &\cong \rho^{-1} \int_{r < R} \langle \delta\rho(0) \delta\rho(\mathbf{r}) \rangle dr \\ &= \frac{2(1 + \sigma_T)(1 - 2\sigma_T) \rho k_B T}{\pi E_T(1 - \sigma_T)} \\ &\quad \times [\text{Si}(k_{\max} R) - \sin(k_{\max} R)]. \end{aligned} \quad (A9)$$

Here $\text{Si}(u)$ is the sine integral function; as its argument increases to infinity it converges to $\pi/2$. However, in the same large-distance limit the sine function in Eq. (A9) continues to oscillate, an artifact due to the sharp cutoff assumed in \mathbf{k} space at k_{\max} . A more realistic approximation would replace the discontinuous cutoff with a continuous dropoff to zero, and would have the effect of damping out such oscillations at large R . A more formal route to the same conclusion would be to introduce either a simple exponential or a Gaussian convergence factor in the integrand of Eq. (A9). Then since

$$\lim_{a \rightarrow 0^+} \int_0^\infty \exp(-ax) \cos(mx) dx = 0, \quad (A10)$$

$$\lim_{a \rightarrow 0} \int_0^\infty \exp(-a^2 x^2) \cos(mx) dx = 0 \quad (A11)$$

for $m \neq 0$, it is clear that as R diverges to infinity the sine function in Eq. (A9) should be replaced by its average value zero.

In view of these considerations, we see that the Debye approximation implies

$$\Delta n(\infty) = \frac{(1 + \sigma_T)(1 - 2\sigma_T)\rho k_B T}{E_T(1 - \sigma_T)}. \quad (\text{A12})$$

If this expression is used in Eq. (4.3) to estimate the glass-phase isothermal compressibility, the result is the following:

$$\kappa_T^{(g)} = \left[\frac{(1 + \sigma_T)}{3(1 - \sigma_T)} \right] \left[\frac{3(1 - 2\sigma_T)}{E_T} \right]. \quad (\text{A13})$$

In view of identity (A1) the bracketed first factor should always be unity. However, it only attains this value when $\sigma_T = 1/2$. Deviations from unity for other σ_T reflect shortcomings of the simple Debye approximation. In spite of this shortcoming, the Debye approximation has the qualitative virtue of demonstrating the connection between vibrational normal modes and the compressibility relation.

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