

The Relationship Between the Elastic Constants and the Instantaneous Normal Modes of Liquids¹

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In the solid state the elastic properties of a substance are related quite simply and directly to its phonon spectrum. However, while it is well-known that liquids possess certain macroscopic elastic properties, their relationship with an analogous set of liquid phonons is far more tenuous. We show here that one candidate for what one might call the phonons of a liquid - its instantaneous normal modes - has a very precise connection with the liquid's high-frequency macroscopic elastic moduli. This connection suggests, moreover, that there is at least some plane-wave-like character to the short-time, long-wavelength dynamics of liquids.

KEY WORDS: elastic constants; instantaneous normal modes; liquids; phonons; short-time; sound speed.

1. INTRODUCTION

The parallel notions that viscosity and elasticity are two different sides of the same phenomenon and that ordinary liquids have to behave elastically at short enough times were first made precise through the efforts of Maxwell in 1867 [1, 2]. Nearly a century later, Zwanzig and Mountain [3] succeeded in putting these compelling ideas on a firm molecular footing. By starting with the Green-Kubo time-correlation function expression for the frequency-dependent viscosity and taking the high-frequency limit, they were able to provide equilibrium statistical mechanical expressions for infinite-frequency elastic constants, emphasizing that there could be nothing intrinsically solid-like about the ability to sustain either shear or compressional waves, at least at sufficiently high frequencies.

An alternative, and probably more natural, approach to the elastic properties of solids, however, relies strongly on the existence of phonons.

¹ Paper dedicated to Professor Edward A. Mason.

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The frequency of a given lattice vibration depends on the stiffness of the lattice—its elastic moduli. Hence it is hardly a surprise that one can extract elastic constants from phonon dispersion relations [4]. For an isotropic amorphous solid, for example, the frequencies ω of the longitudinal (L) and transverse (T) phonons as a function of wavevector \mathbf{k} , determine the longitudinal and transverse sound speeds c_L and c_T . In particular, at long wavelengths, we can write for a neat amorphous material that

$$\omega_{L,T}(k) = c_{L,T}k + \dots \tag{1}$$

where the sound speeds are simply related to the elastic constants c_{11} , c_{12} , and c_{44} ,

$$\begin{aligned} m\rho c_L^2 &= c_{11} = c_{12} + 2c_{44} \\ m\rho c_T^2 &= c_{44} \end{aligned} \tag{2}$$

with m the molecular mass and ρ the number density [4, 5]. Equivalent expressions are available in terms of the Lamé coefficients λ and μ or, equivalently, the bulk and shear moduli K and G :

$$\begin{aligned} m\rho c_L^2 &= \lambda + 2\mu = K + (4/3) G \\ m\rho c_T^2 &= \mu = G \end{aligned} \tag{3}$$

One can also rewrite these formulas by taking advantage of the Cauchy (central-force) condition which relates these elastic coefficients in a solid [4]

$$c_{12} = c_{44} \quad (\text{or equivalently, } \lambda = \mu \text{ or } K = (5/3) G) \tag{4}$$

The infinite-frequency versions of these elastic constants which are suitable for a liquid differ from their solid-state counterpart by virtue of some purely ideal-gas (kinetic energy) contributions [3]. However, if we define infinite-frequency *excess* elastic moduli

$$\begin{aligned} \Delta K_x &\equiv K_x - (5/3) \rho k_B T \\ \Delta G_x &\equiv G_x - \rho k_B T \end{aligned} \tag{5}$$

(with $k_B T$ Boltzmann's constant times the temperature), then a number of direct analogies are possible. Cauchy's condition, for example, becomes

$$\Delta K_x = (5/3) \Delta G_x + 2 \Delta p \tag{6}$$

where $\Delta p \equiv p - \rho k_B T$ is the corresponding excess in the pressure p .

From Zwanzig and Mountain's results [3] it is easy to show that these excess elastic constants can be written, for atomic fluids, in terms of simple integrals over the radial distribution function $g(r)$ and derivatives of the interatomic pair potentials $u(r)$,

$$\begin{aligned}\Delta K_{\epsilon} &= (1/18) \rho^2 \int d\mathbf{r}^2 g(r) [t_{\text{L}}(r) - 2t_{\text{T}}(r)] \\ \Delta G_{\epsilon} &= (1/30) \rho^2 \int d\mathbf{r}^2 g(r) [t_{\text{L}}(r) + 4t_{\text{T}}(r)] \\ t_{\text{L}} &\equiv u''(r), \quad t_{\text{T}}(r) \equiv u'(r)/r\end{aligned}\quad (7)$$

The question, though, is what connections can sensibly be made to phonons in a liquid setting. Unlike crystalline solids, there is no single, unambiguous way with which to define liquid phonons. There is no ideal crystal lattice about which to expand, nor is there any guarantee that long-lived, coherent, vibrational excitations with a well-defined wavevector will even exist in a liquid. Nonetheless, there have been numerous attempts at constructing liquid-state analogies with at least some of the features of crystalline phonons. With a few notable exceptions, however [6–17], these constructs have been prescriptions solely for characteristic liquid frequencies and not for specific molecular motions. Still, there have recently been two explicitly molecular approaches to liquid phonons that have begun to come under scrutiny: the instantaneous [15] and quenched [16] normal modes of liquids. (The differences and similarities between these formulations are explored in Ref. 17.) In this paper, we describe the direct relationship that exists between the precisely defined set of motions spelled out by the instantaneous normal modes [15] and the elastic behavior one would expect from a set of liquid phonons. In some sense, this work may also be viewed as a natural sequel to the previous explorations of the connection between the density fluctuations of liquids as a whole and liquid-state elastic properties [18–20].

2. INSTANTANEOUS NORMAL MODES AND PLANE WAVES

The idea behind instantaneous normal modes is that the matrix of second derivatives of the liquid's potential energy V evaluated at any instantaneous liquid configuration \mathbf{R}_0

$$(\mathbf{D})_{\mu, k\nu} \equiv (\partial^2 V / \partial r_{j\mu} \partial r_{k\nu})_{\mathbf{R}_0} \quad (j, k = 1, \dots, N; \mu, \nu = x, y, z) \quad (8)$$

(with $r_{j\mu}$ the μ th Cartesian coordinate of the j th atom) contains information about the independent collective vibrational motions appropriate at that specific moment in time. Though there are a number of non-solid-like features to these vibrations [15, 21, 22], the equilibrium distribution of the eigenvectors, \mathbf{e}_γ , of this matrix, along with the corresponding eigenvalues, $m\omega_\gamma^2$, ($\alpha = 1, \dots, 3N$ for N atoms) have been shown to describe the sub-picosecond dynamics of liquids reasonably well under ordinary thermodynamic conditions [23–25].

The geometrical characteristics of these eigenvectors are only now starting to be understood [26]. However, one can always look, as with the mathematically analogous quantum problem, at the eigenvalues corresponding to some trial vector that one suspects ought to be physically appropriate. Suppose we assume that we have an atomic liquid, for each configuration of which we define the normalized $3N$ -dimensional plane-wave-like vectors $\mathbf{e}_\gamma(\mathbf{k})$

$$[\mathbf{e}_\gamma(\mathbf{k})]_{j\mu} = (N)^{-1/2} e^{i\hat{\mathbf{k}} \cdot \mathbf{r}_j(\hat{\mathbf{k}})_\mu} \quad (9)$$

where the polarization γ is assumed to be in the longitudinal (L) or in one of the two equivalent transverse (T_1, T_2) directions as defined by three mutually perpendicular unit vectors $\hat{\mathbf{k}} \equiv \mathbf{k}/|\mathbf{k}|$, $\hat{\mathbf{k}}_1$, and $\hat{\mathbf{k}}_2$,

$$\hat{\mathbf{k}}_L \equiv \hat{\mathbf{k}}, \quad \hat{\mathbf{k}}_{T_1} \equiv \hat{\mathbf{k}}_1, \quad \hat{\mathbf{k}}_{T_2} \equiv \hat{\mathbf{k}}_2$$

The expectation value of the dynamical matrix, \mathbf{D} , with these vectors, when averaged over liquid configurations, gives an immediate prediction for the eigenvalues that would arise with plane-wave-like instantaneous normal modes

$$m\omega_\gamma^2(\mathbf{k}) = \langle \mathbf{e}_\gamma(\mathbf{k})^\dagger \cdot \mathbf{D} \cdot \mathbf{e}_\gamma(\mathbf{k}) \rangle \quad (\gamma = L, T_1, T_2) \quad (10)$$

To be more specific, with the aid of the standard formulas for the elements of \mathbf{D} in terms of the 3×3 potential-derivative tensor \mathbf{t} [27],

$$\mathbf{D}_{j\mu, kv} = \begin{cases} -[\mathbf{t}(\mathbf{r}_{jk})]_{\mu, v}, & j \neq k \\ \sum_{i (i \neq j)} [\mathbf{t}(\mathbf{r}_{ij})]_{\mu, v}, & j = k \end{cases}$$

$$\mathbf{t}(\mathbf{r}) \equiv t_T(r) \mathbf{1} + [t_L(r) - t_T(r)] \hat{\mathbf{r}}\hat{\mathbf{r}}$$

we can substitute Eqs. (8) and (9) into Eq. (10), letting us evaluate these eigenvalues in terms of the pair-potential derivatives

$$\begin{aligned} m\omega_{\mathbf{k}}^2(\mathbf{k}) &= \left\langle N^{-1} \sum_{i,j(i \neq j)} [1 - e^{-i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)}] \hat{\mathbf{k}}_i \cdot \mathbf{t}(\mathbf{r}_{ij}) \cdot \hat{\mathbf{k}}_j \right\rangle \\ &= \rho \int d\mathbf{r} g(r) (1 - e^{-i\mathbf{k} \cdot \mathbf{r}}) \{ t_{\mathbf{T}}(r) + (\hat{\mathbf{r}} \cdot \hat{\mathbf{k}})^2 [t_{\mathbf{L}}(r) - t_{\mathbf{T}}(r)] \} \end{aligned}$$

When we then perform the angular parts of the integrations, we find that these frequencies prescribe a longitudinal and a (doubly degenerate) transverse branch for our INM spectrum, with the dispersion relations depending only on the magnitude $k \equiv |\mathbf{k}|$ of the wave vector.

$$m\omega_{\mathbf{L}}^2(k) = \rho \int d\mathbf{r} g(r) \{ t_1(r) [1 - j_0(kr)] + 2t_2(r) j_2(kr) \} \quad (11)$$

$$m\omega_{\mathbf{T}}^2(k) = \rho \int d\mathbf{r} g(r) \{ t_1(r) [1 - j_0(kr)] - t_2(r) j_2(kr) \} \quad (12)$$

Here

$$\begin{aligned} t_1(r) &\equiv (1/3)[t_{\mathbf{L}}(r) + 2t_{\mathbf{T}}(r)] \equiv (1/3) \nabla^2 u(r) \\ t_2(r) &\equiv (1/3)[t_{\mathbf{L}}(r) - t_{\mathbf{T}}(r)] \equiv (1/3) \{ u''(r) - [u'(r)/r] \} \end{aligned} \quad (13)$$

and $j_0(x)$ and $j_2(x)$ are spherical Bessel functions [28].

Though the connection with instantaneous normal modes has never been elucidated before, Eqs. (11) and (12) are extraordinarily familiar. They have been derived in the context of other, completely different, approximations for liquid phonons by Schofield [6], by Zwanzig [7-9], by Hubbard and Beeby [10, 11], and by Takeno and Goda [12-14]. Moreover, the expressions for $\omega_{\mathbf{L}}^2$ and $\omega_{\mathbf{T}}^2$ as defined here are the *exact* second moments of the longitudinal and transverse current correlation functions, respectively [29]—so even independently of any approximation, these quantities have already been widely recognized as plausible candidates for liquid phonon frequencies. Typical numerical results from these formulas are shown in Fig. 1. Experience has shown that the longitudinal curve, in particular, is reasonably accurate in predicting the location of the peak in the longitudinal current correlation function [29], itself commonly regarded as experimental indicator of phonon frequency [30]. (Some more recent examples emphasizing the connection with solid-state phonons are given in Refs. 31 and 32.

We are now in a position to deduce the instantaneous-normal-mode prediction for elastic properties just by generalizing Eq. (1) to its liquid-

state equivalent: Expanding ω_L^2 and ω_T^2 to leading order in k^2 allows us to identify two excess sound speeds, Δc_L and Δc_T ,

$$\begin{aligned} \omega_{L,T}(k)^2 &= (\Delta c_{L,T})^2 k^2 + \dots \\ m(\Delta c_L)^2 &= (1/30) \rho \int d\mathbf{r} r^2 g(r) [3t_L(r) + 2t_T(r)] \\ m(\Delta c_T)^2 &= (1/30) \rho \int d\mathbf{r} r^2 g(r) [t_L(r) + 4t_T(r)] \end{aligned} \tag{14}$$

When we further try to relate these sound speeds to the excess elastic moduli via the liquid-state generalization of Eq. (3), it turns out that we can actually do so—and relevant moduli are *precisely* the infinite-frequency moduli

$$\begin{aligned} m\rho(\Delta c_L)^2 &= \Delta K_\infty + (4/3) \Delta G_\infty \\ m\rho(\Delta c_T)^2 &= \Delta G_\infty \end{aligned} \tag{15}$$

given in Eq. (7). Thus the longest-wavelength instantaneous normal modes—at least to the extent that they are genuinely plane-wave-like—are what determines the high-frequency limits of the macroscopic elastic moduli.

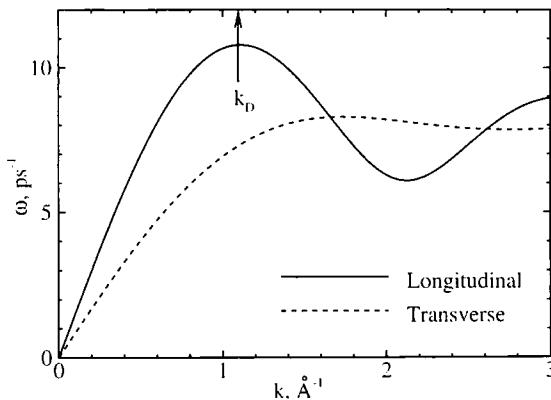


Fig. 1. The plane-wave predictions for instantaneous-normal-mode dispersion relations in a liquid, Eqs. (11) and (12). The arrow labeled k_D indicates the (Debye) maximum wavevector that would pertain if all $3N$ of the modes really were plane waves: $(6\pi^2)^{1/3} \rho = k_D^3$ [19, 22]. The calculations underlying these curves are for a Lennard-Jones liquid at a reduced density $\rho\sigma^3 = 0.8$ and a reduced temperature $k_B T/\epsilon = 1.06 \pm 0.02$, with the actual numerical values shown here derived by scaling with parameters appropriate to liquid Ar ($\sigma = 3.405$ Å, $\epsilon = 119.8$ K). The necessary radial distribution function was computed via a 500-particle molecular dynamics simulation.

3. CONCLUDING REMARKS

The observation that a plane-wave picture of instantaneous normal modes leads to the exact infinite-frequency bulk and shear elastic constants for a liquid is a bit surprising. For one thing, there is no reason to expect instantaneous normal modes to be all that plane-wave-like in an environment as disordered as a liquid. Certainly, at long enough wavelengths, liquids should resemble a featureless continuum in much the same way that amorphous solids do, meaning that plane waves should presumably provide an accurate representation of small k excitations. On the other hand, $D(\omega)$, the density of instantaneous normal modes, goes as ω near $\omega=0$ [27], reflecting a significant excess of modes over the Debye ω^2 dependence that one would have obtained if all of the modes were plane waves [33]. The vast majority of low ω instantaneous normal modes in liquids are evidently *not* plane-wave-like. Still, the $k=0$ limits of our trial vectors are, in fact, exact eigenvectors; the requirements of momentum conservation imply that these three zero-frequency modes correspond to net translation of the entire system [34, 35]. What the findings here suggest is that this plane-wave character must survive at least to wavelengths long enough for an expansion in powers of k to be correct through order k^2 . To go beyond this order, we would no doubt have to allow formally for a *distribution* of k values for each mode—that is, we would have to incorporate matrix elements of the dynamical matrix off-diagonal in k [36].

The second noteworthy point is that the long-wavelength excitations that we do see end up being infinite-frequency excitations. It makes a great deal of sense that an instantaneous approach to a phonon spectrum should correlate with infinite-frequency behavior. But our observation is that the *lowest*-frequency instantaneous normal modes are what correlates with the particular infinite-frequency response we are singling out. The question therefore arises as to what, if anything, can be made of the modes that are slightly higher in frequency, corresponding, in this treatment, to slightly shorter wavelengths? It may very well be the case that there is some precise relationship between such modes and the viscosity of the liquid at finite k and ω [3, 37]. If so, there may be a real connection to be explored between the elastic-continuum [38] and the fully microscopic instantaneous-normal-mode [23–25] theories for nonpolar solvation.

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