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On the validity of using the Debye model to quantitatively correlate the shear modulus with vibrational properties in cubic metals

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ABSTRACT

The relationship between the shear modulus and the flexibility volume has been examined using molecular dynamics simulations in fifteen cubic metallic elements over a range of temperatures. We have observed a universal correlation, and identified the applicability range in which this correlation is quantitatively consistent with the prediction based on the Debye model. Deviation is observed for high modulus metals, and its origin is discussed in terms of the Debye assumptions regarding the vibrational mean squared displacement and the phonon density of states.

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The elastic constants (or the bond force constants) of materials are expected to be reflected by the phonon properties. A recent perspective [1] is that the shear modulus (G) can be regarded as a mechanical manifestation of restricted motion, and the atomic vibrational mean squared displacement (MSD), $\langle r^2 \rangle$, can serve as a measure of the configurational constraint. Similarly, the elastic shoving models of liquids purport that the (instantaneous) G can be directly linked with the MSD, based on the harmonic approximation of solids [2–6]. In particular, quantitative correlation between G and $\langle r^2 \rangle$ has been derived from the isotropic Debye model [7]. This asserted validity of the Debye model for liquids, however, has not been verified with systematic data. For amorphous solids, recent molecular dynamics (MD) simulations for model glasses [8,9] suggest that the Debye model is applicable: combining both the MSD and atomic volume aspects, the newly-defined flexibility volume (v_{flex}) [8,9] parameter has been shown to quantitatively predict the G of all metallic glasses (MGs) as well as covalently bonded amorphous solids.

These correlations for liquids and glasses, either considering MSD or v_{flex} , are derived within the quasi-harmonic scheme based on the following Debye model approximation [10,11]. In the long wavelength approximation (LWA), i.e., when the wavelength of the sound wave is very long compared to the nearest atomic distance in a classical elastic continuum, the Debye temperature at the Debye cutoff wave number [10,11] is related to G (incorporating the transverse sound velocity

and bulk modulus instead of using the approximation below would not cause a difference of more than 3%) [8,9,12],

$$\Theta_{LWA} \propto (\Omega_a)^{-1/3} \sqrt{\frac{G}{\rho}} \quad (1)$$

where $\rho = \frac{M}{\Omega_a}$ is the mass density and M is average atomic weight, and the average atomic volume $\Omega_a = a^3$, where a is the average atomic spacing. Meanwhile, in the “high-temperature approximation”, i.e., when the applied temperature is well above the Debye temperature, Debye temperature scales with the vibrational MSD following [8,9,11]

$$\Theta_{HTA}^2 \propto \frac{k_B T}{M r^2} \quad (2)$$

where k_B is Boltzmann constant. If we assume that the two Debye temperatures are equal, then

$$G = C \frac{k_B T}{r^2 \cdot a} = C \frac{k_B T}{v_{flex}} \quad (3)$$

where C is a universal constant [8,9]. Because the average atomic spacing a increases with temperature T , i.e., there is a temperature-dependent atomic volume at finite temperature, Eq. (3) is in effect the quasi-harmonic approximation replacing the harmonic approximation. By combining a with MSD we can define a flexibility volume, $v_{flex} = \langle r^2 \rangle \cdot a$, which includes both volumetric and dynamics information. In the

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following we correlate G with either the MSD or the v_{flex} . One merit of v_{flex} is that this single new parameter determines the shear modulus according to Eq. (3) for all glasses (e.g., at room temperature) [8].

Although the correlation in Eq. (3) was previously assumed for liquids in terms of the instantaneous shear modulus (G_{∞}) and vibrational MSD (see Eqs. (11) and (12) in [13]), and has been demonstrated with simulation data for amorphous solids [8,9], it remains unclear why the Debye approximation, upon which the derivation is based, would be quantitatively valid (or at least give a good representation of the data), considering that the normalized phonon density of states (PDOS, $g(\omega)$), where ω is the frequency) of amorphous matter obviously differs from the Debye model [14]. It is not even clear under what conditions the simple Debye model $G \sim \langle r^2 \rangle$ correlation would quantitatively hold for crystals. Therefore, before one tackles the issue of general validity, the first step is to examine crystals with cubic structures, in a baseline case study to benchmark the applicability range of the Debye model correlation. This is the purpose of this paper.

In this work, we carry out molecular dynamics (MD) simulations on cubic metallic elements to explore the quantitative correlations between shear modulus and various vibrational properties including MSD, v_{flex} and PDOS. Specifically, we use 15 cubic metals with either the face-centered-cubic (FCC) structure or body-centered-cubic (BCC) structure to build a picture/trend of statistical significance. Our results suggest that a strong correlation between shear modulus and vibrational properties does hold for cubic metals, but those having large shear modulus, beyond 65 GPa, clearly deviate from the Debye prediction. This result helps to establish the validity range of a quantitative prediction of G from v_{flex} and vice versa. The deviation seen for high- G elements is rationalized based on their PDOS and its effect on the Debye temperature relations used in the Debye model.

Our simulations use a system size of 4000 atoms for FCC metals and 4394 atoms for BCC metals under periodic boundary conditions. The interatomic interactions are described by the well-developed embedded atom method (EAM) potentials [15–22]. All samples are equilibrated at desired temperatures for 0.2 ns under NPT conditions (i.e., constant atom number, pressure and temperature). During the equilibration, Nose-Hoover thermostat [23–25] and Parrinello-Rahman method [26] are used to control temperature and pressure (zero pressure in our case), respectively. After initial equilibration, shear modulus and MSD are calculated. The shear moduli of single-crystalline cubic metals are largely anisotropic, i.e., different values of C_{44} are expected after coordinate transformations of C_{44} in the simple [100]-[010]-[001] coordinate system. Thus we adopt the Voigt-Ruess-Hill average as an approximation to the shear modulus of a polycrystalline sample. Specifically, the stiffness tensor \mathbf{C} for a given sample is calculated using the finite deformation method: we apply a strain tensor (with a small value for the component of interest and zero otherwise) each time and record the change of the corresponding stress component (the average Virial stresses are used at a specific temperature). Note that while virial stress has been widely used in atomistic simulations, a direct comparison to experimental measured stress (also experimental elastic constants) may not be straightforward, due to the differences in both stress definitions and specific calculation/measure methods. The sample is relaxed for additional 2 ns before and after applying the strain tensor using a Langevin thermostat and the stress component is averaged over the last 6 ps. For each applied strain tensor, both positive and negative directions are considered. Afterwards the Voigt average and Ruess average shear modulus are obtained from the calculated stiffness tensor and compliance tensor. We consider the Hill average $G = 1/2(G_{\text{voigt}} + G_{\text{ruess}})$ in this work. It should be noted that for cubic metals, the Hill average has been shown to be a good estimate for a non-textured polycrystal and the results are very close to the self-consistent averaging schemes [27]; this is one reason why we limit our current study to cubic elements. The vibrational properties we calculated include MSD, flexibility volume v_{flex} and PDOS. The MSD of i^{th} atom was calculated according to $\langle (x_i(t) - \bar{x}_i) \rangle$, where $x_i(t)$ is the atomic position at time t , \bar{x}_i is

the time averaged position and the angular bracket denotes the time average. Then the flexibility volume can be obtained via $v_{\text{flex}} = \langle r^2 \rangle / a^2 \cdot \Omega_a$. All these parameters were obtained in the microcanonical (NVE) ensemble on the timescale of several picoseconds, so as to exclude diffusive contributions to the vibrational MSD. PDOS was calculated from the dynamical matrix at finite temperatures [28] and is normalized such that $\int_0^{\omega_{\text{max}}} g(\omega) d\omega = 1$. In all simulations, a time step of 1 fs is used for the integrator as implemented in LAMMPS [29].

We first attempt in Fig. 1A to observe if there is a correlation between G and MSD for the 15 cubic metals over a wide range of temperatures, to examine G as a manifestation of configurational constraint [1]. As can be seen, at a specific temperature (along a given dashed line), elements showing larger $\langle r^2 \rangle$ have lower G , which can be fitted linearly with a negative slope in the double-logarithmic plot, suggesting a power-law relation such as $G \sim G_0(T) \langle r^2 \rangle^n$, where the exponent n is a negative constant with a magnitude close to unity and G_0 enters the intercept. This linear relation holds for all temperatures considered here, but the intercept is a function of temperature, i.e., $G_0(T)$ increases with rising temperature. When we scale $\langle r^2 \rangle$ by the corresponding temperature T , all data points collapse onto a single line (Fig. 1B), indicating a universal power law scaling between G and $\langle r^2 \rangle / T$, $G \sim \left(\frac{\langle r^2 \rangle}{T} \right)^m$, where m is a negative exponent. Meanwhile, due to thermal expansion and anharmonic effects, G is lowered with increasing temperature for each of the metals studied (see data for a given shaped symbol in Fig. 1). Interestingly, for almost all the elements studied, the G of each element can also be fitted to decrease linearly in a logarithmic plot (not shown in Fig. 1) with its own increasing MSD, except at high homologous temperatures. The slope may slightly vary from element to element and also differ from that at a fixed temperature for all the elements. Overall, both temperature-specific and element-specific measurements demonstrate softening with increasing MSD. Such MSD-induced softening can be intuitively interpreted as an inverse scaling between flexibility and configurational constraint/rigidity: the less constraint applied or the less rigid the material, the larger sampled configurational space. We also mention in passing that the interplay between flexibility and constraint can be tuned by external conditions such as temperature and pressure [30–32].

The above results lend support to the configurational constraint argument on G and could be useful in predicting the shear modulus of cubic metals based on a simple power law correlation, i.e., $G = C_0 \left(\frac{T}{\langle r^2 \rangle} \right)^{-m}$, where C_0 is a constant independent of temperature and the exponent $-m$ is found to be 1.28 from the fitting in Fig. 1B. However, a major shortcoming of this correlation is that the interpretation is not based on derivation and thus physically less transparent. So next we look into the more physically interpretable correlation of Eq. (3) which is based on the Debye model with quasi-harmonic approximation.

Before testing the G - v_{flex} relationship it is necessary to verify that the “high-temperature limit” assumption used in Eq. (2) is satisfied, meaning the applied temperature T is well above Θ_{HTA} to ensure that all vibrational modes are activated. To test this assumption we calculated the Θ_{HTA} for each metal studied, as summarized in Fig. 2. Most data points are on the right-hand side of the line $T = \Theta_{\text{HTA}}$, in accord with the high temperature approximation. Because the relationship between Θ_{HTA} and MSD is derived using a first-order series expansion of the Debye integral function at high temperature (see ref. [11] Eqs. (7.42)–(7.44)), we would expect smaller error in Eq. (3) at temperatures further above the Debye temperature. Calculations verified that inclusion of the second order term of this expansion had a negligible effect on the relationship between Θ_{HTA} and MSD in Eq. (2).

Fig. 3 shows the plot of G vs. T/v_{flex} for all 15 elements at temperatures that are greater than Θ_{HTA} . We observe that for elements with $G < \sim 65$ GPa, the calculated data is quantitatively consistent with the Debye model prediction of Eq. (3) with the expected slope (i.e., constant C in Eq. (3)). However, data points with $G > \sim 65$ GPa obviously deviate from the prediction. Such a significant deviation has not

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