

Comment on “Emergence and Evolution of the k Gap in Spectra of Liquid and Supercritical States”

It is well known [1] that liquids can support the propagation of transverse (T) acoustic-like excitations at the nanoscale if the T waves “see” the atomic structure of the media as frozen. Under such circumstances, it holds the long-wavelength dispersion relation [2,3]

$$\omega(k) = \sqrt{c_T^2 k^2 - \frac{1}{4\tau_M^2}}, \quad (1)$$

where $\tau_M = \eta/G$ is the Maxwell relaxation time and $c_T = \sqrt{G/\rho}$ is the transverse sound velocity (η , G , and ρ are the viscosity, high-frequency shear modulus, and density, respectively). It immediately follows that while transverse waves can propagate at any frequency the squared root in Eq. (1) implies a T gap in k space below:

$$k_{\text{gap}} = (2\tau_M c_T)^{-1} = \sqrt{\rho G/2\eta}. \quad (2)$$

In a recent Letter, Yang and collaborators [4] proposed a different estimation for the T excitation gap,

$$k_{\text{gap}} = (2\tau_F c_T)^{-1} \quad (3)$$

where, besides using an approximate linear slope of $\omega_T(k)$ as a proxy for macroscopic c_T , they substitute the shear stress relaxation time with a *single-particle time*, “the full period of the particles jump motion equal to twice Frenkel’s” τ_F . Furthermore, in the Supplement Material of Ref. [4], τ_F was identified with the alpha-relaxation time. Since the proposal [4] challenges old and well established paradigms, we performed a check via molecular dynamics (MD) simulation of the applicability of τ_F to calculations of the T gap in supercritical Ar at $T = 280$ K. The k_{gap} value resulting from the simulation (upper inset in Fig. 1) for density 1621.2 kg/m^3 turns out to be $\sim 0.27 \text{ \AA}^{-1}$. From Eq. (2), using the Maxwell relaxation time, obtained via the Green-Kubo integral for shear viscosity of $4 \times 10^{-4} \text{ Pa s}$ (NIST database [5] for fluid Ar at 280 K gives $3.45 \times 10^{-4} \text{ Pa s}$) and the calculated high-frequency shear modulus $G = 2.56 \text{ GPa}$, we obtained $\tau_M \sim 0.156 \text{ ps}$ and T gap $\sim 0.25 \text{ \AA}^{-1}$, in good agreement with MD results. On the contrary, using the calculated Frenkel time by definition [6,7] [i.e., as the timescale required for a particle to reach a distance equal to the position of the first maximum of the pair distribution function, $g(r)$] $\tau_F \sim 4.3 \text{ ps}$ in Eq. (3) results in an order of magnitude smaller T gap $k_{\text{gap}} \sim 0.01 \text{ \AA}^{-1}$. Finally, the cross symbols in Fig. 1 show that the disagreement persists in a wide range of densities due to $\tau_F \gg \tau_M$. This is in line with the large difference between alpha-relaxation and Maxwell relaxation times well documented in the literature [8].

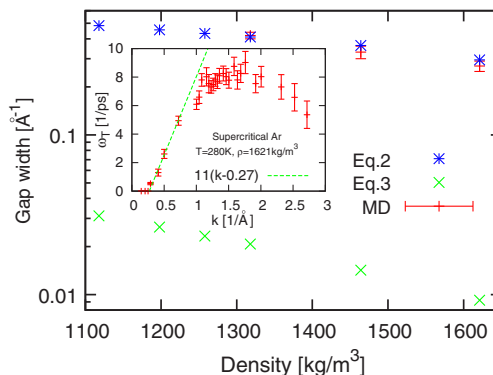


FIG. 1. Dependence of the T gap on density for supercritical Ar at 280 K via Eqs. (2) and (3). The Maxwell time was calculated with NIST data [5] for shear viscosity. Red symbols with error bars correspond to MD results. The inset shows the dispersion of T excitations with the gap $\sim 0.27 \text{ \AA}^{-1}$, calculated from peaks of a T current spectral function $\tilde{C}^T(k, \omega)$.

In summary, the application of the single-particle timescale τ_F in the calculations of the T gap in [4] is inconsistent—with one order of magnitude—with the estimate from the Maxwell relaxation τ_M , which correctly describes the MD observed T gap of dense liquids. Moreover, it contradicts the macroscopic viscoelastic equation for collective T excitations. Accordingly, the proposal of determining the T gap in a collective property (T waves spectrum) using a single-particle timescale (the Frenkel time) turns out to be unjustified.

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