Do we understand the solid-like elastic properties of confined liquids?

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Recently, in polymeric liquids, unexpected solid-like shear elasticity has been discovered, which gave rise to a controversial discussion about its origin (1–3). The observed solid-like shear modulus G depends strongly on the distance L between the plates of the rheometer according to a power law $G \propto L^{-p}$ with a nonuniversal exponent ranging between $p = 2$ and $p = 3$.

Zaccone and Trachenko (4) have published an article in which they claim to explain these findings by a nonaffine contribution to the liquid shear modulus. The latter is represented as

$$\Delta G \propto -\sum_{\lambda=L,T} \frac{1}{V} \sum_{\mathbf{k}} \frac{\omega_{p,\lambda}^2(k)}{\omega_{p,\lambda}^2(k) - \omega^2 + i\omega\nu}, \qquad [1]$$

where $\omega_{p,L}(k)$ and $\omega_{p,T}(k)$ are the longitudinal (L) and transverse (T) phonon dispersions, and ν is a sound attenuation coefficient.

From this, the authors (4) obtain a $\Delta G \propto L^{-3}$ behavior by 1) observing that, for small frequencies, the ω-dependent terms are negligible, and, consequently, the nominator cancels against the denominator, from which follows that the nonaffine contribution becomes just a mode sum $\mathrm{MS} = \frac{1}{V}\sum_{\mathbf{k}} 1$; 2) converting the $\mathbf{k}$ sum $\frac{1}{V}\sum_{\mathbf{k}}$ to an integral over $\mathbf{k}$; and 3) representing the confinement of the sample by restricting the $\mathbf{k}$ integral to values $|\mathbf{k}| \geq L^{-1}$.

However, the authors (4) disregard the fact that the liquid is not confined inside a sphere of diameter L, but between two plates of the rheometer with gap distance L. This means that we are dealing with a slab geometry, in which the sample boundaries L_x and L_y in x and y directions are much larger than the confinement L in the z direction.

Let us assume periodic boundary conditions with respect to L_x, L_y and L. In the limit of $L_x = L_y \to \infty$, the $\mathbf{k}$ sum for MS becomes

$$\mathrm{MS} = \frac{1}{L} \sum_{k_z} \int d^2(k_y, k_y)\ 1. \qquad [2]$$

The k_z sum runs over discrete values labeled as $k_z^{(n)} = 2\pi n/L$. One can now order the summation as $n = 0, \pm 1, \pm 2 \ldots$ and convert the sum $\frac{1}{L}\sum_{k_z}$ for $n \neq 0$ into a k_z integral from $k_z^{(1)} = 2\pi/L$ to $k_{\max}$. This gives a ΔG contribution proportional to L^{-1} instead of L^{-3}.

Apart from the fact that the claimed L^{-3} prediction is at variance with the nonuniversal exponent p, we find that its derivation is in error. We feel that the origin of the observed solid-like properties of confined liquids is still elusive.

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