

1 Universal $G' \sim L^{-3}$ Law for the Low-Frequency Shear Modulus of 2 Confined Liquids

3 Alessio Zaccone* and Laurence Noirez*



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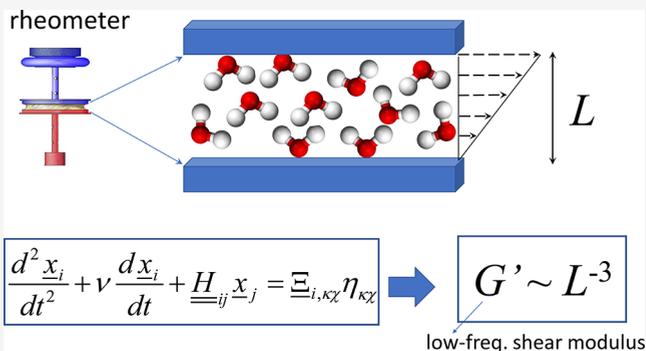
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4 **ABSTRACT:** Liquids confined to sub-millimeter scales have
 5 remained poorly understood. One of the most striking effects is
 6 the large elasticity revealed using good wetting conditions, which
 7 grows upon further decreasing the confinement length, L . These
 8 systems display a low-frequency shear modulus in the order of $1-$
 9 10^3 Pa, contrary to our everyday experience of liquids as bodies
 10 with a zero low-frequency shear modulus. While early experimental
 11 evidence of this effect was met with skepticism and abandoned,
 12 further experimental results and, most recently, a new atomistic
 13 theoretical framework have confirmed that liquids indeed possess a
 14 finite low-frequency shear modulus G' , which scales with the
 15 inverse cubic power of confinement length L . We show that this
 16 law is universal and valid for a wide range of materials (liquid
 17 water, glycerol, ionic liquids, non-entangled polymer liquids, isotropic liquids crystals). Open questions and potential applications in
 18 microfluidics mechanochemistry, energy, and other fields are highlighted.



19 **O**ur daily life experience and education tell us that when a
 20 liquid, e.g., liquid water, is subjected to an infinitesimal
 21 shear stress, it flows. In physics, the absence of noticeable
 22 mechanical resistance can be expressed by saying that the shear
 23 elastic modulus G of liquids is exactly zero, where the shear
 24 modulus represents the proportionality coefficient between the
 25 applied shear stress (σ) and the resulting deformation of a solid
 26 body (γ), i.e., Hooke's law, $\sigma = G\gamma$. Here, a first important
 27 distinction comes into play, as the above statement is true for
 28 nearly static measurements, i.e., at low frequency or low
 29 deformation rate, where the shear modulus is zero, but at high
 30 frequency or high rate of deformation the shear modulus of
 31 liquids is large (as one would experience by diving into a
 32 swimming pool from a considerable height, a possibly painful
 33 experience if one is not an experienced diver!). This observation
 34 reflects the fact that liquids at high frequency of external drive
 35 behave like amorphous solids (e.g., glasses), because the atoms
 36 or molecules are made to oscillate at such high speed by the
 37 external field that they cannot escape the liquid cage made by
 38 their nearest neighbors. This goes along with the ability of
 39 liquids to sustain transverse acoustic waves at sufficiently high
 40 momenta or high frequencies, as predicted in early work by
 41 Yakov Frenkel in the 1940s.¹

42 Besides this basic notion, which defines the essential property
 43 of a liquid, our understanding of the physics of liquids is
 44 incomplete.² This is due to the fact that atoms and molecules in a
 45 liquid are in a state of disorder and random motions, which is
 46 very different from atoms or molecules sitting on a regular lattice

in crystalline solids. Therefore, it is difficult to find a
 47 mathematical description of the atomic or the molecular
 48 dynamics in a liquid, from which quantitative explanations of
 49 the macroscopic properties of liquids could be deduced. 50

As a consequence of this state of affairs, it has been impossible
 51 so far to rationalize the mechanics of liquids on microscopic
 52 scales. Already in 1989–1990, using the newly developed piezo-
 53 quartz resonance device, it was experimentally observed that a
 54 liquid film confined at a several micrometers scale exhibits an
 55 unexpected shear elasticity at low frequency/rate of deformation,
 56 a behavior much more akin to solids than to liquids.^{3,4} In
 57 spite of the fact that these experiments were led by Boris
 58 Derjaguin, one of the most prominent Russian physico-chemists
 59 of the 20th century, the observation was met with skepticism and
 60 abandoned by the scientific community because of the
 61 preconceived notion that liquids must have a zero shear
 62 modulus. From the early 2000s, many other experiments
 63 conducted by different teams across different length scales,
 64 however, resulted in the same observation, extending the
 65 identification of the “Derjaguin” shear elasticity up to the
 66

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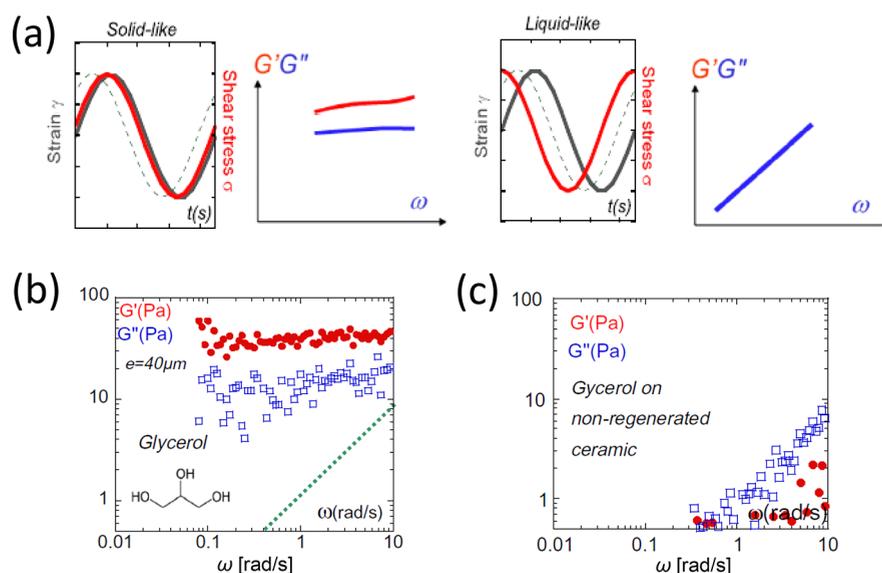


Figure 1. Dynamic viscoelastic response of liquids. Panel (a) shows a schematic depiction of time-dependent shear stress σ and shear strain γ for solid-like (left) and liquid-like (right) systems and the corresponding frequency-dependent viscoelastic curves. The lower set of figures shows the experimentally measured G' and G'' as a function of oscillation frequency ω for glycerol in good (cleaned/thermally regenerated ceramic), panel (b), and poor (non-cleaned ceramic), panel (c), surface-wetting conditions. The measurements are carried out at low gap thickness ($e = 0.04$ mm) and at room temperature. Panel (b), obtained using a surface state perfectly free of impurities, displays higher viscoelastic moduli and leads to $G' > G''$, indicating a solid-like response. In panel (c), where the thermal regeneration of the surfaces has not been applied (hence causing a lower energy of adhesion, thus poor wetting and possibly de-wetting), G'' scales exactly linear with ω , in line with expectations for purely viscous liquids. Reproduced with permission from ref 19. Copyright 2010 Elsevier.

67 millimeter scale,⁵ using different experimental techniques and
 68 different liquids (from liquid water to liquid crystals to ionic
 69 liquids and polymer melts).^{6–12} A theoretical explanation for
 70 these phenomena, however, has remained elusive (despite the
 71 keen interest in this problem by Nobel laureate Pierre-Gilles de
 72 Gennes, a former colleague of one of us, before his untimely
 73 death in 2007).

74 In Figure 1 is shown the typical viscoelastic response of a sub-
 75 millimeter confined liquid (glycerol at room temperature), in
 76 terms of the storage shear modulus $G'(\omega)$ and the dissipative
 77 loss modulus $G''(\omega)$, which represent, respectively, the real and
 78 imaginary parts of the complex shear modulus, $G^* = G'(\omega) +$
 79 $iG''(\omega)$. Here, ω is the frequency of the externally applied
 80 mechanical oscillation field (oscillatory strain), $\gamma = \gamma_0 \sin(\omega t)$.
 81 The shear strain γ is now time-dependent and triggers, under
 82 conditions of the linear response, a stress response, $\sigma = \sigma_0 \sin(\omega t$
 83 $+ \delta)$, where δ is a phase which is $\delta = 0$ for a perfectly elastic
 84 response (Hooke's law) and $\delta = \pi/2$ for a perfectly fluid
 85 response. The situation is summarized in Figure 1a. Exper-
 86 imentally, the solid-like response displays $G' > G''$, and a flat
 87 plateau of G' at low frequency. The hallmark of a liquid-like
 88 viscous response, instead, is that $G' \ll G'' = \eta\omega$ (where η is the
 89 shear viscosity) at low frequency. While bulk liquids have $\delta = \pi/$
 90 2 (perfectly viscous response) for low frequencies of oscillation
 91 (in the range 0.001–10 Hz), liquids in confined geometry and/
 92 or strongly in interaction with the substrate (wetting conditions)
 93 may display δ values much smaller than $\pi/2$, which indicates a
 94 solid-like viscoelastic response. This goes along with a
 95 substantial low-frequency plateau value of storage modulus, G'
 96 $> G''$. An experimental example which illustrates the solid-like
 97 response of confined liquids is provided in Figure 1b,c, showing
 98 the mechanical response of a small-molecule liquid, glycerol, at
 99 low frequency and room temperature. Among other simple
 100 liquids, very similar mechanical responses at low frequency have

101 been measured for water,⁶ for *o*-terphenyl (OTP),⁷ and for ionic
 102 liquids.⁸ Similar solid-like properties have also been observed
 103 with higher-molecular-weight liquids, such as linear alkanes,⁹
 104 isotropic liquids crystals,¹⁰ side-chain liquid crystals,^{11,12}
 105 entangled⁷ and non-entangled polymers,^{10,13} and supercooled
 106 polypropylene glycol.¹⁴ The same phenomena have also been
 107 observed at the nanoscale in nano-confined liquids.^{15–18}

108 It is important to note the role of boundary conditions, i.e., of
 109 the surface energy. For certain solid surfaces in direct contact
 110 with the liquid, the liquid molecules are firmly anchored to the
 111 solid surface. This is typically associated with high wettability, or
 112 good wetting, of the surface, and implies strong attractive
 113 interactions between the liquid molecules and the surface. In
 114 order to implement these conditions, therefore, it is also
 115 necessary to consider the surface energy of the solid, in addition
 116 to cleaned, atomically smooth conditions. If that is not the case,
 117 e.g., for non-wetting surfaces, the liquid molecules in direct
 118 contact with the surface are instead more free in their relative
 119 motion with respect to the solid surface. This makes a big
 120 difference in order to access the elastic response. It turns out
 121 that, in the case of wetting surfaces, the mechanical response of
 122 the confined liquid is higher and solid-like, whereas for non-
 123 wetting surfaces, the standard purely viscous response is
 124 observed. This phenomenon can be mechanistically explained
 125 in terms of plane-wave null boundary conditions for the wetting
 126 surfaces (or absence thereof, for non-wetting surfaces) in the
 127 following theoretical analysis.

128 These experimental findings have recently been rationalized
 129 from the point of view of theory. Theories of liquids have
 130 normally focused on the high-frequency shear modulus for
 131 which atomistic or molecular-level expressions are available,
 132 such as the Zwanzig–Mountain formula,²⁰ precisely because the
 133 low-frequency mechanical of bulk liquids was not supposed to
 134 exist. In the allied field of amorphous solids, such as glasses,

135 instead, the mechanical response has been studied across the
 136 entire frequency range, since amorphous solids obviously exhibit
 137 a finite zero-frequency shear modulus. In particular, lattice
 138 dynamics can be extended to deal with disordered systems
 139 where the positions of atoms/molecules are completely random,
 140 to arrive at theoretical expressions for the elastic constants and
 141 for the viscoelastic moduli.²¹ The resulting theoretical frame-
 142 work is sometimes referred to as non-affine lattice dynamics, or
 143 NALD.^{22,23} The theory has proved effective in quantitatively
 144 describing elastic, viscoelastic, and plastic responses of systems
 145 as diverse as jammed random packings and random networks,²¹
 146 glassy polymers,^{24–26} metallic glass,²⁷ and colloidal glasses.²⁸
 147 Furthermore, NALD intrinsically takes into account long-range
 148 correlation phenomena^{29,30} that are present also in liquids and
 149 give rise to acoustic wave propagation.

150 The usual starting point is the equation of motion of a
 151 microscopic building block, i.e., an atom or a molecule for
 152 atomic liquids or molecular liquids, respectively. In the case of
 153 polymers, the building block could be identified with a monomer
 154 of the polymer chain.²⁴ Following previous literature,^{21,22} we
 155 introduce the Hessian matrix of the system $\underline{\underline{H}}_{ij} = -\partial^2 \mathcal{U} / \partial \underline{\underline{q}}_i \partial \underline{\underline{q}}_j$,
 156 where \mathcal{U} is the internal energy, and the affine force field $\underline{\Xi}_{i,\kappa\chi} =$
 157 $\partial \underline{f}_i / \partial \eta_{\kappa\chi}$, where $\eta_{\kappa\chi}$ is the strain tensor. For example, for simple
 158 shear deformation the xy entry of tensor $\eta_{\kappa\chi}$ is given by a scalar γ ,
 159 i.e., the shear strain introduced above, which coincides with the
 160 angle of deformation.

161 Furthermore, $\underline{\underline{q}}_i$ is the coordinate of atom i in the initial un-
 162 deformed frame (denoted with the ring notation), while $\underline{f}_i =$
 163 $\partial \mathcal{U} / \partial \underline{q}_i$ denotes the force acting on atom i in the affine position,
 164 i.e., in the initial frame acted upon by the macroscopic
 165 deformation, hence the name “affine” force-field. See Figure 2a
 166 for a visual representation of affine positions in a deformed
 167 frame. Greek indices refer to Cartesian components of the
 168 macroscopic deformation (e.g., $\kappa\chi = xy$ for shear). For liquids
 169 (and to a lesser extent, also for glasses²⁴), the Hessian $\underline{\underline{H}}_{ij}$ is
 170 normally evaluated in a reference state obtained from averaging
 171 over MD configurations to include instantaneous normal modes,
 172 or INMs (purely imaginary vibrational frequencies).²⁴ For more
 173 details about INMs, see ref 31.

174 As shown in previous works, the equation of motion of atom i
 175 in a disordered medium subjected to an external small amplitude
 176 strain, in mass-rescaled coordinates, can be written as
 177 follows:^{22,24}

$$178 \quad \frac{d^2 \underline{x}_i}{dt^2} + \nu \frac{d \underline{x}_i}{dt} + \underline{\underline{H}}_{ij} \underline{x}_j = \underline{\Xi}_{i,\kappa\chi} \eta_{\kappa\chi} \quad (1)$$

179 where the summation convention is operative for both Latin and
 180 Greek indices. Also, $\eta_{\kappa\chi}$ are the components of the Green–Saint
 181 Venant strain tensor, and ν is a microscopic friction coefficient
 182 which arises from long-range dynamical coupling between atoms
 183 mediated by anharmonicity of the pair potential. The term on
 184 the right-hand side physically represents the effect of the
 185 disordered (non-centrosymmetric) environment leading to
 186 non-affine motions: a net force acts on atom i in the affine
 187 position (i.e., the position prescribed by the external strain
 188 tensor $\eta_{\kappa\chi}$). The situation is schematically depicted in Figure 2b,
 189 which contrasts a centrosymmetric environment (left panel),
 190 where all atoms are at mechanical equilibrium, even in the affine
 191 position (here for an infinitesimal strain), due to cancellation of
 192 nearest-neighbor forces that are mirror-images of each other

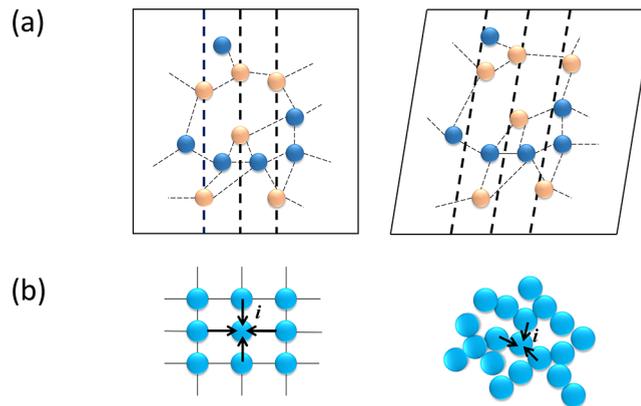


Figure 2. Schematic illustration of non-affine displacements in amorphous media. Panel (a) shows the rearrangements or displacements of atoms upon application of an external shear strain. If the deformation were affine, atoms which sit exactly on the dashed lines in the un-deformed frame (left) would still sit exactly on dashed lines also in the deformed frame (right). However, in a disordered environment this does not happen, and in the deformed frame the atoms that were sitting on the dashed lines in the un-deformed frame are no longer sitting on the dashed lines, but are displaced from them. The distance from the actual positions of the atoms to the dashed line corresponds to the non-affine displacements. Panel (b) provides a visual explanation of the origin of non-affine displacements in disordered environments. The left figure shows a perfect lattice where, upon applying a small deformation, the nearest-neighbor forces from surrounding atoms cancel each other out in the affine positions, so there is no need for non-affine displacements to arise. In the right figure, instead, the tagged atom i is not a center of inversion symmetry, which implies that nearest-neighbor forces from surrounding atoms do not balance in the affine position, and hence a net force arises which triggers the non-affine displacement in order to maintain mechanical equilibrium.

193 across the central particle, with the situation in a disordered
 194 system (liquid or amorphous solid, right panel). In the latter
 195 case, the nearest-neighbor forces do not cancel, thus leading to a
 196 net force acting on the central atom.

197 As a consequence, in order to keep mechanical equilibrium on
 198 all atoms throughout the deformation, an additional *non-affine*
 199 displacement is required in order to relax the force f_i acting in the
 200 affine position. This displacement brings each atom i to a new
 201 (non-affine) position. A schematic depiction of a non-affine
 202 displacement is shown in Figure 2a.

203 The equation of motion eq 1 can also be derived from first-
 204 principles, from a model particle-bath Hamiltonian as shown in
 205 previous work.²⁴ Using standard manipulations (Fourier
 206 transformation and eigenmode decomposition from time to
 207 eigenfrequency²²), and applying the definition of mechanical
 208 stress, we obtain the following expression for the viscoelastic
 209 (complex) elastic constants:^{22,24}

$$210 \quad C_{\alpha\beta\kappa\chi}(\omega) = C_{\alpha\beta\kappa\chi}^{\text{Born}} - \frac{1}{V} \sum_n \frac{\hat{\Xi}_{n,\alpha\beta} \hat{\Xi}_{n,\kappa\chi}}{\omega_{p,n}^2 - \omega^2 + i\omega\nu} \quad (2)$$

211 where $C_{\alpha\beta\kappa\chi}^{\text{Born}}$ is the Born or affine part of the elastic constant, i.e.,
 212 what survives in the high-frequency limit. Here, ω represents the
 213 oscillation frequency of the external strain field, whereas ω_p
 214 denotes the internal eigenfrequency of the liquid (which results,
 215 e.g., from diagonalization of the Hessian matrix²⁴). We use the
 216 notation ω_p to differentiate the eigenfrequency from the external
 217 oscillation frequency ω .

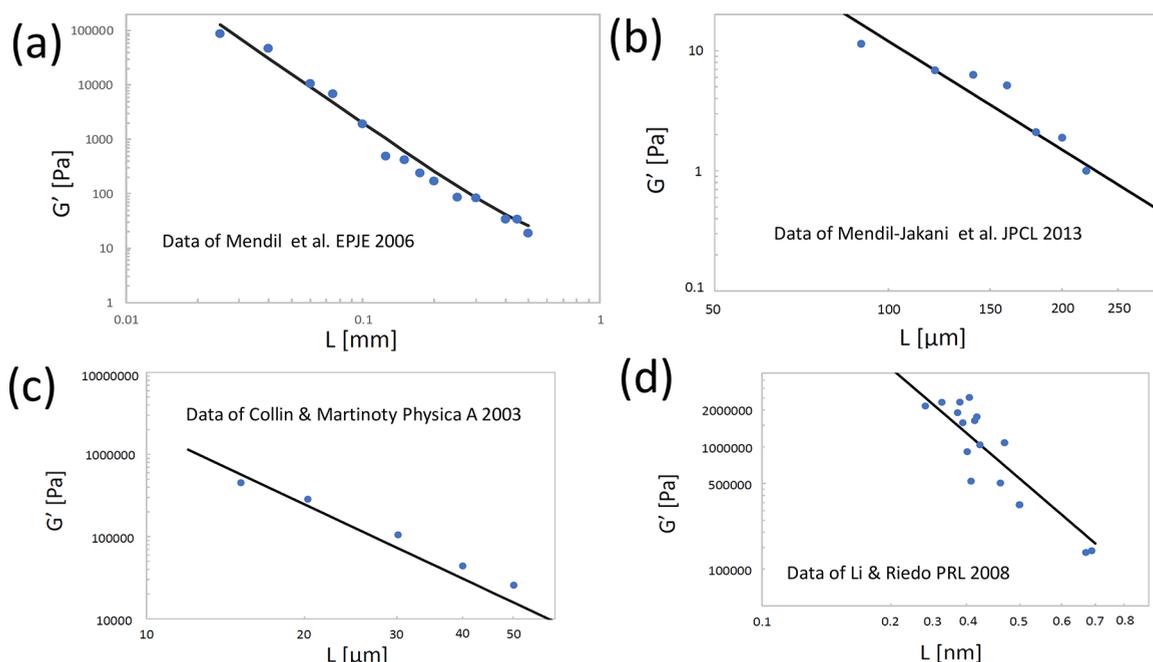


Figure 3. Experimental data of low-frequency shear modulus G' versus confinement length L for different systems, where circles represent experimental data while the solid line is the law $G' \sim L^{-3}$ derived in ref 37. Panel (a) shows the comparison for PAOCH₃, an isotropic liquid crystal system from ref 10; (b) shows the same comparison for ionic liquids, from ref 8; (c) shows experimental data for short-chain (non-entangled) polystyrene melts from ref 13; and (d) shows experimental data for nanoconfined water from ref 15.

218 As already mentioned above, an atomistic expression for $G_{\infty} \equiv$
 219 $C_{\alpha\beta\gamma\chi}^{\text{Born}}$ is provided by the well-known Zwanzig–Mountain
 220 formula,²⁰ in terms of the pair potential $V(r)$ and the radial
 221 distribution function $g(r)$. The sum over n in eq 2 runs over all
 222 $3N$ degrees of freedom (given by the atomic or molecular
 223 building blocks with central-force interactions). Also, we
 224 recognize the typical form of a Green's function, with an
 225 imaginary part given by damping and poles $\omega_{p,n}$ that correspond
 226 to the eigenfrequencies of the excitations.

227 At this point we use a key assumption of plane waves; i.e., we
 228 assume that, at low values of wavenumber k (i.e., for long
 229 wavelengths λ), liquids can support shear elastic waves.
 230 Propagation of longitudinal acoustic waves in liquids is, of
 231 course, a well-known fact to everyone who does snorkeling or
 232 swims under the water level, with firmly established
 233 experimental and theoretical evidence of longitudinal acoustic
 234 dispersion relations.^{32–34} For transverse or shear acoustic waves

235 in liquids, instead, there is no propagation below a characteristic
 236 wavenumber. Indeed, there is an onset value of k , that we shall
 237 denote k_g , above which these modes can propagate in liquids,
 238 known as the k -gap,² again a result due originally to Frenkel,¹
 239 and recently demonstrated by Trachenko and co-workers.^{35,36}

240 Following the analytical steps presented in ref 37, we arrive at
 241 the following expression for the complex shear modulus:

$$G^*(\omega) = G_{\infty} - B \int_{1/L}^{k_D} \frac{\omega_{p,L}^2(k)}{\omega_{p,L}^2(k) - \omega^2 + i\omega\nu} k^2 dk - B \int_{k_{\min}}^{k_D} \frac{\omega_{p,T}^2(k)}{\omega_{p,T}^2(k) - \omega^2 + i\omega\nu} k^2 dk \quad (3)$$

243 where the first integral represents the non-affine (negative or
 244 softening) contribution due to longitudinal (L) acoustic modes,
 245 while the second integral represents the non-affine (also
 246 softening) contribution due to the transverse (T) acoustic

247 modes. The upper integration limit in the k integrals is set, as
 248 usual, by the Debye wavenumber k_D . In the above expression, $k_{\min} = \max(k_g, \frac{1}{L})$ is an “infrared” cutoff for the transverse
 249 modes, with k_g the onset wavenumber for transverse phonons in
 250 liquids (the k -gap) and L the confinement length along the z
 251 direction. In the above treatment, dealing with plane waves in
 252 3D implies the condition $\sqrt{k_x^2 + k_y^2 + k_z^2} = k = 2\pi/\lambda$, which
 253 leads to the spherical integrals of eq 3, with the metric factor k^2 .
 254

255 For the longitudinal modes, one can resort to the Hubbard–
 256 Beeby theory of collective longitudinal modes in liquids,³² which
 257 has been shown to provide a good description of experimental
 258 data, and thus use eq 43 from ref 32 for $\omega_{p,L}(k)$ inside the
 259 integral above. As shown in ref 37, the final result for the low-
 260 frequency G' does not depend on the form of the $\omega_{p,L}(k)$
 261 dispersion relation. However, for the mathematical complete-
 262 ness of the theory, it is important to specify which analytical
 263 forms for the dispersion relations can be used.

264 Anyway, upon taking the real part of G^* , which gives the
 265 storage modulus G' , and focusing on low external oscillation
 266 frequencies $\omega \ll \omega_p$ used experimentally, in both integrals the
 267 numerator and denominator cancel out, leaving the same
 268 expression in both integrals. Therefore, as anticipated above, the
 269 final low-frequency result does not depend on the actual form of
 270 $\omega_{p,L}(k)$, nor of $\omega_{p,T}(k)$, although the latter, due to the k -gap,
 271 plays an important role (see the expression for k_{\min} above) in
 272 controlling the “infrared” cutoff of the transverse integral.
 273 In the experiments where the size effect of confinement is seen,
 274 $k_g \ll \frac{1}{L}$,³⁸ and $k_{\min} = \frac{1}{L}$, thus leading to

$$G' = G_{\infty} - \alpha \int_{1/L}^{k_D} k^2 dk = G_{\infty} - \frac{\alpha}{3} k_D^3 + \frac{\beta}{3} L^{-3} \quad (4)$$

275 For the lower limit of the non-affine integral, we used an
 276 “infrared” cutoff,
 277

$$k_{\min} \equiv |\mathbf{k}_{\min}| = 2\pi\sqrt{(1/L_x)^2 + (1/L_y)^2 + (1/L)^2} \quad (5)$$

by assuming that the liquid is confined along the z direction, such that $L \equiv L_z \ll L_x, L_y$; the lower limit in the non-affine integral over k -space thus reduces to $1/L$, as displayed in eq 4. A rigorous estimate of the k -integral in eq 4, including exact prefactors, can be found in ref 39.

In eq 4, the only term which depends on the system size is the last term, while α and β are numerical prefactors. In liquids that are in thermodynamic equilibrium and for quasistatic deformations, a different version of the non-affine response formalism called the stress-fluctuation formalism can be used. It has been rigorously demonstrated that the two versions of the formalism are equivalent in ref 40. Using the stress-fluctuation non-affine formalism in combination with standard equilibrium statistical mechanics, it has been shown in ref 41 that the affine or high-frequency (Born) term G_∞ and the negative non-affine term (here, $-\frac{\alpha}{3}k_D^3$) cancel each other out exactly, such that $G'(\omega \rightarrow 0) = 0$ for $L \rightarrow \infty$ (bulk liquids). Therefore, for liquids under sub-millimeter confinement, only the third term in the above equation survives, and we finally obtain

$$G' \approx \beta' L^{-3} \quad (6)$$

where $\beta' = \beta/3$ is a numerical prefactor. This law was derived for the first time in ref 37. It is worth noticing that G_∞ is independent of L . This fact can be seen, e.g., through the Zwanzig–Mountain formula, where the main contribution to G_∞ is given as an integral that contains $dV(r)/dr$ as a multiplying factor in the integrand, with $dV(r)/dr = 0$ after a few molecular diameters. This, in turn, implies that no dependencies on length scales much larger than the nearest-neighbor cage can be present in G_∞ .

The above theory clarifies that the liquid confinement between two plates is able to “remove” certain low-frequency normal-mode collective oscillations of molecules, associated with the non-affine motions (i.e., negative contributions to the elasticity), which are responsible for the fluid response of liquids under standard macroscopic (“unconfined”) conditions. These motions are responsible for reducing the shear modulus basically to zero in macroscopic bulk liquids. Under confinement, instead, the shear modulus is non-zero because these collective oscillations modes are suppressed, and the theory of Zaccone and Trachenko³⁷ provides the universal law by which the shear modulus grows upon reducing the confinement (gap) size. In particular, the static shear modulus grows with the inverse cubic power of the gap size.

In ref 37, the law $G' \sim L^{-3}$ was found to provide a perfect description of experimental data measured in an isotropic liquid crystal system (PAOCH₃) upon varying the confinement length using a conventional rheometer. Here, we show that this law appears to be truly universal, and we present theoretical fittings of several, very different systems in Figure 3.

In all these systems, i.e., polymer melts of relatively low molecular weight, isotropic liquid crystals, ionic liquids, and even nano-confined water, the law eq 6 appears robust, as shown in Figure 3. In the case of nano-confined water,¹⁵ one would expect a crossover from $\sim L^{-3}$ into an L^{-1} regime once a 2D monolayer is reached. This is expected because the k -space integral in eq 4 contains a metric factor k in 2D, instead of k^2 for 3D (in fact, k^{d-1} for generic d -dimensional space). This crossover is not seen in the data of Figure 3d, which calls for further investigations, both experimentally and theoretically.

Experimental data have also been reported for OTP, an organic liquid (data not shown here).⁷ Those data also show the $\sim L^{-3}$ behavior, but the data at the shortest confinement length, ~ 0.01 mm, suggest the possible existence of a plateau upon going toward lower L , while the experimental accuracy is lowered as the confinement increases. The paucity of experimental data does not allow for drawing a definitive conclusion on this effect (i.e., the possible existence of a plateau in G' at low L in certain systems), which should also be the object of further investigation, both experimentally and in theory.

As mentioned earlier, a crucial role is played by the surface anchoring. The solid-like response of confined liquids is indeed observed mainly for atomically smooth surfaces (crystal planes) or for conditions of good wetting between liquid and solid surfaces (high energy surfaces). Instead, a standard, purely viscous response is reported for non-wetting or poorly wetting surfaces; see Figure 4 for a schematic illustration of two different

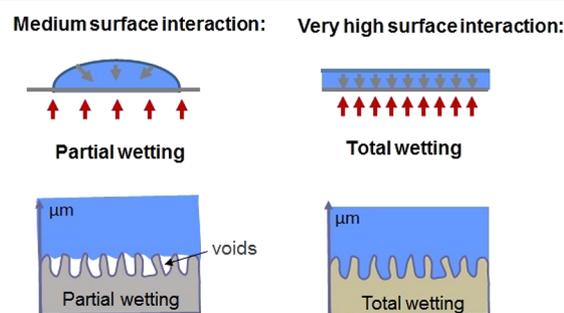


Figure 4. Schematic illustration of different levels of surface interaction between liquid molecules and solid substrate. A not-so-strong attractive interaction leads to partial wetting (left panel), whereas a strong attractive interaction with the solid surface leads to total wetting filling in the rough edges (right panel).

surface wetting conditions. The same observation has been made in the case of nanoconfined water, with a substantially higher viscosity measured in the case of good wetting in ref 16.

From the theoretical point of view, this fact can be explained by referring to the non-affine lattice dynamic framework summarized above. In particular, wettability connects with the assumption of plane waves and with the implicit *null boundary conditions* for the displacement field of plane waves. This leads straightforward to the term $\sim L^{-3}$ in eq 4 above, which is the term responsible for the solid-like elastic response. Without the full wetting boundary conditions between the liquid and the solid surface, the liquid molecules would not be well-anchored to the solid surface, so the null boundary condition for the acoustic waves would not apply, and the very existence of elastic plane waves would then be called into question. Certainly, the above theoretical framework would not be applicable in that case, as it relies on the ability of the liquid to support plane waves. We can speculate that, when molecules are not anchored to the solid surface, the effective “removal” of softening non-affine motions during the displacement and due to confinement is less effective; hence, the rigidifying effect of “cutting” non-affine motions off due to confinement during the deformation, would not be active. A more precise explanation may require a different theoretical approach, possibly working in eigenfrequency domain rather than in k -space, and is an interesting problem for future research.

Finally, it is important to point out that the non-zero low-frequency shear elasticity has been measured in various liquids irrespective of their surface tension (alkanes, ionic liquids, and

polymer melts typically exhibit low surface tension). Since the interfacial (air/liquid) energy scales as the inverse of the surface area, significant contributions to G' would be possible if the sample area changes drastically during the oscillatory shear. Bad filling, bad wetting, and large-amplitude oscillator strain (LAOS) conditions could produce a weak “false” torque by breaking the rotational symmetry in the plane.⁴² In contrast, the genuine low-frequency shear elasticity intrinsic to the confined liquid state is accessible under conditions where the above artifacts are carefully avoided, and by ensuring a good wetting and low strain—that is, as close as possible to the equilibrium conditions. G' then vanishes by increasing the shear strain (at low gap) to make room for the conventional viscous or viscoplastic flow behavior, which could be understood as the non-linear evolution of the finite low-frequency shear elasticity,^{3–7} similar to what happens in amorphous solids upon crossing the yielding/plasticity transition.^{27,28}

A number of outstanding questions remain open for future investigations. For example, it could be interesting to explore what kind of connection exists between the above scenario of solid-like elasticity of confined liquids and the glass transition under confinement. The latter is an intensively studied problem, especially in the context of thin polymer films.^{43,44} Another important issue is the progress that can be made with numerical simulations. In molecular dynamics (MD), the shear modulus of a confined liquid can be measured, but the noise is currently too large (since the size of MD-simulated systems is small) to make predictions for most realistic situations.⁴⁵ Another issue is represented by the small time step used, especially in atomistic simulations (on the order of femtoseconds), which prevents accessing the low-frequency shear modulus. Quasi-static deformation methods implemented atomistically could be a step forward, but they have not demonstrated quantitative predictive power thus far, in comparison with experiments. Also, the power-law nature of the relation $G' \sim L^{-3}$ implies the absence of characteristic length scales (as is typical for power-laws), which suggests that the same mechanisms apply at different length scales; i.e., the same laws apply with L being on the sub-millimeter, micrometer, or nanometer scale. Similarities between trends observed for sub-millimeter¹⁰ and nanoconfined fluids,^{15,16} in terms of both solid-like mechanical properties and role of wetting,⁴⁶ suggest that this may indeed be the case, but further research is required to more firmly establish a complete multi-scale framework.

The potential applications of solid-like elasticity of confined liquids, and its tunability via the control and modulation of the interfacial energy and gap size L , are manifold, encompassing fields as diverse as mechanical stress-assisted manipulation of soft and biological matter in microfluidics,^{47–49} protective equipment,⁵⁰ biomedical flow applications,⁵¹ oil recovery,⁵² heat transfer in liquids,⁵³ and phase transitions under confinement.⁵⁴ Recently, it has been demonstrated that the thermal response of confined liquids is very similar to that of solids,⁵⁵ which opens up new opportunities for exploiting thermoelasticity of confined fluids, e.g., for energy conversion.

Finally, another potential exciting application of this effect is in the emerging fields of mechanochemistry^{56–59} and mechanobiology:⁶⁰ a (confined) liquid with a finite low-frequency shear modulus G' is able to support mechanical stress-transmission much more efficiently and with much lower dissipative losses compared to standard viscous liquids. This fact may open up new avenues for mechanically induced enhancement of chemical reaction kinetics, by combining the force-

transmission efficiency typical of elastic solids with all the favorable solvation and solubility properties of liquids.^{61–64}

AUTHOR INFORMATION

Corresponding Authors

Alessio Zaccone – Department of Physics “A. Pontremoli”, University of Milan, 20133 Milan, Italy; Department of Chemical Engineering and Biotechnology and Cavendish Laboratory, University of Cambridge, CB30AS Cambridge, U.K.; orcid.org/0000-0002-6673-7043; Email: alessio.zaccone@unimi.it

Laurence Noirez – Laboratoire Léon Brillouin (CEA-CNRS), Université Paris-Saclay, CEA-Saclay, 91191 Gif-sur-Yvette, France; Email: laurence.noirez@cea.fr

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.jpcllett.0c02953>

Notes

The authors declare no competing financial interest.

Biographies

Alessio Zaccone

Laurence Noirez

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