The conventional wisdom says that a solid is more rigid than a liquid. In a short time scale, however, it is known that some liquids become ‘rigid’ (or ‘elastic’) \[1,2\]. A natural question is: Are solids ‘rigid’ in such a time scale? More deeply, this leads us to a fundamental question: When comparing liquid and solid phases of the same material, which is more ‘rigid’ at high frequencies? The purpose of this paper is to give a universal answer to this question.

The term ‘rigid’ refers to the ability of a material to resist deformation by an applied force \( f \). However, this does not define the rigidity uniquely, because the ability depends strongly on the nature of \( f \), such as its strength, frequency, and spatial variation \[2\]. Furthermore, in general, two or more types of deformations are induced, such as displacement and rotation \[2\]. According to the types of deformation and the nature of \( f \), the ability to resist the deformation is quantified by various measures, such as the elastic modulus, stiffness and viscosity \[1,4\]. Therefore, we must first specify the type of deformation, the nature of \( f \), and the measure that defines the rigidity.

To study the above fundamental question, we assume a simple case where \( f \) is sufficiently weak, so that neither hysteresis nor creep occurs and the material responds to \( f \) linearly \[2,3\]. We also assume that \( f \) is uniform spatially but varies as a function of time with frequency \( \omega \). Physically, \( f \) can be an electric field, gravitational or inertial force, and so on. To probe rigidity of a material by applying such a simple force, we assume that microscopic ‘pinning centers’ exist \[3,5\], such as impurities and roughness of walls of the container. This leads to a reasonable measure of rigidity. Using it, we show that if a material is more rigid in a solid phase than in a liquid phase at low frequencies then in a certain high-frequency region it is more rigid in the liquid phase than in the solid phase. Since this result is derived from a universal sum rule, it is a universal result that holds for wide classes of materials, including electron systems and cold atoms \[10,13\]. We also explore physics of this counterintuitive result. We show that the frequency region in which a solid becomes more flexible than a liquid is not purely determined by intrinsic properties of the solid. It depends also on extrinsic factors such as the density of pinning centers.

Liquid is More Rigid than Solid in a High-Frequency Region

Naoki Hasegawa,\(^1\) Tatsuro Yuge,\(^2\) and Akira Shimizu\(^3\)

\(^1\)Department of Basic Science, University of Tokyo, 3-8-1 Komaba, Meguro, Tokyo 153-8902, Japan
\(^2\)Department of Physics, Osaka University, 1-1, Toyonaka, Osaka, 560-0043, Japan

(Dated: December 30, 2014)

We compare rigidity of materials in two phases, liquid and solid phases. As a measure of the rigidity, we employ the one characterizing how firmly the material is fixed by low density of pinning centers, such as impurities and rough surfaces of walls, against a weak force. Although a solid is more rigid than a liquid against a low-frequency force, we find that against a high-frequency force the liquid becomes more rigid than the solid of the same material. Since this result is derived from a universal sum rule, it is valid for wide classes of materials, and for both quantum and classical systems. To explore its physics, we perform nonequilibrium molecular dynamics simulations. We find that the frequency region in which a solid is more flexible than a liquid is not purely determined by intrinsic properties of the solid. It depends also on extrinsic factors such as the density of pinning centers.

PACS numbers: 62.90.+k, 64.70.D-, 05.70.Fh, 72.90.+y

\[ I = \frac{1}{L_x} \sum_{j=1}^{N_x} \hat{p}_x^j m_e, \]

where \( N_e \) is the number of particles that respond to \( f(t) \), \( \hat{p}_x^j \) is the \( x \) component of the momentum operator of the \( j \)-th particle, whose mass is \( m_e \). Under the aforementioned assumptions, the Fourier components of \( f(t) \) and \( I(t) \) are related as

\[ I_\omega = \Xi(\omega) f_\omega. \]

Here, \( \Xi(\omega) = \Xi'(\omega) + i \Xi''(\omega) \) is the complex admittance, which is a continuous function of \( \omega \) \[4,6\]. Its real part \( \Xi'(\omega) \) determines the rate of dissipation, whereas the imaginary part \( \Xi''(\omega) \) is related to non-dissipative displacement \[6\]. Hence, according to the second law of thermodynamics, \( \Xi''(\omega) \geq 0 \) for all \( \omega \).

We note that one can fix a rigid material firmly to a board by hammering a small number of nails into it, whereas one can hardly fix a flexible material. When one
In this case, the following sum rule holds rigorously: \[ \int_{-\infty}^{\infty} \Sigma'(\omega) \frac{d\omega}{\pi} = \left\langle \frac{1}{i\hbar} \left[ \sum_{j=1}^{N_e} \hat{q}_j^2, \hat{I} \right] \right\rangle = \frac{N_e}{m_e L_x}, \] (4)

where \( \langle \cdot \rangle \) denotes the equilibrium expectation value, and \( m_e \) is the mass of the particle. We note that the right-hand side is independent of the state of the system, i.e., whether the system is in a liquid or solid phase. Hence, although \( \Sigma'(\omega) \) at each \( \omega \) changes drastically across a phase transition, its sum over all \( \omega \) does not change at all. Since \( \Sigma'(\omega) \geq 0 \) for all \( \omega \), this is a strong restriction on possible values of \( \Sigma'(\omega) \). In particular, if a solid phase has smaller \( \Sigma'(\omega) \) at low \( \omega \) (than a liquid phase, as expected) then it must have larger \( \Sigma'(\omega) \) at high \( \omega \). That is, if a solid is more rigid at low frequencies, then, counterintuitively, a liquid is more rigid at high frequencies.

The same can be said about classical systems, because the sum rule (4) holds also for classical systems [3–7].

Note that the sum rule relies only on the forms of the observable of interest, Eq. (1), and the interaction with \( f \), Eq. (2), which are typical forms in both quantum and classical (nonrelativistic) mechanics. It holds rigorously irrespective of interactions among particles, even when pinning centers are present. It holds also for thermal pure quantum states [14, 16]. Although phenomenological models sometimes fail to satisfy it, they should be modified at high frequencies in such a way that the sum rule is satisfied [3]. Therefore, the above result is a universal one, which holds for wide classes of materials.

**Model to explore physics.**—We have drawn the counterintuitive conclusion from the sum rule. However, the sum rule does not tell what is going on because it refers only to the sum. To clarify the physics, we must answer the following questions: Regarding the frequency region in which a solid is more flexible than a liquid, is it an intrinsic property of the solid? That is, is it insensitive to extrinsic factors such as the density and configuration of pinning centers? If not, what happens if pinning centers are completely absent? To answer these questions, we perform nonequilibrium (NE) molecular dynamics (MD) simulations for a classical model. Since the sum rule (4) takes the same form for both quantum and classical systems, we expect that bare essentials are common to both systems.

The model for the MD simulations should undergo a liquid-solid phase transition. Furthermore, it should have stable NE states in the presence of \( f(t) \), because otherwise \( \Sigma(\omega) \) could not be well-defined. To meet these requirements, we generalize the models of Refs. [17, 20], which have stable NE states and are free from problems due to the long-time tails [21, 26].

As shown in Fig. 1 our model consists of three types of particles, which are called e, p and i after a typical case where they are electrons, phonons and impurities, respectively. Their radii are taken 1, 0 and 0, respectively. For interactions between these particles, we assume those...
close to the hard-core interactions. Hence, with increasing the volume filling factor \( \rho_e = (4\pi/3)N_e/(L_xL_yL_z) \), \( e \) particles undergo a first-order transition of the Alder type \(^{27,28} \), from a liquid phase (\( \rho_e < \rho_e^{l1} \)) to a solid phase (\( \rho_e > \rho_e^{l1} \)). Both phases coexist for \( \rho_e^{lq} \leq \rho_e \leq \rho_e^{l1} \). For hard-sphere particles of unit radius, \( \rho_e^{lq} = 0.494 \) and \( \rho_e^{l1} = 0.545 \) \(^{28} \). By contrast, neither \( p \) nor \( i \) particles undergo such a transition because they have vanishing volume filling factor (because of vanishing radii). The \( p \) particles are particles of the ‘environment,’ which is attached to a heat reservoir. Through \( e-p \) interaction \( p \) particles tend to drive the temperature of \( e \) particles to that of the reservoir, \( T \) (which we take 1). The \( i \) particles are ‘impurities,’ which are fixed at random positions, and scatter \( e \) particles via static potentials. They work as pinning centers. A force \( f(t) \) acts only on \( e \) particles.

Work done by \( f(t) \) on \( e \) particles is distributed among \( e \) and \( p \) particles, through the \( e-e \) and \( e-p \) interactions, and finally dissipated to the reservoir. As a result, a stable NE state is realized in the presence of \( f(t) \), and the system has well-defined \( \Xi(\omega) \). Details of the model is described in Ref. \(^{29} \).

Results.— We first study the liquid phase by taking \( \rho_e = 0.223 \) (< \( \rho_e^{l1} = 0.494 \)), in the presence of impurities of number density \( n_i = N_i/(L_xL_yL_z) = 80/6000 = 0.0133 \cdots \). The circles in Fig. 2 show \( \Xi'(\omega) \) in this case. Its behavior is almost of the Drude type, \( \Xi'(\omega) \approx \Xi'(0)/(1 + (\omega \tau)^2) \), which is typical to liquid phases. [The least square fit gives the collision time \( \tau \simeq 5 \).] As expected, the liquid is flexible at low frequencies \( \omega \lesssim 0.2 \).

Numerical integration of \( \Xi'(\omega) \) gives 2.0 \times 10^3 for the left-hand side of Eq. (1), which agrees fairly well with the right-hand side = \( N_e/(m_eL_z) = 320/15 = 21.33 \cdots \) (we take \( m_e = 1 \)) \(^{30} \).

We now study the solid phase by increasing \( \rho_e \). To keep the sum value \( N_e/(m_eL_z) \) constant, we squeeze \( L_y \) and \( L_z \) from 20 to 12, while keeping \( L_x = 15 \). This yields \( \rho_e = 0.621 \) (> \( \rho_e^{l1} = 0.545 \)). In Fig. 3 we plot the structure factor \( S(k) = \sum_{j,l=1}^{N_e} e^{-i(k-q_j-k_l)} \), obtained by the MD simulation, where \( q_j \) is the position of the \( j \)-th \( e \) particle. It clearly shows that \( e \) particles are in a solid phase. We have computed \( \Xi'(\omega) \) of this state, as shown by squares in Fig. 2. It is seen that \( \Xi'(\omega) \to 0 \) as \( \omega \to 0 \), i.e., the solid is much more rigid than the liquid at low frequencies. With increasing \( \omega \), on the other hand, \( \Xi'(\omega) \) of the solid (squares) increases whereas that of the liquid (circles) decreases. As a result, \( \Xi'(\omega) \) of the solid becomes much larger than that of the liquid around \( \omega \sim 1 \), at which \( \Xi'(\omega) \) of the solid has a peak. That is, the solid is much more flexible in this frequency region. We have thus confirmed the universal conclusion that is derived from the sum rule (1). Furthermore, numerical integration of \( \int \Xi'(\omega) d\omega/\pi = 2 \int \omega \Xi'(\omega) d\ln(\omega)/\pi \) for the solid gives 2.0 \times 10^3 \(^{30} \), and the sum rule itself is again confirmed.

![FIG. 2. Real part of \( \Xi(\omega) \), for the liquid phase with \((L_x, L_y, L_z) = (15, 20, 20) \) and \( N_i = 80 \) (circles), and for the solid phase with \((L_x, L_y, L_z) = (15, 12, 12) \) and \( N_i = 80 \) (squares). \( N_i = 40 \) (triangles), and \( N_i = 0 \) (crosses). For all of them, \( N_e = 320 \), \( N_p = 160 \) and \( T = 1 \).](image)

![FIG. 3. Structure factor in the solid phase \((N_i = 80)\), computed at \( t = 8000 \), for \( k = (k,0,0),(0,k,0),(0,0,k) \).](image)

Physics.— We have seen that in a solid phase \( \Xi'(\omega) \) has a peak at a high frequency, which makes the solid more flexible than the liquid. The peak also keeps the sum value constant, compensating for reduction of \( \Xi'(\omega) \) at low frequencies. To explore physics of the peak, we study its dependence on the configuration and the number density \( n_i \) of impurities. The peak would be insensitive to them, as long as \( n_i \ll n_e = N_e/(L_xL_yL_z) \) \(^{31} \), if it came purely from intrinsic excitation modes in the solid of \( e \) particles.

When the impurity configuration is changed, we find that the peak position shifts slightly (by \( \sim 0.2 \), typically). This indicates that the peak is not intrinsic to the \( e \)-particle solid. To see this more clearly, we study the cases of lower \( n_i \), keeping \( n_e \) constant. In the above case of solid, we have taken \( n_i = 80/2160 = 0.0370 \cdots \) and \( n_e = \cdots \)
The triangles in Fig. 2 show $\Xi'(\omega)$ for lower $n_i$, where $n_i = 40/2160 = 0.148 \cdots$. The triangles in Fig. 2 show $\Xi'(\omega)$ for lower $n_i$, where $n_i = 40/2160 = 0.148 \cdots$. Numerical integration of $\Xi'(\omega)$ gives $2.0 \times 10^1$ [34], and the sum rule is satisfied also in this case. It is seen that the peak shifts significantly to a lower frequency. For confirmation, we further decrease $n_i$ to $n_i = 0$. Although our measure of rigidity is not applicable to this limiting case, we can see the physics. The crosses in Fig. 2 show $\Xi'(\omega)$ for $n_i = 0$. Numerical integration of $\Xi'(\omega)$ gives $2.0 \times 10^1$ [34], and the sum rule is again confirmed. It is seen that the peak of $\Xi'(\omega)$ at a high frequency almost disappears. Hence, we have confirmed that the peak is not purely intrinsic to the solid of $e$-particles. On the other hand, obviously, it is not purely extrinsic, either (because, e.g., it disappears in the liquid phase). Therefore, the peak is determined by many factors, including both intrinsic ones (such as phonon modes) and extrinsic ones (such as the density and configuration of pinning centers).

Interestingly, $\Xi'(0)$ for the solid with $n_i = 0$ does not vanish, and $\Xi'(\omega)$ behaves as if $e$-particles were in a liquid phase. This is understood as due to the ‘sliding motion’ of the solid [35, 36]. That is, the solid can slide (i.e., move without deformation) if any pinning centers are absent. As a result, $\Xi'(0)$ for the solid becomes finite for $n_i = 0$, and $\Xi'(\omega)$ behaves like that of a liquid. When $n_i > 0$, on the other hand, such a sliding motion is impossible because the solid is pinned by impurities, and $\Xi'(0)$ vanishes. By contrast, a liquid has finite $\Xi'(0)$ even when $n_i > 0$, as shown by circles of Fig. 2 because it is flexible at $\omega \approx 0$ so that it is not pinned.

**Nonequilibrium phases.**—Recently, phase transitions between NE states have been attracting much attention [32, 33]. The sum rule [31] originally assumed that the system was in an equilibrium state before $f$ is applied [32, 33]. However, it was recently shown that it holds rigorously even when the system was in a NE state, which is driven by some driving force $F$, before $f$ is applied [32, 33]. In this case, the admittance $\Xi'(\omega)$ of an equilibrium state to $f$ is replaced with the admittance $\Xi'_F(\omega)$ of a NE state to $f$. Therefore, the above results should apply also to NE states if $\Xi'(\omega)$ is replaced with $\Xi'_F(\omega)$, the real part of $\Xi'_F(\omega)$. That is, in a certain high-frequency region a material is more flexible in a NE solid phase than in a NE liquid phase, in the sense that $\Xi'_F(\omega)$ is larger in that region of $\omega$. Note, however, that $\Xi'_F(\omega)$ can take negative values when $F \neq 0$, unlike $\Xi'(\omega)$ of an equilibrium state. Hence, larger $\Xi'_F(\omega)$ does not necessarily imply larger $|\Xi'_F(\omega)|$.

**Discussions.**—Since the above results are universal, they can be tested experimentally in diverse systems, such as electron systems and cold atoms [10, 13]. Note that measured $\Xi'(\omega)$ often contains contributions not only from particles of interest (which undergo a phase transition) but also from other particles or excitations. Hence, it is necessary to extract the contribution from particles of interest.

One sometimes extracts contributions only from a single band. Since the energy scale is strongly restricted in such a case, the ‘restricted sum rule’ holds instead of the ‘full sum rule’ [31]. In a way similar to derivation of the restricted sum rule for the optical (transverse) conductivity [39, 44], we obtain the one for the longitudinal admittance as

$$
\int_{-\infty}^{\infty} \Xi'(\omega) \frac{d\omega}{\pi} = \frac{1}{L_x} \sum_{k, \sigma} n^{-1}(k) \langle \hat{n}_{k\sigma} \rangle,
$$

and similarly for $\Xi'_F(\omega)$. Here, $m^{-1}(k)$ is a (diagonal element of) the inverse mass tensor, and $\langle \hat{n}_{k\sigma} \rangle$ is the occupation of the Bloch state with wavevector $k$ and spin $\sigma$. In such a case, only when electrons occupy low-energy states of the band (in all phases) the sum value becomes constant, because $\sum_{k, \sigma} n^{-1}(k) \langle \hat{n}_{k\sigma} \rangle = m^{-1}(0) \sum_{\sigma} \langle \hat{n}_{k\sigma} \rangle = m^{-1}(0) N_e$. Under this condition, all the results of the present paper hold also in such a single-band case.

Our measure of rigidity is clearly related to other measures, such as viscosity, at low $\omega$. At high $\omega$, however, relations among different measures (including ours) are not well understood yet. This will be a subject of future studies.

We are grateful to K. Asano, Y. Kato and H. Hayakawa for helpful discussions. This work was supported by KAKENHI from the Japan Society for the Promotion of Science, Grant Nos. 22540407, 24540393 and 26287085.
[12] Z. Hadzibabic, P. Krüger, M. Cheneau, B. Battelier, and J.B. Dalibard, Nature 441, 1118 (2006).
[13] M. Lewenstein, A. Sanpera, V. Ahufinger, B. Damski, A. Sen(De), U. Sen, Adv. Phys. 56, 243 (2007).
[14] S. Sugiuara and A. Shimizu, Phys. Rev. Lett. 108, 240401 (2012).
[15] S. Sugiuara and A. Shimizu, Phys. Rev. Lett. 111, 010401 (2013).
[16] M. Hyuga, S. Sugiuara, K. Sakai, A. Shimizu, Phys. Rev. B 90, 121110(R) (2014).
[17] T. Yuge, N. Ito and A. Shimizu, J. Phys. Soc. Jpn. 74, 1895 (2005).
[18] T. Yuge and A. Shimizu, J. Phys. Soc. Jpn. 76, 093001 (2007); Erratum: J. Phys. Soc. Jpn. 77, 028001 (2008).
[19] T. Yuge and A. Shimizu, Prog. Theor. Phys. Suppl. 178, 64 (2009).
[20] T. Yuge and A. Shimizu, J. Phys. Soc. Jpn. 78, 083001 (2009).
[21] B. J. Alder and T. E. Wainwright, Phys. Rev. Lett. 18, 988 (1967).
[22] M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, Phys. Rev. Lett. 25, 1254 (1970).
[23] J. R. Dorfman and E. D. G. Cohen, Phys. Rev. Lett. 25, 1257 (1970).
[24] R. Zwanzig and M. Bixon, Phys. Rev. A 2, 2005 (1970).
[25] K. Kawasaki, Phys. Lett. A 32, 379 (1970).
[26] Y. Pomeau and P. Részibois, Phys. Rep. 19, 63 (1975).
[27] B. J. Alder and T. E. Wainwright, J. Chem. Phys. 27, 1208 (1957).
[28] W. G. Hoover and F. H. Ree, J. Chem. Phys. 49, 3609 (1968).

[29] Supplemental Material at http://as2.c.u-tokyo.ac.jp/archive/hys2014sm.pdf

[30] The integral value of $\Xi'(\omega)$ is slightly underestimated because we have computed it by taking the upper bound of the integral to $\omega = 10$, above which $\Xi'(\omega)$ is vanishingly small (and hence relative errors are large).

[31] Recall that an impurity has vanishing radius. In a solid phase, we distribute impurities in vacant spaces among $e$ particles.

[32] S. Nakamura, Phys. Rev. Lett. 109, 120602 (2012).
[33] H. Barghathi and T. Vojta, Phys. Rev. Lett. 109, 170603 (2012).
[34] C. Carr, R. Ritter, C. G. Wade, C. S. Adams, and K. J. Weatherill, Phys. Rev. Lett. 111, 113901 (2013).
[35] S. Genway, W. Li, C. Ates, B. P. Lanyon, and I. Lesanovsky, Phys. Rev. Lett. 112, 023603 (2014).
[36] J. Barrè, B. Marcos, and D. Willkowski, Phys. Rev. Lett. 112, 133001 (2014).
[37] T. Yuge, Phys. Rev. E 82, 051130 (2010).
[38] A. Shimizu, J. Phys. Soc. Jpn. 79, 113001 (2010).
[39] P. C. Martin: Phys. Rev. 161 (1967) 143.
[40] S. Chakravarty: Eur. Phys. J. B 5 (1998) 337.
[41] L. Benfatto, S. G. Sharapov, N. Andreanucci, and H. Beck: Phys. Rev. B 71 (2005) 104511.
[42] D. N. Basov and T. Timusk: Rev. Mod. Phys. 77 (2005) 721.
[43] V. Vescoli, J. Favaud, F. Mila, and L. Degiorgi: Eur. Phys. J. B 3 (1998) 149.
[44] A. Shimizu and T. Yuge, J. Phys. Soc. Jpn. 80, 093706 (2011).