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LETTER TO THE EDITOR

Shear modulus collapse of lattices at high pressure

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Abstract

It is shown that metals would be liquid at high pressure at absolute zero temperature due to the vanishing of the shear modulus. The lowest shear modulus collapse pressures P_G occur for low-Z metals. The shear modulus collapse of the lattice for Li, Be, and B ($Z < 6$) may occur at pressure $P < 3$ Mbar, i.e. at pressures which can be distinguished now by the diamond-anvil technique. Our calculations show that hydrogen transforms to liquid metal at the molecular–monatomic transition.

Whether a material would be solid or liquid at ultrahigh pressure is one of the main problems in high-pressure physics, geophysics, planetary physics, and astrophysics. Some evidence exists that these materials would be liquid at extreme pressure. (i) Calculation of the ground-state energy for a system of interacting electrons and positive ions shows that at extreme pressure the liquid state is more stable than the solid, at least for alkali metals [1]. (ii) A solid would be destroyed at extreme pressure by zero-point quantum vibration at absolute zero temperature (so called 'cold melting') when the energy of zero-point quantum vibration of atoms becomes greater than the Coulomb energy [2]. (iii) Recently, it was shown that the melting temperature dependence on pressure P has the form $T_m = F(P)D(P)$, where $F(P)$ is the rising and $D(P)$ is the damping function, which slopes downward asymptotically under pressure [3]. (At low temperatures, the quantum effects should be taken into account. The zero-point vibration destroys the lattice when T_m approaches zero temperature.) This form predicts that solids must be liquid at high pressure.

On the other hand, for inverse power potentials, $\phi(r) \sim r^{-n}$, melting temperature at high density has the form $T_m \sim r^{-n/3}$, with n lying in the interval from 6 to 12 for the majority of materials [4]. From one-component plasma theory [5], it follows that $T_m \sim Z^{5/3}r^{-1}$. All of these forms predict that the melting temperature rises continuously under compression. In other words, material will remain a solid at all pressures. (It is believed that only hydrogen and helium will be liquid due to zero-point quantum vibration. This because the densities required for heavier elements are such that the sizes of the nuclei become important [2].)

In the present letter we consider the behaviour of the shear modulus of materials under pressure. Note that the shear modulus $G > 0$ for the solid state whereas $G = 0$ for the liquid state. Voigt [6] has shown that the shear and bulk moduli of crystals can be expressed in terms of the elastic constants c_{ij}. It should be emphasized that the Voigt relationships hold at any pressure as long as the matter is solid. The Voigt relationships are widely employed in geophysical research [7]. For cubic crystals (the more stable structures at high pressure), the Voigt shear modulus has the form $G_V = (c_{11} - c_{12} + 3c_{44})/5$ which can be written as

$$G_V = \tfrac{3}{5}(B - 2P - \delta), \tag{1}$$

where $B = (c_{11} + 2c_{12})/3$ is the bulk modulus and $\delta = c_{12} - c_{44} - 2P$ is the deviation from the Cauchy relation. If the Cauchy relation in a material holds—that is, if the pair potential exists (the interatomic force is central)—then deviation $\delta = 0$. All materials become metals at high pressure due to the expanding and overlapping of energy bands. Effects due to many-body forces in metals cause deviation from $\delta = 0$ (for metals $\delta > 0$). It is convenient to rewrite equation (1) in the form

$$G_V = \tfrac{3}{5}(\beta B - 2P) \tag{2}$$

where the dimensionless parameter $\beta = 1 - \delta/B$, $\beta \leqslant 1$. Experimental data [7–9] at $P = 0$ show that $\beta = 1 - (c_{12} - c_{44})/B = 5G/(3B) = 0.7 \pm 0.2$ for cubic (fcc, bcc) metals. Equation (2) predicts that *the lattice should be destroyed at extreme pressure due to the vanishing of the shear modulus*. Indeed, in the high-density limit $B/P = 5/3$ and $G_V/P = (5\beta - 6)/5 < 0$. Therefore *the shear modulus collapse pressure,* P_G exists, when the Voigt shear modulus G_V vanishes. At pressures $P > P_G$ all materials would be liquid even at absolute zero temperature [10][1].

We calculate the shear modulus collapse pressure P_G for different elements at 0 K using equation (2) and the quantum statistical model (QSM) for the equation of state. The QSM model includes the kinetic pressure of a uniform degenerate Fermi gas, the Madelung (Coulomb), the exchange and the quantum corrections [11]. The interpolation equation for metals has the form

$$P = 294.2\left[\frac{1}{5}(3\pi^2)^{3/2}\rho^{5/3} - \frac{13}{16}\left(\frac{\pi}{3}\right)^{-1/3}\rho^{4/3}\right] \text{Mbar}, \tag{3}$$

$$B = -v\,\mathrm{d}P/\mathrm{d}v = 32.7\left[(3\pi^2)^{3/2}\rho^{5/3} - \frac{13}{4}\left(\frac{\pi}{3}\right)^{-1/3}\rho^{4/3}\right](3 + ar_s + br_s^2) \text{ Mbar}, \tag{4}$$

where

$$\rho = \frac{Z}{v}\exp[-a(Z)r_s - b(Z)r_s^2]$$
$$a(Z) = 0.1935Z^{0.495-0.038\log Z}$$
$$b(Z) = 0.068 + 0.078\log Z - 0.086(\log Z)^2$$

r_s is the ratio of the radius of the equivalent sphere to the volume per atom in units of the Bohr radius, and Z is the atomic number.

The results of calculations of the shear modulus collapse pressure P_G as a function of the atomic number Z for the mean value $\beta = 0.7$ are shown in figure 1. It should be noted that Z could be considered not only as an atomic number, but also more generally as a number of electrons (protons) per atom. In this case the P_G versus Z dependence in figure 1 can be applied not only to elements, but also to the isoelectronic compounds (having the same number of electrons per atom), since the equations of state of isoelectronic materials converge at high pressure [12].

[1] Wigner crystal is the opposite case: electrons arrange in a crystal lattice when the volume of the electron liquid expands.

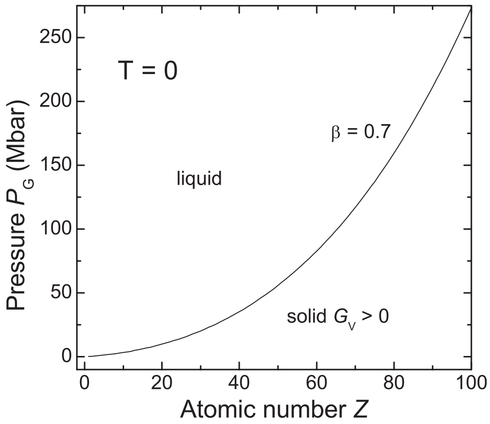

Figure 1. The shear modulus collapse pressure P_G, which corresponds to the vanishing of the shear modulus, versus atomic number Z at 0 K. Calculations were based on the Voigt equation for the shear modulus, $G_V = 3(\beta B - 2P)/5$, where B is the bulk modulus and $\beta = 0.7$. The quantum statistical model for the equation of state of matter was used.

It should be emphasized that the shear modulus collapse pressures in figure 1 correspond to the *metallic state of materials*. For nonmetals, the dependence P_G versus Z at pressure below the transition to the metal state corresponds to the *metastable metallic phase*. Therefore, if the shear modulus collapse pressure, P_G, is less than the nonmetal–metal transition pressure, $P_G < P_{n-m}$, then the nonmetal–metal transition corresponds simultaneously to a transition from the solid to the liquid state.

The lowest shear modulus collapse pressures P_G are for low-Z metals. Theory predicts that hydrogen ($Z = 1$) should dissociate at high pressure from its molecular state to form monatomic metal. The nonmetal–metal transition is expected to occur at pressures in the neighbourhood of $P_{n-m} = 4$ Mbar [13]. Many theorists have attempted to predict the structure of metallic hydrogen. Many studies supported low-coordination-number anisotropic structures, others concluded that high-coordination-number isotropic structures are favoured, and yet others considered the possibility of a quantum liquid state [14]. Our calculations show that the lattice of metallic hydrogen is destroyed at $P_G = 0.23$ Mbar, if $\beta = 0.7$ (the collapse pressure P_G varies from 2.9 to 0.05 Mbar when β varies from 0.9 to 0.5, respectively), i.e. $P_G < P_{n-m}$ in all cases. Hence hydrogen after the nonmetal–metal transition would be liquid. This conclusion is in agreement with previous calculations by McDonald and Burges [15]. They argued that, because of the differing roles of electronic screening in solid and fluid states, metallic hydrogen will remain a liquid at all pressures. Recently, we calculated the melting curve of metallic hydrogen and found that metallic hydrogen would be liquid at all pressures at absolute zero temperature as a result of the zero-point quantum vibration of atoms [16]. Jaffe and Ashcroft [17] have concluded that metallic hydrogen can become a new state of matter: a superconducting liquid.

Unlike hydrogen (and other diatomic molecular insulators), monatomic insulators, such as the rare-gas solids (He, Ne, Ar, Kr, and Xe), are metallized under pressure as a result of the band overlap. Band theory calculations for helium indicate $T = 0$ metallization at $P_{n-m} = 112$ Mbar [18]. Our calculations show that the lattice of metallic helium would be destroyed at $P_G = 0.46$ Mbar, i.e. $P_G < P_{n-m}$. Correspondingly, at the nonmetal–metal transition, molecular helium, as in the case of hydrogen, would transform directly to the metallic liquid state. LiH and CH_4 are isoelectronic to helium. For them, as for helium,

$P_G = 0.46$ Mbar and $P_G < P_{\text{n-m}}$. All of them transform to liquid at the nonmetal–metal transition. For the other rare-gas solids (except neon), $P_G > P_{\text{n-m}}$. At $P = P_{\text{n-m}}$ these materials transform to solid metal; then at $P = P_G$ they transform to liquid metal.

The lattice of lithium ($Z = 3$) would be destroyed at $P_G = 0.7$ Mbar (figure 1). In this connection, it is interesting to note that the superconducting critical temperature of lithium [19] at 0.7 Mbar drops down from 16 to 11 K. It seems plausible that lithium at pressure 0.7 Mbar would transform to the liquid superconducting state (like hydrogen).

Beryllium ($Z = 4$) and boron ($Z = 5$) are more suitable for high-pressure experiments, in comparison with lithium, because of its active diffusion into diamond anvils. Our calculations show that beryllium and boron would be liquid metals at pressures above 1.1 and 1.3 Mbar, respectively, if $\beta = 0.7$ (the pressures are doubled if $\beta = 0.75$). Boron transforms from a nonmetal to a superconductor at 1.6 Mbar [20]. It may well be that the nonmetal–metal transition in boron coincides with the solid–liquid transition.

The present results should be considered as qualitative. All collapse pressures P_G in this letter are based on the QSM equation of state, which is not well defined at low compression. The shear modulus collapse pressure P_G is very sensitive to the value of the parameter β. Clearly, small differences in β yield large variations in the estimates of the collapse pressure. In general, the parameter β is specific to each material. Furthermore, the value of β depends on the pressure. Experiments show that the parameter β decreases (the deviation δ increases) under pressure, i.e. the noncentral nature of the bonding becomes enhanced at high pressure. In fact, the P_G versus Z dependence should not be a smooth line; it is more likely to be a line which oscillates, because to every Z there should correspond a specific β. Nevertheless, the main result is unchanged: the Voigt equation predicts that the lattice should be destroyed at extreme pressure due to the vanishing of the shear modulus.

In conclusion, it is shown that all materials would be liquid at high pressure at absolute zero temperature due to the vanishing of the shear modulus. The shear modulus collapse pressure depends on the atomic number Z and on the parameter β. The lowest shear modulus collapse pressures P_G are for low-Z metals. Our calculations show that hydrogen ($Z = 1$), helium, LiH and CH_4 ($Z = 2$) transforms to liquid at the nonmetal–metal transition. The possibility of the shear modulus collapse of lattices ('shear modulus melting') at high pressure may be important in the evolution and composition of giant planets of solar systems, as well as of white and brown dwarfs.

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