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LETTER TO THE EDITOR

Sound velocity in liquid metals and the hard-sphere model

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Abstract. It is pointed out that two, approximately 'universal', *dimensionless* major characteristics of the sound velocity in liquid metals are also shared by the hard-sphere system as *intrinsic* properties of that simple model.

In recent reviews [1] of some of the more important thermodynamic properties of liquid metals it was noted that the sound velocity, c, divided by the thermal velocity has about the same value for many liquid metals near their melting point. Typically [1, 2],

$$\left(c\Big/\left(\frac{k_B T}{M}\right)^{1/2}\right)_{T=T_m} \sim 10 \tag{1}$$

where T_m is the melting temperature and M is the atomic mass, with a spread of values between $\sim$6 and $\sim$12. Except for a few anomalous cases [3] like Sb, Te, and Ce, the sound velocity *decreases very slowly* with the temperature, and typically [1, 2, 4],

$$\left(\frac{T}{c}\frac{\partial c}{\partial T}\right)_{T\approx T_m} \sim -0.2 \tag{2}$$

with a spread of values between ~ -0.1 and ~ -0.3. The velocity of sound is given by

$$Mc^2 = \left(\frac{\partial P}{\partial \rho}\right)_S = \left(\frac{\partial P}{\partial \rho}\right)_T + \frac{T((\partial P/\partial T)_V)^2}{\rho^2 C_V/N} \tag{3}$$

where P, S, $\rho = N/V$, N, V, and C_V denote the pressure, entropy, density, number of particles, volume, and heat capacity at constant volume, respectively. Even the so-called 'simple' liquid metals represent complicated many-body nucleus–electron systems [5]. No simple model system can provide *detailed* agreement with the thermodynamics of liquid metals that will thus also reproduce the 'quasi-universal' magnitudes (1) and (2), especially since they require also the knowledge of the *melting temperature*. In turn, this quasi-universality by itself, in view of the differences in the details of the thermodynamic properties between classes of liquid metals, 'invites' one to seek a simple model system which can provide a general intuitive feeling for how the magnitudes (1) and (2) come about. The hard-sphere model has a long history of useful applications to the structure and thermodynamics of liquid metals [4, 6], mainly playing the role of a reference system in perturbation theories, but there was no reason to expect such general trends and values as (1) and (2) for liquid metals to also happen to be *intrinsic* properties of the simple hard-sphere system.

The purpose of this short letter is to point out that these two major 'quasi-universal' *dimensionless* characteristics of liquid metals are also shared by a collection of classical hard spheres. The classical system of hard spheres, perhaps the simplest classical system with

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pairwise interactions which exhibits the freezing transition, certainly cannot reproduce the detailed thermodynamics of liquid metals in detail, yet by coincidence it provides a representative simple generic model for these quasi-universal features.

For a classical system of hard spheres of radius R the heat capacity is purely kinetic, $C_V = \frac{3}{2}Nk_B$, and the compressibility factor

$$\frac{P}{\rho k_B T} = p(\eta) \tag{4}$$

is a function of only the packing fraction

$$\eta = \left(\frac{4\pi}{3}R^3\right)N/V.$$

A good fit to the simulation data is given by the Carnahan–Starling expression

$$p(\eta) = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{5}$$

and the fluid density at the melting temperature is $\eta_F = 0.494$ [7].

Using (4) and (5) we can obtain η as function of the ratio P/T from the equation

$$\left(\frac{4\pi}{3}R^3\right)P/(k_B T) = \eta p(\eta) \equiv \psi(\eta). \tag{6}$$

Using (3) we obtain

$$c\Big/\left(\frac{k_B T}{M}\right)^{1/2} = s(\eta) \tag{7}$$

and

$$M^{1/2}c\Big/\left(\left(\frac{4\pi}{3}R^3\right)P\right)^{1/2} = \frac{s(\eta)}{(\eta p(\eta))^{1/2}} \equiv f(\eta) \tag{8}$$

where

$$s(\eta) = \left(p(\eta) + \eta\frac{\mathrm{d}p(\eta)}{\mathrm{d}\eta} + \frac{2}{3}p(\eta)^2\right)^{1/2}. \tag{9}$$

In view of the physical significance of the packing fraction we display the results using η as a parameter. The function $s(\eta)$ is shown in figure 1(a) where we plot $c/(k_B T/M)^{1/2}$ (using equation (7)). In particular, we see that near melting ($\eta \sim 0.5$) it is about 12. In most mappings of liquid metals onto the hard-sphere system their melting points correspond to η between $\sim$0.4 to $\sim$0.5, for which $s(\eta)$ varies between $\sim$6 to $\sim$12, in general agreement with (1). For a given pressure, the function $f(\eta)$ describes the velocity of sound as function of temperature: $\eta \sim 0.5$ corresponds to the melting temperature T_m, while $\eta \ll 1$ corresponds to the ideal-gas limit of $T \gg 1$ for which

$$f(\eta) = \left(\frac{5}{3\eta}\right)^{1/2}$$

and thus

$$c = \left(\frac{5}{3}\frac{k_B T}{M}\right)^{1/2}.$$

The overall behaviour is shown in figure 1(b) where we plot the ratio

$$c(T)/c(T_m) = f(\eta)/f(\eta = 0.494)$$

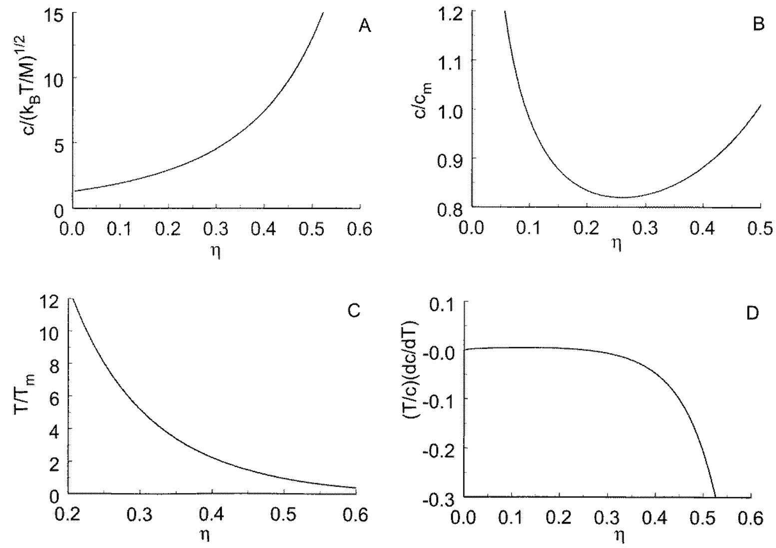

Figure 1. Various 'constant-pressure' properties of the hard-sphere system as a function of the packing fraction η. (a) The ratio of the sound velocity to the thermal velocity $c/(k_B T/M)^{1/2}$. (b) The ratio c/c_m of the velocity of sound to its value at melting $c_m = c(T_m)$. (c) The ratio T/T_m. (d) The logarithmic temperature derivative of the sound velocity, $\partial \ln c/\partial \ln T = (T/c)\,\partial c/\partial T$. See the text.

using (8). The sound velocity decreases from the melting temperature (i.e. $\eta \sim 0.5$), and after passing through the *minimum* value at about $\eta \sim 0.26$ it then increases eventually like $\eta^{-1/2}$ for $\eta \ll 1$. In figure 1(c) we plot the ratio

$$T/T_m = \psi(\eta = 0.494)/\psi(\eta)$$

using (1). By comparison of figure 1(b) with figure 1(c) we find that the minimum in the sound velocity is at $T \approx 7T_m$, and we see that as η varies from 0.494 to 0.415, T/T_m varies from 1 to about 2, while the velocity of sound changes only by about 10%. Correspondingly, the temperature derivative

$$\frac{\partial \ln c}{\partial \ln T} = \frac{T}{c}\frac{\partial c}{\partial T}$$

(using equations (6) and (8)) given in figure 1(d) varies from about -0.3 near $\eta \sim 0.52$ to about -0.1 near $\eta \sim 0.45$, and it is about -0.2 near $\eta = \eta_F = 0.494$ (i.e. $T = T_m$) in agreement with (2).

The hard-sphere pressure and heat capacity are certainly not adequate models for the corresponding properties for liquid metals. The hard-sphere system serves only as a reference system in thermodynamic perturbation theory, which defines an *effective hard-sphere packing fraction*, $\eta(\rho, T)$. However, that effective packing itself is also useful when considering experimental results for the structure factor and transport coefficients in terms of a collection of hard spheres [4, 6]. The present observation that the hard-sphere values for

$$\left(c\Big/\left(\frac{k_B T}{M}\right)^{1/2}\right)_{T=T_m} \qquad \text{and} \qquad \left(\frac{T}{c}\frac{\partial c}{\partial T}\right)_{T\approx T_m}$$

are so close to the experimental values for many liquid metals should likewise be useful. Anomalous behaviour in systems like Sb, Te, and Ce can also be interpreted in terms of effective hard-sphere diameters as affected by structural changes resulting from electronic transitions.

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