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THE SOFT-SPHERE MODEL FOR METALS NEAR THE CRITICAL POINT*

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ABSTRACT

The soft-sphere model is convenient and accurate for predicting fluid phase thermodynamics. The validity of the model for describing the equation-of-state derivatives, Grüneisen's gamma and sound velocity, is shown.

KEY WORDS

High pressure fluids, liquid metals, soft-sphere model

The soft-sphere model for fluids was developed in order to model the dense liquid thermodynamics better than it is described by the van der Waals' equation. In the van der Waals' equation the excluded volume is treated crudely, so although this equation works well for low-density fluids, there is an unphysical singularity in the equation of state for densities approaching the normal liquid. In order to better describe the dense fluid an analytic fit to Monte Carlo simulations of particles interacting with a $\epsilon(\sigma/r)^n$ repulsion has been augmented with a phenomenological term accounting for the attractive tail in real potentials (Hoover et al., 1975 and Shaner, 1988).

The form of the equation of state for this model is

$$P = \frac{NkT}{V}\left\{1 + \frac{1}{3}nC_n\rho^{n/3}\left(\frac{\epsilon}{kT}\right) + \frac{1}{18}n(n+4)\rho^{n/9}\left(\frac{\epsilon}{kT}\right)^{1/3} - m\rho^m\left(\frac{\epsilon}{kT}\right)\right\}$$

and (1)

$$E = NkT\left\{\frac{3}{2} + C_n\rho^{n/3}\left(\frac{\epsilon}{kT}\right) + \frac{1}{6}(n+4)\rho^{n/9}\left(\frac{\epsilon}{kT}\right)^{1/3} - \rho^m\left(\frac{\epsilon}{kT}\right)\right\} \quad .$$

In these equations, n is the exponent of the repulsive part of the potential, C_n is the fcc static lattice Madelung energy, $\rho = n\sigma^3/\sqrt{2}V$, and m is a phenomenological parameter which describes the attractive part of the interaction. For $m = 1$ we recover the classical, mean-field van der Walls' form. We have shown that molecular fluids can be described by Eq. (1) augmented by terms in the energy equation describing the internal degrees of freedom (Shaner, 1988).

One of the consequences of the soft-sphere model is that one of the equation-of-state derivatives, Grüneisen's gamma, can be expressed analytically as

$$\gamma_G = \frac{2}{3}\left\{\frac{1 + 1/27(n+4)n\rho^{n/9}(\epsilon/kT)^{1/3}}{1 + 2/27(n+4)\rho^{n/9}(\epsilon/kT)^{1/3}}\right\} \quad . \tag{2}$$

This expression shows that γ_G depends on both density and temperature explicitly. By contrast, the quasiharmonic model of the solid phase gives only an explicit

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density dependence for γ_G.

We have measured γ_G for liquid lead (Hixson et al., 1986a and Boness et al., 1988a) and tantalum (Brown and Shaner, 1984 and Hixson et al., 1986b) both in shock compression and isobaric expansion. These data are shown along with a soft-sphere calculation for $n = 8$ in Fig. 1. The basic feature of the inversion of the density dependence between expansion and compression are clear in this figure. Since the temperature is increasing with density for the shock compression part of the curve and decreasing with density for the isobaric expansion part of the curve the non-monotonic density dependence of γ_G is attributed to the intrinsic temperature dependence of Eq. (2).

For the $n = 8$ repulsive potential, which is a reasonable approximation for many liquid metals, one can show that the sound velocity around the normal liquid density is (Shaner, 1988)

$$C = 0.5\left(\frac{A}{M}\frac{kT_c}{4.14 \times 10^{-4}}\right)^{1/2} \tag{3}$$

where A is Avagadro's number, M is the atomic weight, and T_c is the critical temperature. We show in Fig. 2 sound velocity data at the melting temperature of a number of metals (Webber and Stephens, 1968). One sees for groups in the same column of the periodic table the dominant $M^{-1/2}$ dependence. The $T_c^{1/2}$ dependence is also clear as T_c increases slightly for the lighter alkali metals.

The soft-sphere model has proven to be both a useful interpolative equation of state over a wide density range of molecular and metallic fluids and a useful guide to interpreting experimental data. Systematic adjustment of the parameters in the model should make it even more useful for describing specific fluid systems.

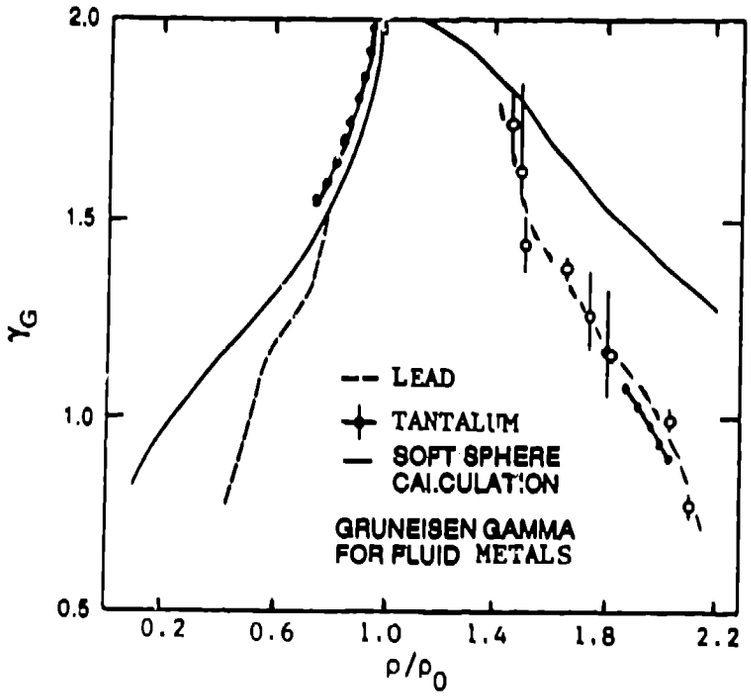

Fig. 1. Grüneisen gamma for liquid Pb and Ta compared with the soft-sphere model.

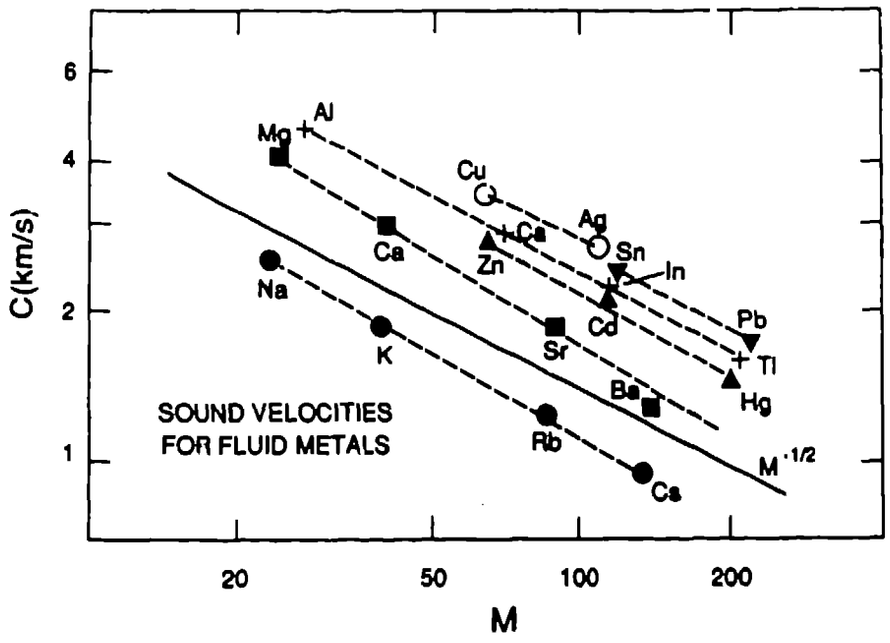

Fig. 2. Sound velocity of liquid metals.

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