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Pseudo-Grüneisen Parameter for Liquids*

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The dimensionless parameter $V_h^2\alpha/C_p$ is investigated for liquids, where V_h is the velocity of sound, and α/C_p the ratio of the coefficient of thermal expansion to the specific heat at constant pressure. For both Hg and H_2O, this quantity increases with increasing compression, contrary to the behavior for solids. For H_2O, this parameter becomes substantially independent of temperature. For a model in which compaction is assumed to take place by an increase of long-range positional order and growth of clusters, the pseudo-Grüneisen parameter is predicted to be temperature independent.

A DIAGNOSTIC parameter which has been found to be useful in the theory of the lattice dynamics of solids is the Grüneisen parameter. In one version, this parameter can be written as the dimensionless combination

$$\Gamma(V,T)=K_s\alpha V/C_p, \tag{1}$$

where K_s is the adiabatic bulk modulus, α is the coefficient of thermal expansion, V is the specific volume, and C_p is the specific heat at constant pressure. Let Γ be independent of temperature; we call $\Gamma=\gamma$. Then, by integration of (1),

$$P(V,T)=P_0(V,0)+\gamma(V)[U(V,T)/V], \tag{2}$$

which is Grüneisen's equation of state with U/V the internal energy density. Equation (2) was originally derived on the basis of the lattice dynamics of a crystalline solid. For most solids, Γ is nearly independent of temperature.

It is of interest to investigate whether Γ as defined in (1) is a suitable parameter to study the internal structure of liquids. For liquids, (1) can be written as

$$\Gamma=V_h^2\alpha/C_p, \tag{3}$$

with V_h the velocity of sound.

Accurate thermodynamic parameters are available for water at pressures up to 7.5 kbar.[1,2] We can test to determine whether Γ is independent of temperature (Fig. 1), as it is usually taken to be for solids. There is an indication that Γ does become substantially independent of temperature at sufficiently high pressures. The calculation has been made for water because thermodynamic data are presently available over a wide range of P and T. However, as may be expected, water has some anomalous properties. The values of Γ are significantly lower than for solids. Furthermore, Γ increases with decreasing V, contrary to the behavior of γ for metals.

Additional information is available from observations of the thermodynamic parameters for mercury.[3] Values of Γ for Hg also increase with increasing compression (Fig. 2). In this case, the values of Γ that are obtained are in the range of γ for solids. For these data, Γ does not seem to be independent of temperature over the limited range of volumes available; Hg appears to behave much like water at small compressions. One may attribute the differences in behavior between H_2O and Hg to the significantly greater incompressibility of Hg.

We assume that the lack of dependence of Γ upon T for part of the range of volumes of H_2O implies that the methods of lattice dynamics, developed originally for solids, can be applied to the liquid in this range. It has already been inferred that clustering occurs in liquids.[4] We treat the problem of the lattice dynamics of a cluster; in our model, we assume that the number of atoms in the cluster is a function of the compression. Thus, we are assuming that an increase in positional order is a mechanism for providing the compaction of the fluid. Evidently $N(V)$, the average number of par-

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[1] R. Vedam and G. Holton, J. Acoust. Soc. Am. **43**, 108 (1968).

[2] W. E. Sharp, University of California, Lawrence Research Laboratory Technical Report No. 7118, 1962 (unpublished).

[3] L. A. Davis and R. B. Gordon, J. Chem. Phys. **46**, 2650 (1967).

[4] A. R. Ubbelohde, *Melting and Crystal Structure* (Oxford U. P., New York, 1965).

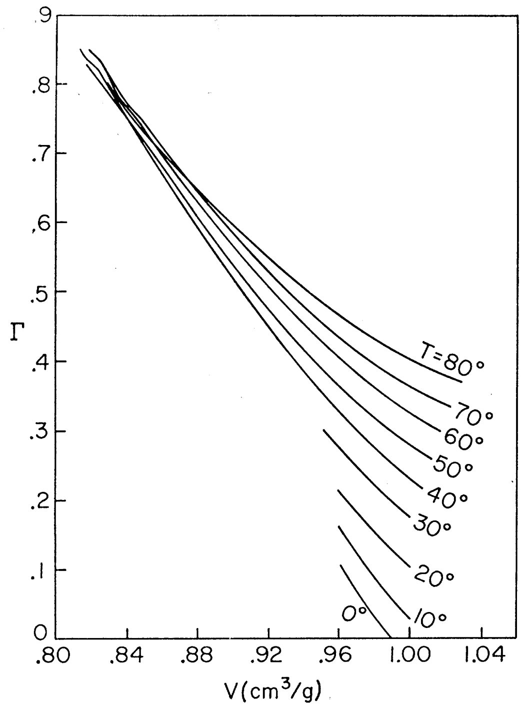

FIG. 1. Γ for water. Thermodynamic parameters for $30° \leq T \leq 80°$, from Ref. 1; for $0° \leq T \leq 20°$, from Ref. 2.

ticles in a cluster, is a monotonically decreasing function.

In order to obtain a qualitative explanation of the reversal of slope of $\gamma(V)$ between liquids and solids, we invoke the following argument based on the lattice dynamics of a one-dimensional monatomic crystal of finite dimensions which we take as an elementary model of a cluster. The theory can also be extended to the three-dimensional case but, in view of the approximations made and the simplicity of the algebra for the present case, this will not be done here.

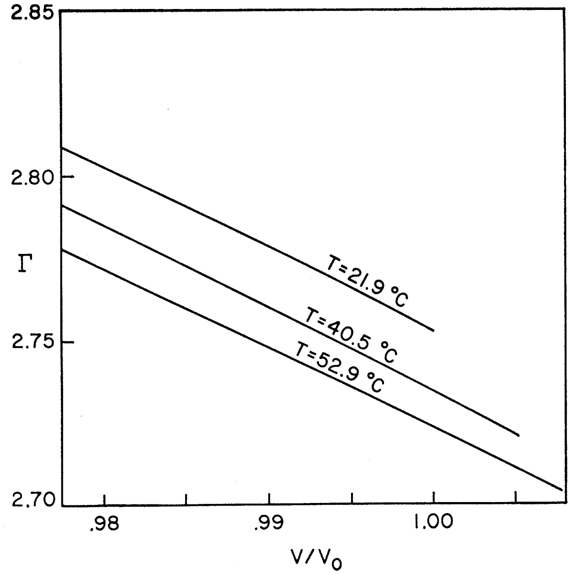

FIG. 2. Γ for mercury; V_0 is the volume at standard conditions.

Assuming nearest-neighbor interactions, the vibrational eigenfrequencies of a chain with equilibrium spacing d are well known to be

$$\omega_m = 2\omega_0 \sin(m\pi/2N), \quad m = 1, 2, \ldots, N-1 \tag{4}$$

where $\omega_0^2 = U''(d)/M$, $U(x)$ is the potential function, and M is the atomic mass. The internal energy is

$$E = \sum_{m=1}^{N-1} \frac{\hbar\omega_m}{e^{\hbar\omega_m/kT}-1}. \tag{5}$$

The pressure at temperature T is

$$P = P_0 + \frac{1}{V} \sum_{m=1}^{N-1} \frac{\hbar\omega_m\gamma_m}{e^{\hbar\omega_m/kT}-1}, \tag{6}$$

where $P_0(V)$ is the pressure at $T=0$ and

$$\gamma_m = -\left.\frac{\partial \ln\omega_m}{\partial \ln V}\right|_T. \tag{7}$$

From the usual Grüneisen theory, the Grüneisen parameter is

$$\gamma = \frac{(P-P_0)V}{E} = \sum_1^{N-1} \frac{\hbar\omega_m\gamma_m}{e^{\hbar\omega_m/kT}-1} \Big/ \sum_1^{N-1} \frac{\hbar\omega_m}{e^{\hbar\omega_m/kT}-1}. \tag{8}$$

Operating with (7) on (4) we get

$$\gamma_m = \gamma_D + \frac{m\pi}{2N} \left.\frac{\partial \ln N}{\partial \ln V}\right|_T \cot\frac{m\pi}{2N}, \tag{9}$$

where γ_D is the term usually derived from Debye theory, i.e.,

$$\gamma_D = -\left.\frac{\partial \ln\omega_D}{\partial \ln V}\right|_T, \tag{10}$$

with ω_D the Debye frequency; $\omega_D = \pi\omega_0$.[5] γ_D is evidently independent of m, since it is the term corresponding to the infinite lattice. By direct substitution of (4) and (9) into (8), we get

$$\gamma = \gamma_D + \xi \left.\frac{\partial \ln N}{\partial \ln V}\right|_T,$$
$$\xi(a,N) = \sum_1^{N-1} \frac{m\nu \cos m\nu}{e^{a \sin m\nu}-1} \Big/ \sum_1^{N-1} \frac{\sin m\nu}{e^{a \sin m\nu}-1}, \tag{11}$$

with $a = 2\hbar\omega_0/kT$, and $\nu = \pi/2N$. For temperatures

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[5] M. Blackman, Proc. Roy. Soc. (London) **A148**, 365 (1934).

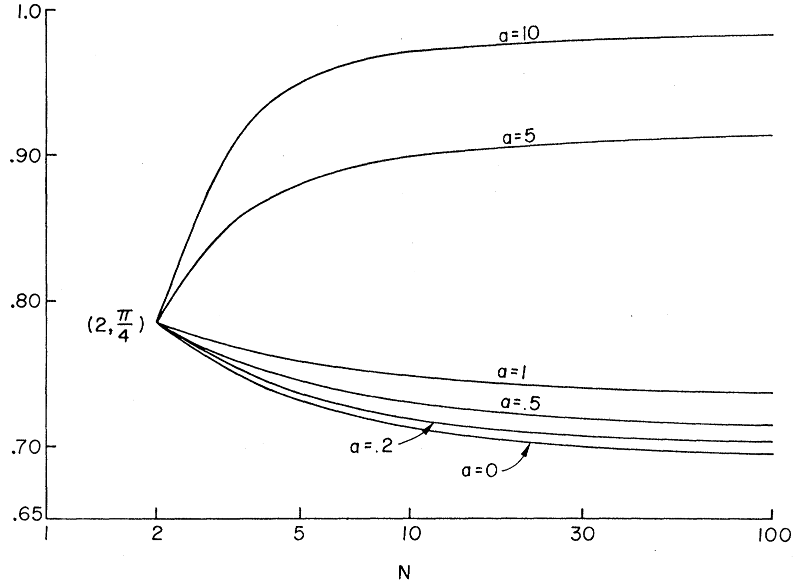

FIG. 3. Function $\xi(a,N)$. $\xi(a,2)=\frac{1}{4}\pi$.

large compared with the Debye temperature, i.e., $a \ll 1$, and for large N,

$$\xi=\int_{\nu}^{\pi/2-\nu} x \cot x dx \Big/ (\tfrac{1}{2}\pi-2\nu)+\cdots$$

$$=0.6942+\frac{0.3780}{N}+\cdots. \quad (12)$$

The function ξ in Eq. (11) can be evaluated directly by summation for N small or by integration for N sufficiently large. Figure 3 displays curves of $\xi(a,N)$.

The result (11) indicates that, if $dN/dV=0$, $\gamma=\gamma_D$, and indeed $\gamma(V)$ can have the reverse slope if N decreases with V sufficiently strongly. This theory also implies

$$\left.\frac{\partial\gamma}{\partial T}\right|_V >0,$$

in support of the observations for H_2O, but is inadequate to account for those for Hg. There are a number of other features not accounted for by this theory, including the apparent disappearance of the dependence of γ on temperature in the range where $\gamma(V)$ has a negative slope. This model can only be considered to be qualitative at best, and its main virtue is that it accounts for the reversal of slope in terms of accretion of particles onto clusters. We do not expect that an analysis of three-dimensional models will diminish the importance of the term dN/dV in the calculation of γ