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Application of Soft-Sphere Equation of State to Liquid Mercury

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INTRODUCTION

In a previous article with J. E. Lind, we describe PVT data for liquid mercury obtained over the temperature and pressure ranges 30 to 150°C and 0 to 8,000 bars respectively.¹ These data were fitted by expressing pressure as a single quadratic equation in density and temperature following a previous example.^{2,3} Using this equation, in conjunction with the calorimetric properties of Douglas, Ball and Ginnings,⁴ we then computed thermodynamic properties.

At that time we attempted to interpret the equation of state in terms of the hard-sphere model-not very satisfactorily since, although we made a first order allowance for the variation of hard-sphere diameter with temperature and pressure, there did not appear to be an adequate method of taking care of higher order effects, though this has been attempted.⁵

Subsequently, computer-derived equation-of-state data became available for the soft-sphere model for various values of the soft-sphere exponent n .⁶ In this article, an attempt is made to apply this model to the experimental data and thereby extract quantitative information about the components making up the internal energy.

Previous approaches at analysing the equation of state of mercury have been chiefly concerned with correlating experimental data and make use of, for example, the Huddleston equation⁷ which has a quasi theoretical basis and whose parameters are ostensibly related to intermolecular forces. In

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contrast, this approach is mainly concerned with testing the applicability of a specific molecular model and deducing quantitatively the molecular parameters.

SOFT-SPHERE MODEL

Suppose that the soft-sphere or repulsive potential has the form $\epsilon(\sigma/r)^n$ and that the attractive potential may be represented by a sum of potentials φ_i having the form $\epsilon_i(\sigma/r)^{m_i}$. It then follows that the internal energy is given by:

$$U = \langle K \rangle + \langle \Phi_r \rangle + \sum_i \langle \Phi_i \rangle \quad (1)$$

where $\langle K \rangle$ is the canonical ensemble average kinetic energy of atoms and free electrons and $\langle \Phi_r \rangle$ and $\sum_i \langle \Phi_i \rangle$ the corresponding quantities for the potential energy. It is not thought that the simplifying assumption of pairwise additive energy will materially affect the general conclusions reached in applying the model. See, for example, Rowlinson for a discussion of this approximation.⁸

The virial theorem gives:

$$2\langle K \rangle = 3PV - n\langle \Phi_r \rangle - \sum_i m_i \langle \Phi_i \rangle \quad (2)$$

Eliminating $\langle \Phi_r \rangle$ from (1) and (2) and differentiating yields:

$$\begin{aligned} d\langle K \rangle = & ((3V(\partial P/\partial T)_V - nC_V)/(2 - n)) dT \\ & + (((3 + n)P + 3V(\partial P/\partial V)_T - nT(\partial P/\partial T)_V) \\ & + \sum_i (m_i - n)(\partial \langle \Phi_i \rangle / \partial V)_T)/(2 - n)) dV \end{aligned} \quad (3)$$

This neglects the differential of $\langle \Phi_i \rangle$ with respect to temperature; but it is thought to be a fair approximation since the potentials φ_i depend on lower powers of r than φ_r .

Since $\langle K \rangle = \langle K_a \rangle + \langle K_e \rangle = (3/2)RT + \langle K_e \rangle$, where $\langle K_a \rangle$ is the atomic and $\langle K_e \rangle$ the electronic kinetic energy, equating coefficients of dT in Eq. (3) gives:

$$\frac{n}{3} = (V(\partial P/\partial T)_V - R)/(C_V - 3R/2 - C_V^e) \quad (4)$$

where C_V^e is the electronic contribution to the total specific heat C_V .

Equation (4) gives a means of empirically evaluating n from the experimentally determined quantities $V(\partial P/\partial T)_V$, C_V and C_V^e . This has been done for two points at the extremes of the author's PVT data, at 30°C, 8,000 bars and 150°C, 0 bars respectively. At the former points, $V = 14.41 \text{ cm}^3/\text{g} \cdot \text{atom}$, $C_V = 24.63 \text{ J/g} \cdot \text{atom} \cdot \text{C}$, $(\partial P/\partial T)_V = 4.77 \text{ J/cm}^3 \cdot \text{C}$, $C_V^e = 0.57 \text{ J/g} \cdot \text{atom} \cdot \text{C}^9$ giving $n = 15.6$. At the latter point, $V = 15.16 \text{ cm}^3/\text{g} \cdot \text{atom}$, $C_V = 22.89 \text{ J/g} \cdot \text{atom} \cdot \text{C}$, $(\partial P/\partial T)_V = 3.83 \text{ J/cm}^2 \cdot \text{C}$, $C_V^e = 0.80 \text{ J/g} \cdot \text{atom} \cdot \text{C}$

giving $n = 15.5$. The range has been extended from the melting point to the boiling point by using the tabulated values of Vukalovich *et al.*¹⁰ At the former point, $n = 15.1$ and at the latter, $n = 16.1$, turning out to be fairly constant. These values of n contrast with the preferred value 9 of Epstein and Powers¹¹ derived by a number of methods.

SOFT-SPHERE DENSITY

The model may be applied to determine the density by two methods. One method compares the soft-sphere excess entropy with the experimental values. The other method compares compressibility factors.

Figure 1 shows the soft-sphere excess entropy plotted against the dimensionless density $\omega = \rho(\epsilon/kT)^{3/n}$ for various values of n . It was computed by

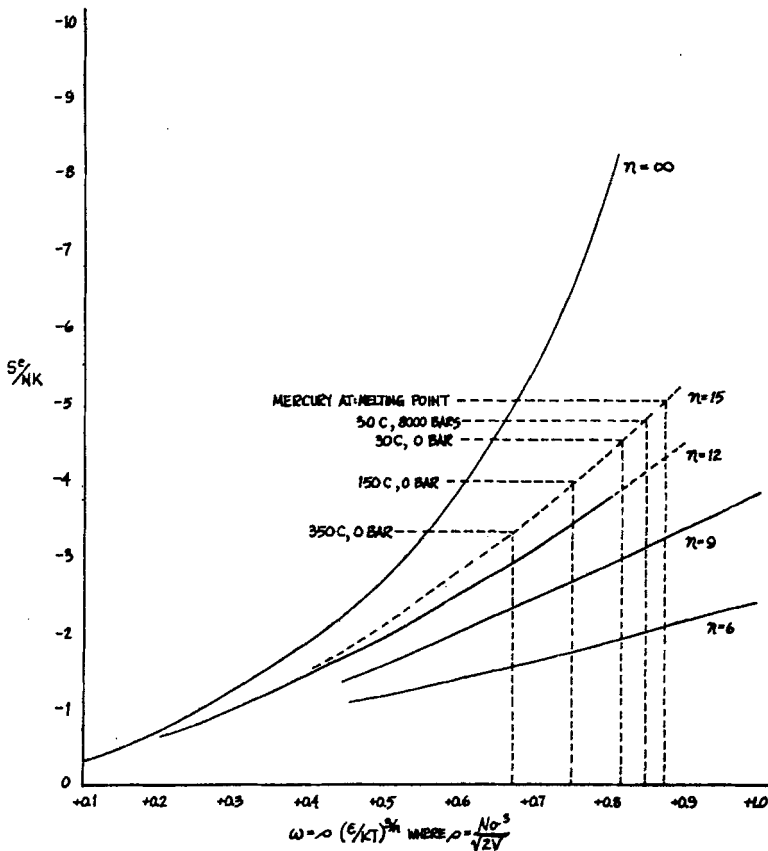


FIGURE 1 Excess entropy for hard and soft spheres (relative to an ideal gas at the same density and temperature) $S^e/Nk = (3/n)(Z - 1) - \int_0^Z (Z - 1) d \ln \rho$ for $\epsilon/kT = 1$. — Starling for $n = \infty$ and Hoover *et al.* for $n = 6, 9, 12$; ---- Extrapolated.

graphically integrating Hoover *et al.*'s equation-of-state data for $\epsilon/kT = 1$ utilizing the formula:

$$\frac{S^e}{NK} = \frac{3}{n} (Z - 1) - \int_0^{\rho} (Z - 1) d \ln \rho$$

The equivalent quantity for hard spheres is shown for comparison.¹² The $n = 15$ curve was obtained by extrapolation from the others and is the one applied to the mercury data.

S^e/Nk has been computed for liquid mercury from our data at three points: 30°C, 0 bars; 30°C, 8,000 bars; and 150°C, 0 bars making use of ideal gas entropies calculated by the Sackur-Tetrode Eq. (13). Vukalovich's tabulated

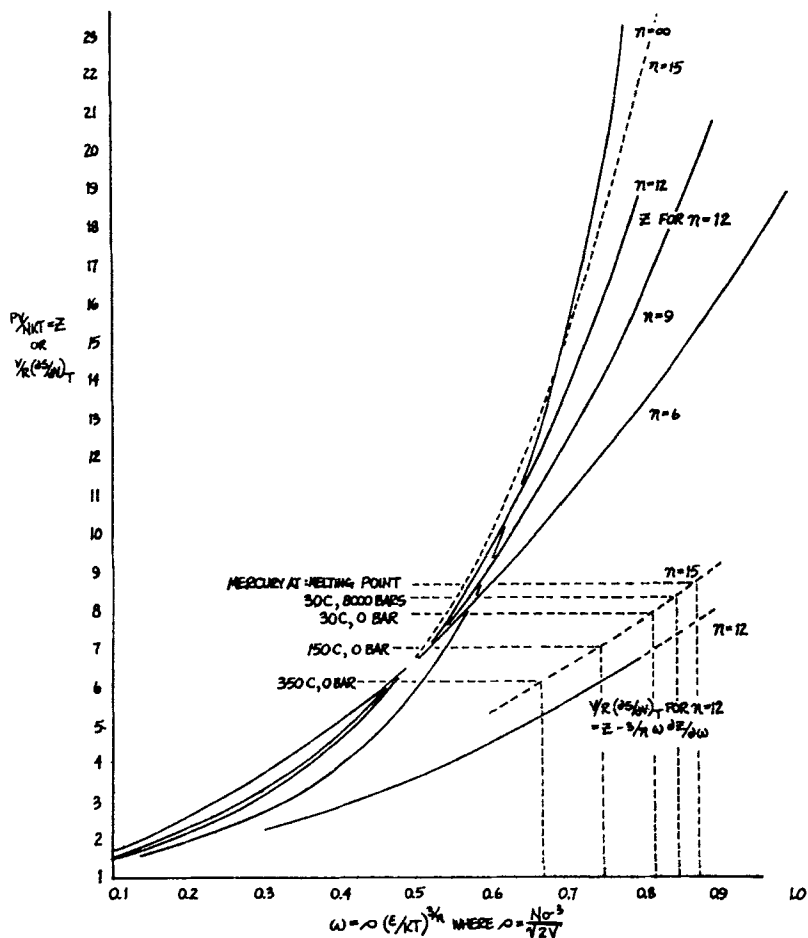


FIGURE 2 Compressibility factor for hard and soft spheres. — Starling for $n = \infty$ and Hoover *et al.* for $n = 6, 9, 12$; --- Extrapolated.

values have been used to extend the range from the melting point to the boiling point.

At 30°C, 0 bars the soft-sphere density turns out to be approximately $N\sigma^3/\sqrt{2}V(\epsilon/kT)^{3/n} = 0.82$ giving $\sigma = 3.05 (303.15k/\epsilon)^{1/15}$ Å. It is not possible to evaluate σ and ϵ/k from this expression since they only have separate significance for a combined attractive and repulsive potential. Using a theoretical two-parameter expression for the Van der Waals potential,¹⁴ $\epsilon_0/k = 875C$, $\sigma_0 = 2.76$ Å and $r_0 = 3.06$ Å where ϵ_0 is the depth of the potential well, σ_0 is the interatomic distance where the potential is zero and r_0 that where it is a minimum. These values are comparable with the literature values cited by Epstein and Powers.

In Figure 2 the compressibility factor is plotted against ω for both soft and hard spheres. Again the data is that of Hoover *et al.* and Carnahan and Starling respectively. Data for $n = 15$, as before, is extrapolated.

Since, in addition to a repulsive energy, there are a number of attractive terms making up mercury's total energy it is not possible to directly compare compressibility factors. But if one assumes that all the terms except the repulsive one are temperature insensitive, the quantity $(V/R)(\partial S/\partial V)_T$ may be used instead. It is related to the compressibility factor by the equation: $(V/R)(\partial S/\partial V)_T = Z - (3/n)\omega(\partial Z/\partial \omega)$ and is shown for $n = 12$ and 15 as derived graphically. Values of $(V/R)(\partial S/\partial V)_T$ for mercury for the same points as before are shown on the graph and it may be seen that the resulting densities correspond closely with those resulting from application of the excess-entropy method. This is in contrast to the disagreement when applying the hard-sphere model.

SEPARATION OF ENERGY COMPONENTS

Equations (1) and (2) provide two simultaneous equations from which two energy components may be calculated. The preceding application of soft-sphere theory yields a value for the repulsive energy $\langle \Phi_r \rangle$. The Van der Waals energy $\langle \Phi_a \rangle$ has also been calculated from the formula for the interatomic energy:¹⁵

$$U(r) = -2.296 \times 10^{-58} r^{-6} - 1.252 \times 10^{-73} r^{-8} \\ - 6.487 \times 10^{-89} r^{-10} - 4.234 \times 10^{-104} r^{-12},$$

where $U(r)$ is the attractive part of the interatomic energy in ergs and r is the interatomic distance in cm. This means that the free-electron kinetic energy $\langle K_e \rangle$ and the coulombic energy $\langle \Phi_c \rangle$ may be estimated.

In calculating $\langle \Phi_a \rangle$ it has been assumed that the mercury atoms are on a face-centered cubic lattice. In this case, the relationship between the interatomic potential and the lattice energy are given by Hirschfelder *et al.*,

p. 1035 *et seq.*¹⁶ An independent way of calculating the free-electron kinetic energy is from the Fermi energy¹⁷ which may serve to corroborate the result. Computations have been done at the melting point.

U may be calculated from the heat of vaporization¹⁸ and is approximately $-59,800$ J; $\langle\Phi_r\rangle$ obtained graphically from Figure 2 is approximately $10,500$ J and $\langle\Phi_a\rangle$ is approximately $-151,800$ J, all on a molar basis. Substitution of values for U , $\langle\Phi_r\rangle$, $\langle\Phi_a\rangle$, and PV in Eqs. (1) and (2) yield $\langle K_e\rangle = 882,150$ J and $\langle\Phi_c\rangle = -800,650$ J.

Alternatively $\langle K_e\rangle$ may be approximated by $(3/5)NzE_F$ which Ascarelli computes to be $910,000$ J which is in fair agreement.

CONCLUSION

Computation of the same atomic density by two methods, one based on excess entropy and the other on the thermal pressure coefficient tend to validate application of the soft-sphere model to liquid mercury. It is further supported by the agreement of two independent estimates of the free-electron kinetic energy.

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