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UCRL-52352

A SOFT-SPHERE MODEL FOR LIQUID METALS

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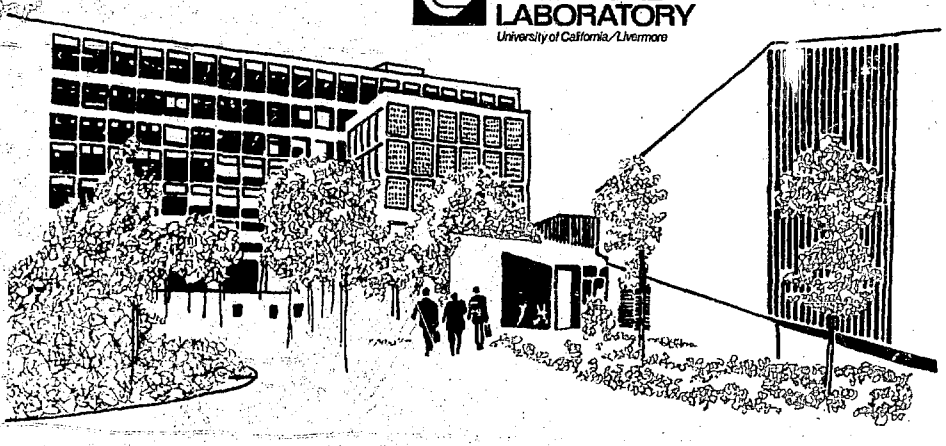
November 8, 1977

Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48



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UCRL-52362

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ABSTRACT

A semi-empirical soft-sphere model of fluids is modified for application to the thermodynamic properties of liquid metals. Enthalpy, volume, and sound speed are computed as functions of temperature for 13 metals and compared with experimental data. Critical points and coexistence curves are also computed and compared with experimental data, where these have been measured. Strengths and weaknesses of the model are discussed.

INTRODUCTION

In recent years, both the demands of new technologies (e.g., the breeder reactor) and continuing interest in the development of adequate theory have led to a great increase in research into the properties of liquid metals over a wide range of density. An especially important development has been the solution to the problem of containing liquid refractory metals in the isobaric expansion experiment,[1] which made it possible to measure the thermodynamic characteristics of liquid metals along isobars up to 400 MPa (4 kbar) and 7000 K. Further increases in pressure and temperature are expected from use of the technique, which allows the critical region to be approached for even the highest melting metals.

Despite these advances, however, no sufficiently rigorous body of theory is available that describes liquid metal behavior over the entire liquid-vapor range. Consequently, in the absence of an adequate theoretical model, we must rely on a semi-empirical model to systematize data from recent liquid metal experimentation.

HARD-SPHERE MODEL

A recent attempt to provide an approximate treatment of liquid metals in the liquid-vapor and critical regions was the hard-sphere van der Waals model of liquid metals published in 1971.[2] In this model the pressure and energy as functions of volume and temperature are given by

$$p = \frac{NkT}{V}\,\frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{V^2} \qquad (1)$$

and

$$E = \frac{3}{2}\,NkT - \frac{a}{V} + E_{coh}\ , \qquad (2)$$

where k is Boltzmann's constant, N is the number of atoms, σ is the hard-sphere diameter, $y = \pi N\sigma^3/6V$, and E_{coh} is the cohesive energy. The two parameters σ and a were determined from experimental data. From the standpoint of liquid metals research this model has several important limitations:

- The model is based on impenetrable hard spheres; it is clearly inadequate for compressed liquids.
- The heat capacity lacks configurational and electronic terms.
- The corresponding states principle obeyed by this model is clearly untrue for metals.

- The model does not quantitatively fit available liquid metal thermodynamic data.

Accordingly, a more general equation-of-state model is called for.

SOFT-SPHERE MODEL

To improve the agreement between theory and experiment, I have chosen the soft-sphere model of Hoover *et al.* [3] This model is based on Monte Carlo calculations for particles interacting with pair potentials of the form $\phi(r) = \epsilon(\sigma/r)^n$, where $4 \leq n \leq 12$. It uses a fairly simple configurational heat capacity term

$$\frac{\delta\Phi}{NkT} = \frac{1}{6}(n+4)\,\rho^{n/9}\,(\epsilon/kT)^{1/3}\,, \qquad (3)$$

which is obtained from the Monte Carlo energy value by subtracting the kinetic energy 3/2 NkT and a static-lattice term $C_n \rho^{n/3}$ (where C_n is the fcc Madelung constant for the potential and $\rho = N\sigma^3/\sqrt{2}$ V). Equation (3) permits the thermodynamic properties of fluids with repulsive $1/r^n$ potentials to be accurately determined for a wide range of n values.

Two further modifications are needed to make the model usable for liquid metals. First, a cohesive term must be added to the energy and pressure. Since the form of the attractive part of the effective pair potential in metals is complex and only poorly known, a mean-field term must suffice. Secondly, some liquid transition metals have very large electronic contributions to the heat capacity that cannot be fitted with the soft-sphere configurational term alone. Hence I multiply the configurational term by a factor Q, which can be greater than 1.0. This correction crudely accounts for the electronic effects, which are assumed to be slowly varying functions of temperature similar in form to the configurational term itself.

The final forms of the modified soft-sphere pressure and energy are

$$p = \frac{NkT}{V}\left[1 + \frac{1}{3}\,n\,C_n\,\rho^{n/3}\,(\epsilon/kT) + \frac{1}{18}\right.$$

$$\left. \times\, Qn\,(n+4)\,\rho^{n/9}\,(\epsilon/kT)^{1/3} - m\,\rho^m\,(\epsilon/kT)\right] \qquad (4)$$

and

$$E = NkT\left[\frac{3}{2} + C_n\,\rho^{n/3}\,(\epsilon/kT) + \frac{1}{6}\,Q\,(n+4)\right.$$

$$\left. \times\, \rho^{n/9}\,(\epsilon/kT)^{1/3} - \rho^m\,(\epsilon/kT)\right] + E_{coh}\,. \qquad (5)$$

Five parameters are adjustable: ϵ, σ, n, m, and Q. Primary emphasis is given to fitting enthalpy, volume, and sound speed isobars. Additional data, such as critical points or coexistence curves, are then "predicted" by the model. However, the physical basis of the model places some constraints on the values of the parameters. The value of n should be such that $(n+2)/6 \cong \gamma_0$, the Grüneisen parameter at the normal solid volume. (This is the prediction of harmonic lattice theory with $1/r^n$ potential particles.) Similarly, in general $m \cong 1.0$ in accord with the van der Waals equation of state and its generally good fits to molecular fluid data. Finally, $Q \cong 1$ except where electronic corrections are clearly warranted.

LIQUID METAL DATA

To test the model I selected 13 liquid metals for which substantial experimental data are available. As a group, the 13 metals constitute a good cross section of the periodic table: Li, Na, Al, K, Ga, Rb, Nb, Mo, Cs, Ta, Hg, Pb, and U.

The experimental data are in the form of isobars of enthalpy, volume, and sound speed. For a few metals the volume along several isobars, the coexistence curve, and the critical point have been measured. These data come from different sources (primarily Soviet, American, and German) that are not always consistent with one another. Also, some measurements are intrinsically more difficult to perform than others. For example, the measured

sound-speed data should be considered less accurate than volume or enthalpy data.

For the comparison of soft-sphere and experimental isobars, a basic set of experimental data is required. This set includes the atomic weight, the room temperature volume (V_o), the cohesive energy (E_{coh}), the melting temperature (T_m), enthalpy at melt referred to the room temperature value (H_m), and the density at melt ($\rho_m = 1/V_m$). These values are given in Table 1. Finally, a list of temperatures with corresponding experimental values of volume, enthalpy, and sound speed are required for comparison with model calculations.

Table 1. **Experimental data for 13 liquid metals.**

Metal	Atomic Weight (kg/mol)	Volume at room temperature V_0 (m^3/kg)	Cohesive energy E_{coh} (J/kg)	Melting temperature T_m (K)	Enthalpy at melt H_m (J/kg)	Density at melt ρ_m (kg/m^3)
Li	6.939×10^{-3}	1.876×10^{-3}	2.303×10^{7}	4.537×10^{2}	1.034×10^{6}	5.180×10^{2}
Na	2.299×10^{-2}	1.035×10^{-3}	4.659×10^{6}	3.710×10^{2}	2.067×10^{5}	9.270×10^{2}
Al	2.698×10^{-2}	3.706×10^{-4}	1.220×10^{7}	9.332×10^{2}	1.068×10^{6}	2.380×10^{3}
K	3.910×10^{-2}	1.166×10^{-3}	2.282×10^{6}	3.364×10^{2}	8.967×10^{4}	8.300×10^{2}
Ga	6.972×10^{-2}	1.694×10^{-4}	3.901×10^{6}	3.029×10^{2}	8.204×10^{4}	6.100×10^{3}
Rb	8.547×10^{-2}	6.560×10^{-4}	9.463×10^{5}	3.126×10^{2}	4.184×10^{3}	1.480×10^{3}
Nb	9.291×10^{-2}	1.166×10^{-4}	7.764×10^{6}	2.740×10^{3}	1.160×10^{6}	7.775×10^{3}
Mo	9.594×10^{-2}	9.784×10^{-5}	6.860×10^{6}	2.883×10^{3}	1.280×10^{6}	9.158×10^{3}
Cs	1.329×10^{-1}	5.206×10^{-4}	5.723×10^{5}	3.016×10^{2}	1.656×10^{4}	1.840×10^{3}
Ta	1.810×10^{-1}	5.968×10^{-5}	4.319×10^{6}	3.270×10^{3}	7.200×10^{5}	1.443×10^{4}
Hg	2.006×10^{-1}	7.407×10^{-5}	3.061×10^{5}	2.982×10^{2}	0.0	1.350×10^{4}
Pb	2.072×10^{-1}	8.818×10^{-5}	9.414×10^{5}	6.006×10^{2}	6.389×10^{4}	1.067×10^{4}
U	2.380×10^{-1}	5.240×10^{-5}	2.197×10^{6}	1.405×10^{3}	2.450×10^{5}	1.671×10^{4}

FITTING PROCEDURE

The soft-sphere isobar calculation first uses chosen values of n, m, and Q and computes ϵ and σ by an iteration scheme that solves the equations $p(V_m, T_m) = 0$ and $E(V_m, T_m) = H_m$. Subsequently, a search routine locates the critical point and T_c, V_c, p_c, and $Z_c = p_c V_c / R T_c$ are printed out. This calculation is helpful as a check for those metals with experimentally determined critical points. Finally, another iterative calculation takes the isobar pressure and a list of expanded volumes and determines the corresponding values of temperature, enthalpy, and sound speed. These calculated values are then plotted together with the experimental points.

If, as always happens, the first trial values of n, m, and Q lead to disagreement with experimental data, a series of systematic changes in these parameters is made until agreement is satisfactory. I have not, however, carried this process to an extreme precision of fit because the model is only semi-empirical and the experimental data are probably not accurate enough to warrant the effort.

A separate calculation is used to compute the coexistence curve for K, Rb, Cs, and Hg, metals for which experimental data are available. This is done by locating for given temperatures the coexisting densities for which the Maxwell equal-area rule is satisfied. This code plots out T vs ρ, p vs T, and $\ell n(p/p_c)$ vs T_c/T.

RESULTS

Lithium

The soft-sphere fit to lithium data is shown in Fig. 1. The enthalpies were obtained from Hultgren *et al.*[4] The volumes were obtained from Gol'tsova[5] and from Shpil'rain and Yakimovich.[6] The sound speeds are from Novikov *et al.*[7] All data are for p = 0.1 MPa (1 bar).

The best fit to experiment was found for n = 4, m = 0.7, and Q = 1.30. The most noticeable discrepancy lies in the incorrect slope predicted for the sound speed isobar.

The soft-sphere critical point occurs at T_c = 3741 K, V_c/V_0 = 5.86, p_c = 114 MPa, and Z_c = 0.28. The V_c and Z_c values are probably too large, since the other alkalis have rather small experimental values for Z_c. The predicted Grüneisen parameter at $V = V_0$ is 1.0, and the measured value[8] is 0.9.

Sodium

The soft-sphere fit to sodium data is shown in Fig. 2. The experimental enthalpies were obtained from Hultgren *et al.*[4] The volumes were obtained from Gol'tsova.[5] The sound speeds were obtained from Leibowitz *et al.*[9] and from Chasanov *et al.*[10] The volume and sound speed measurements were made along the saturation curve rather than along a 0.1 MPa isobar. The deviations from isobaric behavior become significant only above the boiling point (1154 K), as seen in the experimental volume data. The soft-sphere fit is adequate except in this region. In general, the greater the range of variables being fitted, the poorer the overall fit will be.

The best fit to experiment was found for n = 8, m = 0.58, and Q = 0.95. The predicted critical point is compared with the hard-sphere prediction[2] and with the measurement[11] in Table 2. As with lithium, the soft-sphere V_c and Z_c values are too large. The predicted Grüneisen parameter at $V = V_0$ is 1.7, and the measured value[8] is 1.3.

Aluminum

The soft-sphere fit to aluminum data is shown in Fig. 3. The experimental enthalpies were obtained from Hultgren *et al.*[4] The volumes were obtained from Gol'tsova.[12] The sound speeds were obtained from Stremousov and Tekuchev.[13]

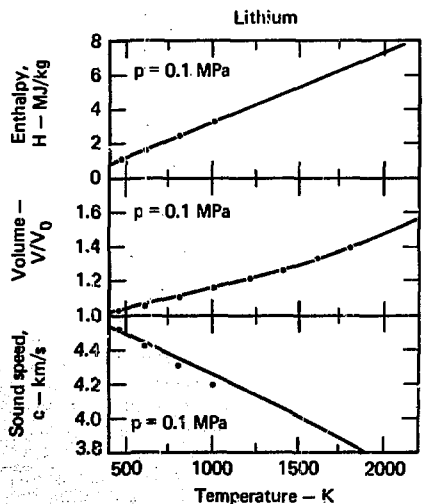

Fig. 1. Soft-sphere fit (smooth curves) to experimental lithium thermodynamic data (points).

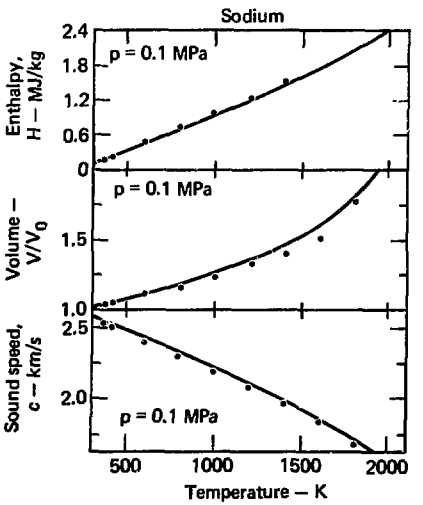

Fig. 2. Soft-sphere fit (smooth curves) to experimental sodium thermodynamic data (points).

Table 2. Comparison of hard-sphere, soft-sphere, and measured values (Ref. 11) of the critical constants for sodium.

	T_c(K)	V_c/V_0	p_c(MPa)	Z_c
Soft-sphere	2429	5.85	30	0.21
Experiment	2503	4.53	25	0.13
Hard-sphere	2635	3.59	92	0.36

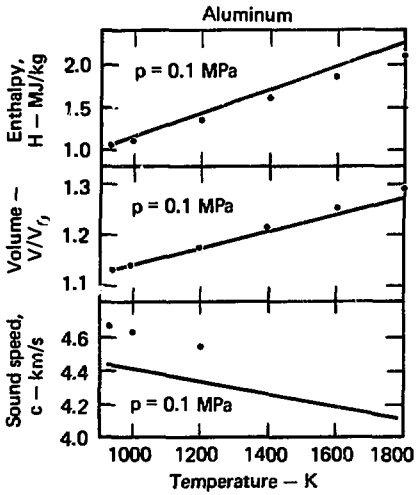

Fig. 3. Soft-sphere fit (smooth curves) to experimental aluminum thermodynamic data (points).

The best fit to experiment was found for n = 8, m = 0.7, and Q = 1.40. The enthalpy and volume fits are adequate. The predicted sound speeds are 4% too small. All data are for p = 0.1 MPa.

The predicted critical point occurs at T_c = 5726 K, V_c/V_0 = 6.37, p_c = 182 MPa, and Z_c = 0.24. The predicted Grüneisen parameter at V = V_0 is 2.2, and the measured value[8] is 2.1.

Potassium

The soft-sphere fit to potassium data is shown in Figs. 4 and 5. The experimental enthalpies were obtained from Hultgren *et al.*[4] The volumes were obtained from Gol'tsova.[5] The sound speeds were obtained from Trelin *et al.*[14] These data are plotted in Fig. 4. As with sodium, the volume measurements were made along the saturation curve rather

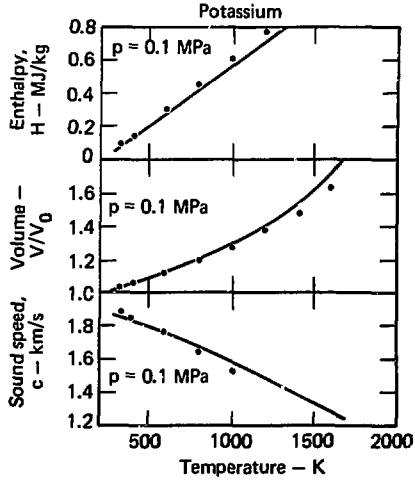

Fig. 4. Soft-sphere fit (smooth curves) to experimental potassium thermodynamic data (points).

than along an isobar so that higher temperatures could be reached. Thus the pressures rise well above 0.1 MPa at the highest temperatures, and mismatch with the isobar calculation is expected.

The liquid-vapor coexistence data are obtained from Jerez *et al.*[15] At present only p-T data near the critical point are available, and these are shown in Fig. 5.

The best fit to experiment was found for n = 7, m = 0.7, and Q = 1.0. The enthalpy and volume fits are adequate. The predicted sound speed isobar is approximately the right size but has the wrong slope.

The predicted critical point is compared with the hard-sphere calculation[2] and with measurement[11,15] in Table 3. The calculated coexistence curve pressure is noticeably too large and the reduced variable plot of $\ell n\ (p/p_c)$ vs T_c/T has the wrong slope. The critical pressure and volume computed from the soft-sphere model are sensitive functions of the parameter set and cannot be changed without changing the fit to the thermodynamic data. Th . Grüneisen parameter at V = V_0 is 1.5, and the measured value[8] is 1.3.

Gallium

The soft-sphere fit to gallium data is shown in Fig. 6. The experimental enthalpies were obtained

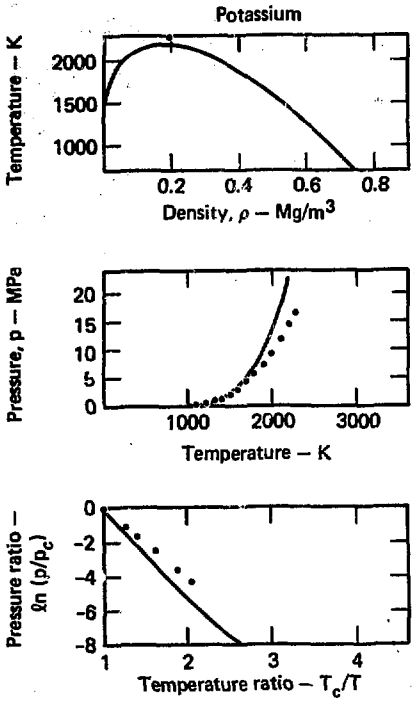

Fig. 5. Soft-sphere fit (smooth curves) to experimental potassium coexistence curve data (points).

Table 3. Comparison of hard-sphere, soft-sphere, and measured values (Refs. 11 and 15) of the critical constants for potassium.

	T_c(K)	V_c/V_0	p_c(MPa)	Z_c
Soft-sphere	2195	4.82	22.5	0.27
Experiment	2281	4.56	16.4	0.18
Hard-sphere	2185	3.62	39.6	0.36

from Hultgren *et al.*[4] The volumes were obtained from Köster *et al.*,[16] who measured volumes for a series of isobars. The p = 0.1 MPa and 250 MPa experimental volume isobars are shown in Fig. 6. The sound speeds were obtained from Magomedov *et al.*[17]

The best fit to experiment was found for n = 8.8, m = 0.75, and Q = 0.95. I found that a consistent fit

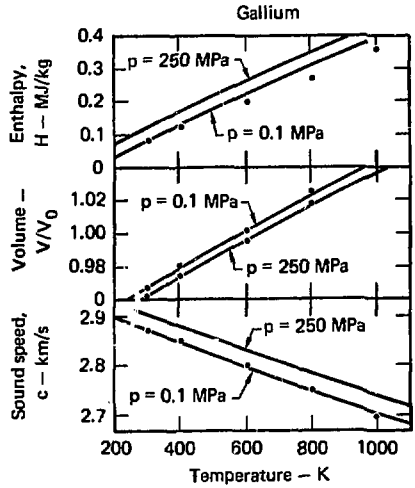

Fig. 6. Soft-sphere fit (smooth curves) to experimental gallium thermodynamic data (points).

to the enthalpy and volume isobars was not possible. Hence in Fig. 6 the enthalpy fit is poor, while the volume fit to the two isobars is good. The calculated sound speed is in excellent agreement with experiment.

The predicted critical point occurs at T_c = 6322 K, V_c/V_0 = 4.68, p_c = 254 MPa, and Z_c = 0.27. The predicted Grüneisen parameter at V = V_0 is 1.6, and the measured solid value[8] is 1.4.

Rubidium

The soft-sphere fit to rubidium data is shown in Figs. 7 and 8. The experimental enthalpies were obtained from Shpil'rain and Kagan[18] and Novikov *et al.*[19] The volumes were obtained from Steinberg.[20] The sound speeds were obtained from Novikov *et al.*[21] These data are shown in Fig. 7. All data are for p = 0.1 MPa. Coexistence curve data were obtained from Bhise and Bonilla[22] and Chung and Bonilla[23], and are shown in Fig. 8.

The best fit to experiment was found for n = 8, m = 0.70, and Q = 1.0. The fits are adequate, although the predicted sound speed is too high by about 5%.

The predicted critical point is compared with the hard-sphere calculation[2] and with measurements[22,23] in Table 4. The soft-sphere critical temperature is too low and the volume is too large, but

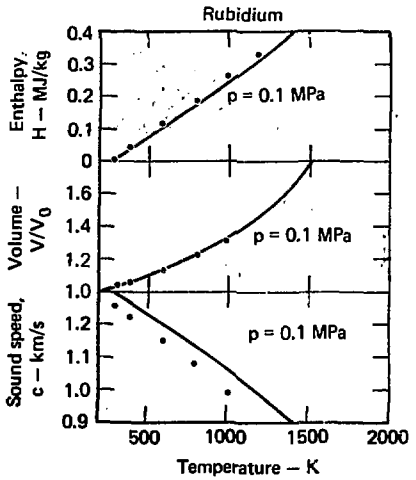

Fig. 7. Soft-sphere fit (smooth curves) to experimental rubidium thermodynamic data (points).

Table 4. Comparison of hard-sphere, soft-sphere, and measured values (Refs. 22 and 23) of the critical constants for rubidium.

	T_c(K)	V_c/V_0	p_c(MPa)	Z_c
Soft-sphere	1995	4.90	15.5	0.26
Experiment	2106	4.39	13.4	0.19
Hard-sphere	2061	3.57	30.8	0.36

the pressure is close to the measured value. These discrepancies show clearly in Fig. 8. The predicted Grüneisen parameter at $V = V_0$ is 1.7, and the measured value[8] is 1.8.

Niobium

The soft-sphere fit to niobium data is shown in Fig. 9. The experimental enthalpies and volumes were obtained from the isobaric expansion experiments of Gathers.[24] Sound speeds in the liquid have not yet been measured. All data are for p = 200 MPa.

The best fit to experiment was found for n = 6, m = 1.0, and Q = 2.10. The fits are adequate. Here the high value of Q is indicative of a large electronic contribution to the heat capacity.

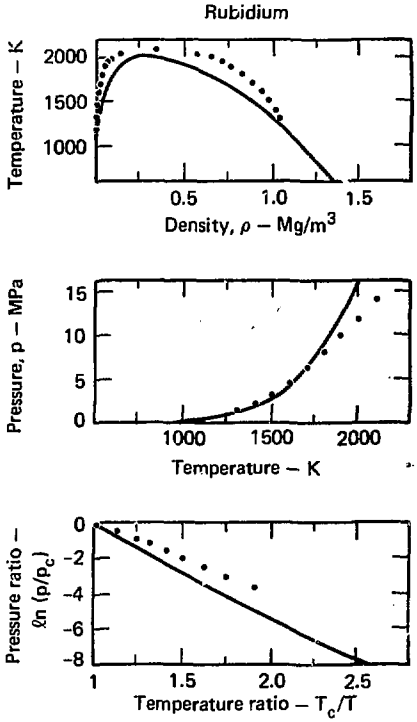

Fig. 8. Soft-sphere fit (smooth curves) to experimental rubidium coexistence curve data (points).

The predicted critical point occurs at T_c = 9989 K, V_c/V_0 = 4.25, p_c = 963 MPa, and Z_c = 0.53. There is a major discrepancy between the soft-sphere T_c and the hard-sphere prediction of approximately 16000 K. This must be due to the large measured heat capacity in liquid Nb. The predicted Grüneisen parameter at $V = V_0$ is 1.7, and the measured value[8] is 1.6.

Molybdenum

The soft-sphere fit to molybdenum data is shown in Fig. 10. The isobaric expansion experimental enthalpies and volumes were obtained from Gathers.[25] Sound speeds in the liquid have not yet been measured. All data are for p = 200 MPa.

The best fit to experiment was found for n = 8, m = 1.1, and Q = 2.1. The fits are adequate. The high

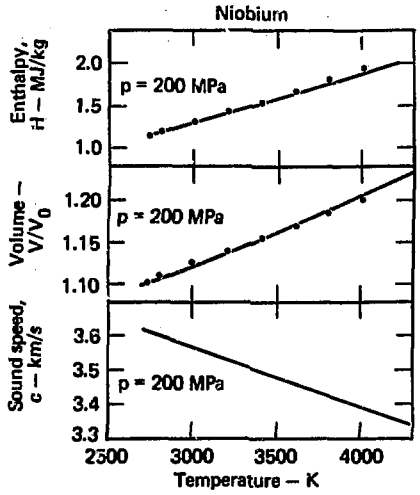

Fig. 9. Soft-sphere fit (smooth curves) to experimental niobium thermodynamic data (points).

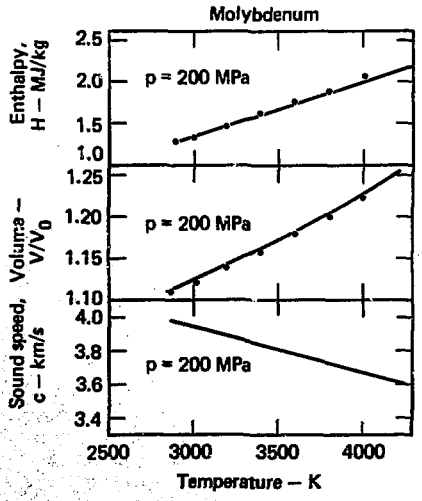

Fig. 10. Soft-sphere fit (smooth curves) to experimental molybdenum thermodynamic data (points).

Q value again indicates a large electronic contribution to the heat capacity.

The predicted critical point occurs at T_c = 8002 K, V_c/V_0 = 4.43, p_c = 970 MPa, and Z_c = 0.61. As with Nb, there is a discrepancy between the soft-sphere T_c and the much higher hard-sphere prediction. The predicted Grüneisen parameter at $V = V_0$ is 2.2, and the measured value[8] is 1.6.

Cesium

The soft-sphere fit to cesium data is shown in Figs. 11 and 12. The experimental enthalpies were obtained from Hultgren *et al.*[4] The volumes were obtained from Shpil'rain and Yakimovich[6] and from Korshunov *et al.*[26] Korshunov *et al.* measured the volume along a large number of isobars. The sound speeds were obtained from Novikov *et al.*[27] These data are shown in Fig. 11. Coexistence curve data were obtained from Das Gupta *et al.*[28] and are shown in Fig. 12.

The best fit to experiment was found for n = 7, m = 0.7, and Q = 0.90. The fits to thermodynamic data for p = 0.1 MPa and p = 12.2 MPa are shown in Fig. 11. The soft-sphere fit to the thermodynamic data is surprisingly poor. Most difficult to understand is the failure to fit the two volume isobars. The model does not compute the correct separation between isobars, even though the sound speed and

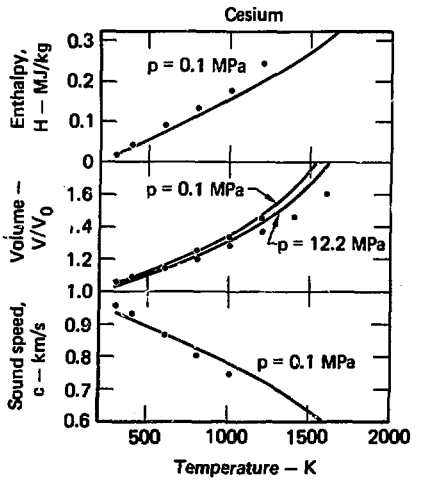

Fig. 11. Soft-sphere fit (smooth curves) to experimental cesium thermodynamic data (points).

hence the compressibility are approximately the correct size. The problem might have to do with the well-known anomalous behavior of cesium, with its electronic phase transition, or with possible inconsistencies in the experimental data.

The predicted critical point is compared with the hard-sphere calculation[2] and with measurements[28] in Table 5. Despite the rather poor fit to thermodynamic data in Fig. 11, the fit to the coexistence curve shown in Fig. 12 is adequate. Although the predicted critical volume is as usual too large, the predicted temperature and pressure are close to the experimental values. The predicted Grüneisen parameter at $V = V_0$ is 1.5, and the measured value[8] is 1.5.

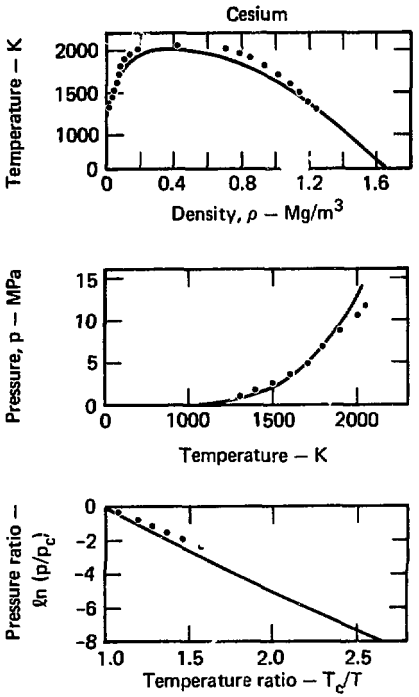

Fig. 12. Soft-sphere fit (smooth curves) to experimental cesium coexistence curve data (points).

Table 5. Comparison of hard-sphere, soft-sphere, and measured values (Ref. 28) of the critical constants for cesium.

	T_c(K)	V_c/V_0	p_c(MPa)	Z_c
Soft-sphere	2018	5.40	13.6	0.30
Experiment	2048	4.57	11.6	0.22
Hard-sphere	1942	3.60	23.3	0.36

Tantalum

The soft-sphere fit to tantalum data is shown in Fig. 13. The isobaric expansion experimental enthalpies and volumes were obtained from Gathers.[25] Sound speeds in liquid tantalum have not yet been measured. All data are for p = 100 MPa.

The best fit to experiment was found for n = 8, m = 1.1, and Q = 2.2. The fits are adequate. The high Q value implies a large electronic contribution to the heat capacity.

The predicted critical point occurs at T_c = 9284 K, V_c/V_0 = 3.93, p_c = 999 MPa, and Z_c = 0.55. The predicted Grüneisen parameter at $V = V_0$ is 2.2, and the measured value[8] is 1.7.

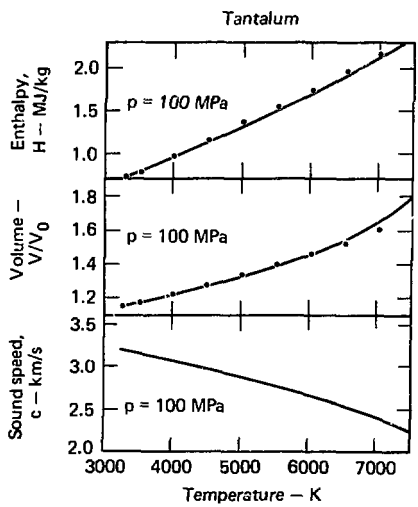

Fig. 13. Soft-sphere fit (smooth curves) to experimental tantalum thermodynamic data (points).

Mercury

The soft-sphere fit to mercury data is shown in Figs. 14 and 15. The experimental enthalpies were obtained from Hultgren *et al.*[4] The volumes were obtained from Spetzler *et al.*[29] and from Kikoin and Senchenkov,[30] who measured the volume along a large number of isobars. The sound speeds were obtained from Spetzler *et al.*[29] These data are shown in Fig. 14. Critical point and coexistence curve data were obtained from Hubbard and Ross,[31] who adjusted the data of Kikoin and Senchenkov, and from Hensel and Franck.[32] These data are shown in Fig. 15.

The best fit to experiment was found for n = 15, m = 1.5, and Q = 0.65. The fits to thermodynamic data for p = 0.1 MPa and p = 150 MPa are shown in Fig. 14. The fits to the enthalpy and volume at p = 0.1 MPa are adequate, but the fit to the volume at p = 150 MPa fails at large expansions. The computed sound speeds lie above the experimental values.

The predicted critical point is compared with the hard-sphere calculation and with experiment in Table 6. In this case, the hard-sphere result is somewhat better than the soft-sphere, probably because the experimental and hard-sphere values of Z_c are nearly equal. The discrepancies between predicted and measured critical constants show up clearly in Fig. 15. For a given density or pressure, the coexistence temperatures are too high. Oddly enough, the $\ell n(p/p_c)$ vs T_c/T fit is very accurate. The predicted Grüneisen parameter at $V = V_0$ (in the liquid) is 2.8, and the measured value is 2.9.

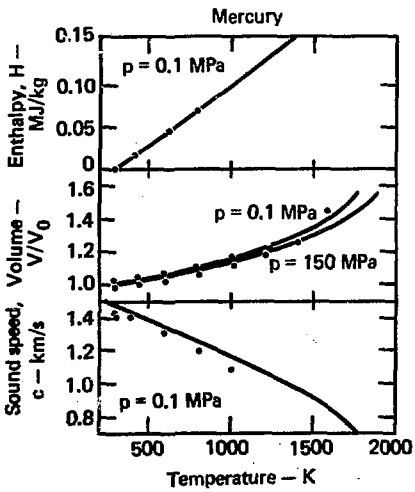

Fig. 14. Soft-sphere fit (smooth curves) to experimental mercury thermodynamic data (points).

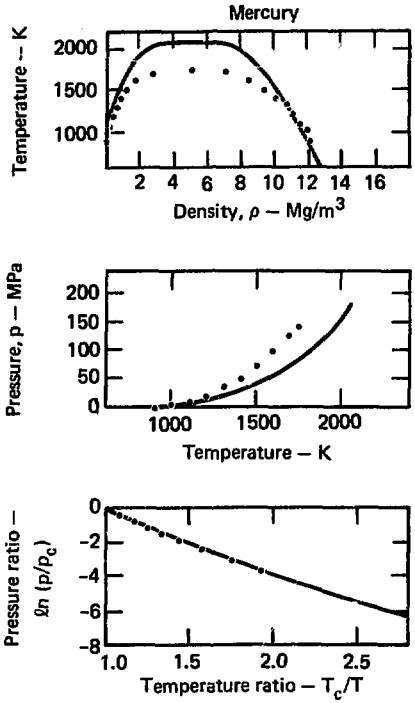

Fig. 15. Soft-sphere fit (smooth curves) to experimental mercury coexistence curve data (points).

Table 6. Comparison of hard-sphere, soft-sphere, and measured values (Ref. 30 and 31) of the critical constants for mercury.

	T_c(K)	V_c/V_0	p_c(MPa)	Z_c
Soft-sphere	2074	3.46	178	0.53
Experiment	1740	2.70	141	0.39
Hard-sphere	1563	3.40	92	0.36

Lead

The soft-sphere fit to lead data is shown in Fig. 16. The experimental enthalpies and volumes were obtained from Hodgson.[33] These are isobaric expansion data taken at 300 MPa. The sound speed data were obtained from Markov,[34] who made measurements at 0.1 MPa.

The best fit to experiment was found for $n = 11$, $m = 1.05$, and $Q = 0.85$. The fits are only fair, primarily due to the very large temperature range of the experimental data.

The predicted critical point is compared with the hard-sphere calculation[2] and with an experimental estimate[35] based on the behavior of release adiabats of shock-compressed porous lead samples in Table 7. The agreement is satisfactory. The predicted value of the Grüneisen parameter at $V = V_0$ is 2.1, and the measured value[8] is 2.7.

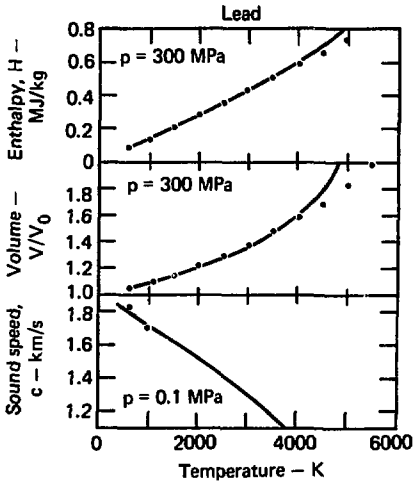

Fig. 16. Soft-sphere fit (smooth curves) to experimental lead thermodynamic data (points).

Uranium

The soft-sphere fit to uranium data is shown in Fig. 17. The experimental enthalpies and volumes were obtained from Shaner.[36] These are isobaric expansion data taken at 200 MPa. The enthalpy data

Table 7. Comparison of hard-sphere, soft-sphere, and measured values (Ref. 35) of the critical constants of lead.

	T_c(K)	V_c/V_0	p_c(MPa)	Z_c
Soft-sphere	5158	3.70	226	0.36
Experiment	5300	4.9	170	0.34
Hard-sphere	4668	3.66	208	0.36

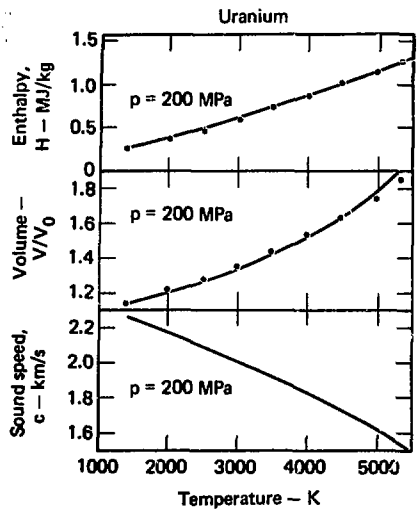

Fig. 17. Soft-sphere fit (smooth curves) to experimental uranium thermodynamic data (points).

of Stephens[37] were used to extrapolate Shaner's data to the melting point. Sound speeds have not yet been measured in liquid uranium.

The best fit to experiment was found for $n = 8$, $m = 1.0$, and $Q = 2.0$. The fits are adequate. The large value of Q implies a large electronic contribution to the specific heat.

The predicted critical point occurs at $T_c = 6618$ K, $V_c/V_0 = 4.60$, $p_c = 416$ MPa, and $Z_c = 0.43$. This value of T_c is half the value predicted[38] when only H-V isobaric data were available and Q was assumed to be 1.0. The predicted Grüneisen parameter at $V = V_0$ is 2.3, and the measured value[8] is 1.8.

DISCUSSION

On the whole, the soft-sphere model seems capable of accurately fitting experimental liquid metal data for many different metals. It appears that liquid metals are not essentially different from other fluids in their thermodynamic behavior.

Although it has weaknesses, the soft-sphere model is a significant improvement over the hard-sphere model on both theoretical and empirical grounds. Theory leads us to expect that the ions in liquid metals behave more like soft spheres than hard spheres. Also, we expect that metallic fluids will have both configurational and electronic contributions to the heat capacity, features that were not included in the hard-sphere model. The need for such terms is illustrated by the requirements of fitting the experimental enthalpy data.

Also, the constraint of corresponding-states behavior imposed by the two-parameter hard-sphere model has been relaxed in the soft-sphere model. This is required by the very different values of Z_c found in metals. Thus for sodium $Z_c = 0.13$, while for mercury $Z_c = 0.39$. In the hard-sphere model, the value is fixed at 0.36.

The parameter spectrum for the 13 metals is $4 \leq n \leq 15$, $0.58 \leq m \leq 1.5$, and $0.65 \leq Q \leq 2.2$. The n values correspond to Grüneisen parameter values of $1.0 \leq (n+2)/6 \leq 2.8$, which accurately covers the experimental range. The m values bracket $m = 1.0$, the classical van der Waals result. The Q values cluster around 1.0, as expected, except where electronic effects are important.

An important consequence of adding the Q term to account for electronic effects is the reduction of the predicted critical temperature as Q is increased. Thus for uranium, with $Q = 2.0$, the soft-sphere critical temperature is 6618 K, while the hard-sphere prediction is 11934 K. Is the lower temperature more nearly correct, or is it merely an artifact of the soft-sphere model? Experimental evidence indicates that the critical temperature of uranium is considerably lower than the hard-sphere prediction. The argument is sketched in Fig. 18. Here I assume that the experimental densities measured at $p \approx 200$ MPa lie very close to the liquid-vapor coexistence curve. This assumption is probably valid, since liquid uranium is relatively incompressible, and the density increase upon changing from the vapor pressure to 200 MPa is insignificant. The rectilinear diameter, which is the average of the liquid and vapor densities, is plotted in Fig. 18, and is typically close to a straight line in fluids where the coexistence curve has been measured. Thus the critical temperature of uranium can be estimated by extrapolating the rectilinear diameter to the estimated critical density. The critical density typically lies in the range $\rho_0/3$ to $\rho_0/5$, and this leads to $6000 \text{ K} \leq T_c \leq 8000 \text{ K}$ for uranium. The coexistence curve would have to take on a very unusual shape in order to achieve $T_c = 12000$ K. All this suggests that corrections to the normal soft-sphere heat capacity can have a decisive effect on the location of the critical point.

The soft-sphere model has a number of significant weaknesses. One is the rather poor prediction of V_c and Z_c for the alkali metals and mercury. The mean-field approximation obviously offers only a crude description of the complex physics which occurs in the critical region of metals.

The difficulties encountered in fitting mercury data (Figs. 14 and 15 and Table 6) illustrate another weak point. The large value of n (15) required to fit the dense-liquid thermodynamic properties produces a large configurational heat capacity term as a result. But the experimental heat capacity is *not* large, so a small value of Q (0.65) is needed to compensate for the large n value and to fit the experimental enthalpy. The resulting parameter set then produces a rather poor fit to the critical point.

Although some improvement in the model could be made by introducing better functional forms for the various terms, the real need now is for accurate first-principles calculations of liquid metal properties.

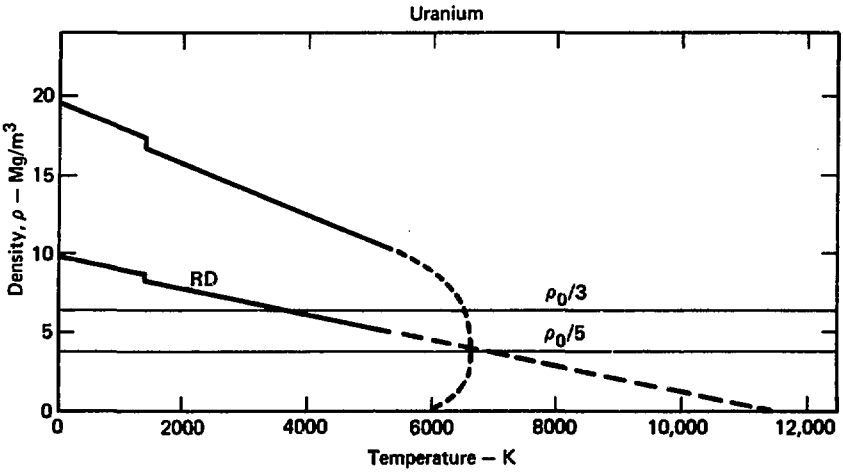

Fig. 18. Technique for estimating the critical point of uranium. The upper solid curve is the experimental uranium density, which lies very close to the true coexistence curve. The lower curve is the rectilinear diameter (RD), which intersects the critical density bounds $\rho_0/3$ at 3700 K and (ω, extrapolation) $\rho_0/5$ at 7000 K. The dashed curve is the soft-sphere prediction, with T_c = 6618 K.

ACKNOWLEDGMENTS

I thank R. Gathers, M. Hodgson, and J. Shaner for the use of their unpublished isobaric expansion data, and R. Grover for valuable discussions.

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