

Thermodynamic calculations for bcc sodium at high pressures

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Molecular-dynamic calculations for bcc pseudopotential sodium are compared to experiment for the 300-K pressure-volume curve to 300 kbar, and for the adiabatic pressure derivative of temperature, and the Grüneisen parameter, to 32 kbar. This comparison supports both the pseudopotential model of sodium, and the use of molecular dynamics to calculate anharmonic contributions to thermodynamic functions for crystals at high temperatures.

I. INTRODUCTION

This paper is a continuation of our work in testing molecular dynamics and pseudopotential theory for calculating thermodynamic properties of metallic sodium. Our model pseudopotential contains parameters that were previously determined by requiring agreement between theory and experiment for the crystal binding energy and its first two volume derivatives, at zero temperature and pressure.¹ This potential was successful in calculating thermodynamic properties for the solid phase,^{2,3} for the fluid phase,⁴ and also the melting behavior of metallic sodium.^{5,6} In the present paper, our calculations are compared with experiment for bcc sodium at high pressures. The experiments are those of Fritz and Olinger⁷ for the 300-K isotherm to 90 kbar, Aleksandrov *et al.*⁸ for the 300-K isotherm to 300 kbar, and Boehler⁹ for the adiabatic pressure derivative of temperature, and the Grüneisen parameter, to a pressure of 32 kbar.

II. CALCULATIONAL METHOD

Our system consists of N ions and Nz electrons in a volume V , and is described by an adiabatic potential Φ evaluated in the pseudopotential perturbation formulation. The principal characteristic of Φ is that it consists of two parts: a volume-dependent term $\Omega(V)$, and a sum over all distinct pairs of ions of the effective ion-ion potential $\phi(r;V)$. Specifically,

$$\Phi - NI_z = \Omega(V) + \sum \phi(r;V), \tag{1}$$

where the zero of Φ corresponds to a system of neutral atoms at infinite separation, and I_z is the ionization energy. Expressions for $\Omega(V)$ and $\phi(r;V)$ are given by Eqs. (2) and (3) of Ref. 2.

The volume per atom is $V_A = V/N$, and the value at zero temperature and pressure is $V_0 = 256a_0^3$, where a_0 is the Bohr radius. Figure 1 shows a plot of the ion-ion potential $\phi(r;V)$ at some of the different volumes used in the present study. The different curves are the potentials for compressions ranging from $V_A/V_0 = 0.78$ at $V_A = 200a_0^3$, to $V_A/V_0 = 0.39$ at $V_A = 100a_0^3$. As the volume decreases, the attractive well in $\phi(r;V)$ decreases, continuing the trend previously reported for volumes greater than V_0

(see Fig. 1 of Ref. 4). The corresponding nearest-neighbor distances are listed in Table I.

We use the technique of molecular-dynamics simulation to solve the coupled classical equations of motion for the sodium ions, in the central finite-difference approximation. The calculational cell consists of 686 particles in a cubic volume, with periodic boundary conditions in all directions. The energy, volume, and translational momentum of the cell are constants of the motion, and the center-of-mass translational momentum is zero. We take the body-centered-cubic crystal structure for solid sodium. The thermodynamic internal energy is

$$U = \langle E_{\text{kin}} \rangle + \langle \Phi \rangle, \tag{2}$$

the temperature T is given by

$$\frac{3}{2}NkT = \langle E_{\text{kin}} \rangle, \tag{3}$$

and the pressure P is

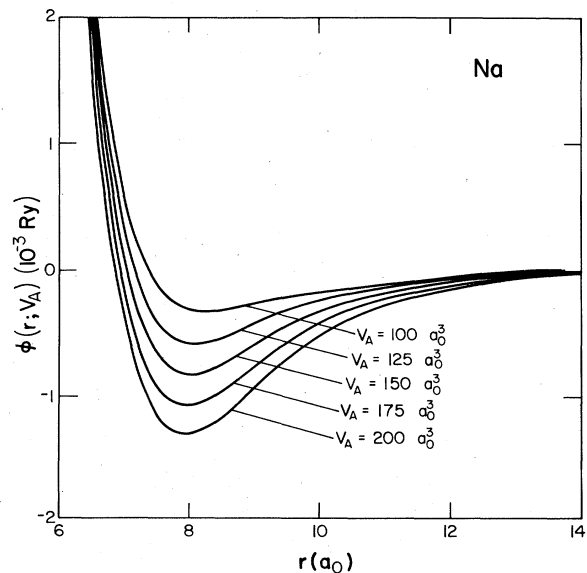


FIG. 1. Total effective pair potential for Na calculated from the modified-point-ion pseudopotential.

TABLE I. Theoretical quantities for pseudopotential sodium in the compressed bcc structure. r_1 is the nearest-neighbor distance.

V_A (a_0^3 /atom)	r_1 (a_0)	$\Theta_{H\infty}$ (K)	$-\frac{d\Omega}{dV}$ (kbar)	$\frac{NkT}{V}$ (kbar)
256	6.93	168	-22.7	1.1
232	6.70	188	-24.5	1.2
200	6.38	222	-27.3	1.4
175	6.10	254	-30.0	1.6
150	5.80	294	-33.4	1.9
125	5.46	348	-37.4	2.2
100	5.06	423	-41.7	2.8

$$P = -\frac{d\Omega}{dV} + \frac{NkT}{V} - \left\langle \sum \left[\frac{\partial\phi}{\partial V} + \frac{r}{3V} \frac{\partial\phi}{\partial r} \right] \right\rangle. \quad (4)$$

Here k is Boltzmann's constant, and the sum in (4) is again over all distinct pairs of ions. The angular brackets denote a time average for the equilibrium molecular-dynamics system; the time average is presumed equal to the molecular-dynamics ensemble average, according to the quasiperiodic hypothesis.

Corrections of relative order N^{-1} in Eqs. (3) and (4), which account for the difference between the molecular-dynamics and the generalized-canonical ensembles,¹⁰ are neglected in the present work. In comparing our calculations with experiment, we also neglect thermodynamic contributions from thermal excitation of conduction electrons; these contributions are important at higher temperatures, where they have been included.⁴ Finally, while quantum effects of the motion of the ions are neglected, the classical nonlinear dynamical motion is calculated accurately in molecular dynamics, and this gives us accurate results for the thermodynamic functions in the classical (high-temperature) region. The classical region corresponds to $T \gtrsim \Theta_{H\infty}$, where $\Theta_{H\infty}$ is the infinite-temperature harmonic Debye temperature, given by¹¹

$$k\Theta_{H\infty} = \frac{5}{3} \langle \hbar^2 \omega^2 \rangle_{BZ}, \quad (5)$$

where the brackets $\langle \rangle_{BZ}$ denote a Brillouin-zone average. Our values of $\Theta_{H\infty}$ for sodium are listed in Table I.

III. COMPARISON WITH EXPERIMENT

The pressure as a function of volume is plotted in Fig. 2 for an isotherm at 300 K. The solid circles are the data of Fritz and Olinger from diamond cell work to about 90 kbar.⁷ The pluses are from the analytic fit of Aleksandrov *et al.* to their experimental data, which extends to about 300 kbar.⁸ The agreement between theory and experiment for the pressure isotherm is quite good; note there is a systematic deviation between the two sets of experimental data between 40 and 90 kbar. Contributions to the pressure from the first two terms of Eq. (4) are listed separately in Table I. In Fig. 3 we have plotted the isothermal bulk modulus B_T as a function of volume. The pluses are again taken from the fit to experimental data of Aleksandrov *et al.*,⁸ and they cover the same range of

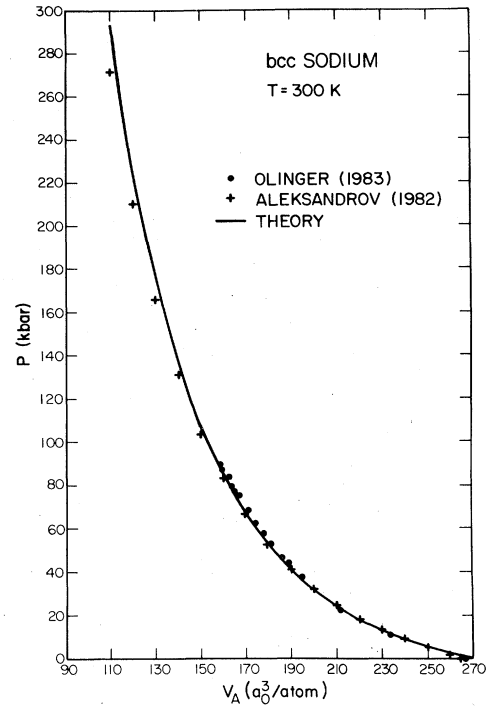


FIG. 2. Pressure as a function of volume at $T=300$ K. The solid circles are the data of Fritz and Olinger (Ref. 7), and the crosses are from the data of Aleksandrov *et al.* (Ref. 8).

pressure as Fig. 2. The theoretical curve for the bulk modulus is also in good agreement with experiment, particularly considering that the bulk modulus increases more than an order of magnitude, while the maximum theoretical-experimental deviation is about 10%.

Since $T/\Theta_{H\infty}$ becomes less than 1 on the isotherm at 300 K (see Table I), we need to check quantum correc-

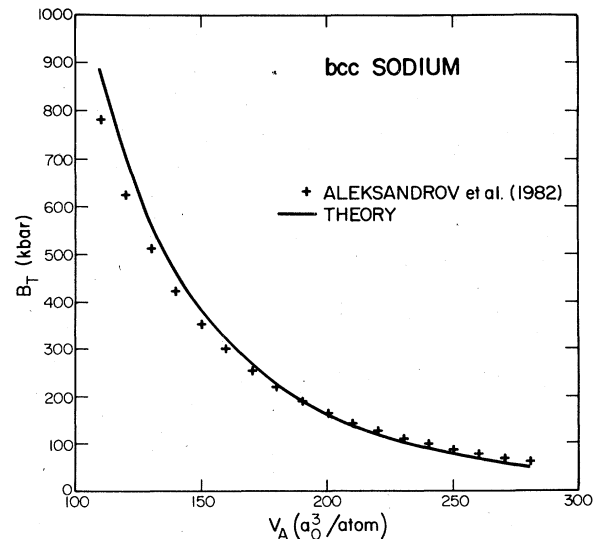


FIG. 3. Isothermal bulk modulus B_T as a function of volume, and compared with the experimental results of Aleksandrov *et al.* (Ref. 8).

tions to our molecular-dynamics results. The leading high-temperature quantum correction to the harmonic free energy is¹²

$$\Delta F = \frac{3N}{40} \frac{K \Theta_{H\infty}^2}{T}$$

This gives a small correction to the vibrational parts of P and B_T ; in the total calculated P and B_T at 300 kbar, the corrections are 0.2% and 0.1%, respectively.

Using a pressure pulse method, Boehler⁹ measured the adiabatic pressure derivative of temperature, $(\partial T/\partial P)_S$, to a pressure of 32 kbar. We can calculate this quantity from the expression

$$\left(\frac{\partial T}{\partial P} \right)_S = \frac{\gamma T}{B_S}, \quad (6)$$

where γ is the Grüneisen parameter, and B_S is the adiabatic bulk modulus. Results for $(\partial T/\partial P)_S$ versus pressure are shown in Fig. 4, and the thermodynamic Grüneisen parameter γ is shown in Fig. 5. The experimental points for both figures are taken from Boehler.⁹ Comparison between theory and experiment for $(\partial T/\partial P)_S$ is perhaps more interesting than for the Grüneisen parameter. First, $(\partial T/\partial P)_S$ is the quantity that was directly measured, while γ was obtained by including additional information, namely the adiabatic bulk modulus, according to Eq. (6). Second, $(\partial T/\partial P)_S$ changes by a factor of three on the isotherm at 298 K, while γ changes by only 25% over the same compression range. This difference is due to the large increase in B_S under compression, which effectively cancels the decrease in $(\partial T/\partial P)_S$, as may be seen from Eq. (6). Our theoretical curves of $(\partial T/\partial P)_S$ and of γ are in reasonably good agreement with experiment, and exhibit the correct pressure and temperature dependences. It should be noted that these quantities, in contrast to the pressure and bulk modulus, are essentially anharmonic vibrational quantities.

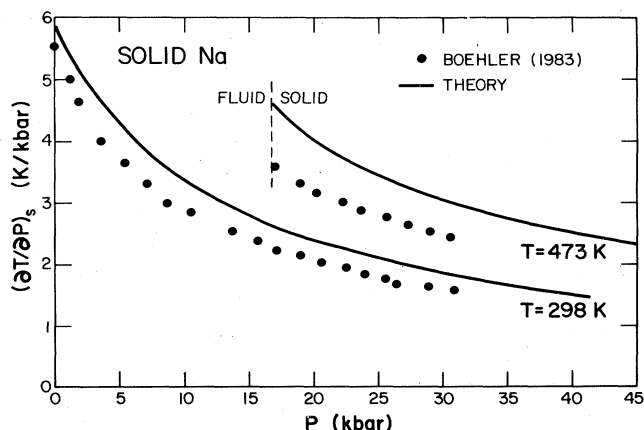


FIG. 4. $(\partial T/\partial P)_S$ vs pressure for the solid phase of sodium for isotherms at $T=298$ and 473 K. The experimental points are from Boehler (Ref. 9). The dashed vertical line represents the approximate solid-fluid phase boundary for the $T=473$ -K isotherm.

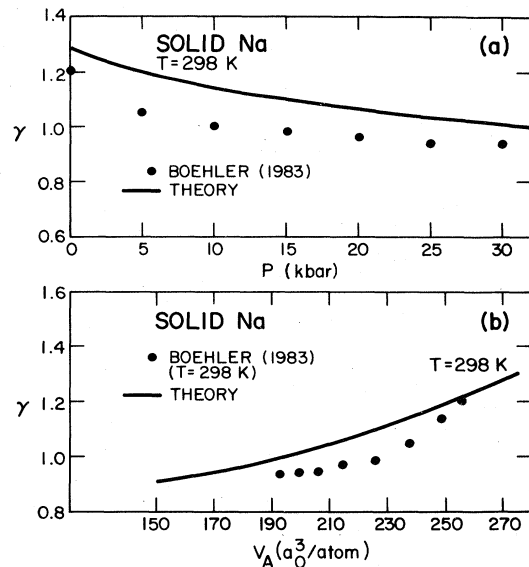


FIG. 5. Thermodynamic Grüneisen parameter at $T=298$ K as a function of (a) pressure and (b) volume. The experimental points are from Boehler (Ref. 9).

IV. DISCUSSION AND CONCLUSIONS

First we should comment on the status of pseudopotential theory. Compared to current standards of band-structure calculations, pseudopotential-perturbation theory represents a crude approximation for the electronic structure of the simple metals. Within this approximation, there are many variations the theory can take. Our pseudopotential is a parametrized model, our wavefunction basis is plane wave, and we include a Born-Mayer repulsion to account for the direct interaction between ion cores. In comparison, the pseudopotential of McMahan and Moriarty¹³ is based on "first principles," includes d states in the wave function basis, and does not include Born-Mayer repulsion. Both theories go to second order in the pseudopotential, but in fitting our parameters to experimental data, we presumably include some representation of higher-order terms. The point is that pseudopotential-perturbation theory is approximate and can be expected to account for the properties of simple metals only to an approximate degree. On the other hand, the great value of this theory is that it allows us to calculate the electronic structure, and hence the total adiabatic potential, for arbitrary positions of the ions, so that we can study the motion of the ions in the solid and fluid phases of a real metal.

We should comment also on the question of the existence of ion core-core repulsion. In pseudopotential theory, or in any theory in which the core electrons are taken as rigid, the core-core repulsion is present in principle. This follows from the observation that compression of the material will cause electrons to transfer from the cores to the bands, and the energy which drives this "ionization" is the core-core repulsion. The magnitude and form of core-core repulsion in compressed matter is an unsolved problem. We note that Harrison's¹⁴ procedure

for estimating overlap interaction from tight-binding theory gives an estimate for sodium which is roughly the same as our empirical Born-Mayer term. We also note that the Born-Mayer term increases strongly with compression, and in the present calculations it becomes approximately 20% of the total for P and B_T at 300 kbar and 300 K.

The main results of the present calculations are summarized by the following conclusions.

(1) When the atomic interaction potentials are known, the problem of calculating the anharmonic contributions

to thermodynamic functions for a crystal in the high-temperature region ($T \gtrsim \Theta_{H\infty}$) is solved easily and accurately by molecular dynamics.

(2) Within the expected accuracy of pseudopotential-perturbation theory, our calculations for bcc sodium agree with experiment for the room-temperature isotherm to 300 kbar, and for the anharmonic quantities γ and $(\partial T/\partial P)_S$ to 32 kbar at temperatures of 298 and 473 K. From this agreement we infer that our theoretical potentials $\Omega(V)$ and $\phi(r;V)$ are accurate representations of the potentials which operate in metallic sodium.

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