MASTER

TITLE: THE THERMAL PROPERTIES OF METALLIC SODIUM NEAR MELT FROM
MOLECULAR-DYNAMICS CALCULATIONS

AUTHOR(S): Galen K. Straub, Richard E. Swanson, Brad L. Holian,
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**The Thermal Properties of Metallic Sodium Near Melt
From Molecular Dynamics Calculations**

**Galen K. Straub, Richard E. Swanson, Brad L. Holian,
and Duane C. Wallace**

Los Alamos National Laboratory, Los Alamos, NM 87545

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Abstract

Molecular dynamics simulations of the thermal properties of metallic sodium were performed in the high temperature anharmonic region near the melting point. The ion-ion interaction potential was derived from pseudopotential theory. From the molecular dynamics results, the anharmonic thermal energy was determined directly without the use of thermodynamic perturbation theory. Comparison of the calculated melting temperature, latent heat of fusion, fluid phase diffusion coefficient, and the atomic distribution function are all in good agreement with experiment.

I. INTRODUCTION

The calculational technique of using a molecular dynamics (MD) simulation on a classical system of particles was used to study the thermal behavior of sodium near its melting point. The MD calculations consist of solving the time dependent, coupled, classical equations of motion for N particles interacting via a potential. Calculations were done over a wide temperature range that included both the solid and fluid phases of sodium. This work was motivated by the need to understand the high temperature anharmonic behavior of metals near the melting point where thermodynamic perturbation theory is not appropriate.

The physical basis for the interatomic potential is the adiabatic approximation in which the electron energy is calculated as a function of the ionic positions. The pseudopotential model for simple metals provides the means of applying the adiabatic approximation to determine an effective interatomic potential between ions.⁽¹⁾ From the pseudopotential expansion for the electronic energies, one can write the total system energy (ion cores plus conduction electrons) as the sum of a two-body central force interaction between ions plus contributions that depend only on the total volume of the system. The total volume of the system does appear as an explicit parameter in the two-body interaction and hence a change in volume alters the pair-wise interaction between ions. Three-body and higher terms result from third and higher order terms in the perturbation expansion of the electron-ion pseudopotential interaction.⁽²⁾ The utility of pseudopotential theory for molecular dynamics arises from the property that at fixed volume the ions may take any arrangement without changing the effective ion-ion interaction.

The total potential energy for the system of ions plus electrons may be written as

$$\phi = \phi_v + \sum \phi(r,V) \quad , \quad (1)$$

where ϕ_v depends only on the total system volume and not the individual ionic positions. The second term represents the sum of contributions from all two-body interactions at a distance r , but it is also a function of the total volume V . For our study of sodium, we have included in ϕ a core-core repulsion term of the Born-Mayer form, $\alpha \exp(-\gamma r)$. A modified point-ion model pseudopotential was used and all parameters were chosen as in reference 3 by requiring agreement with experiment of the crystal binding energy and its first two volume derivatives at zero temperature and pressure.

Figure 1 is a plot of the total effective ion-ion interaction $\phi(r,V)$ as a function of separation at the volume per particle $\Omega_0 = 256 a_0^3/\text{ion}$ (a_0 = Bohr radius). The contribution to the total potential energy from the second term in Eq. (1) is small, being about 2.5% of the total for sodium.

The remainder of this chapter discusses further details of the MD calculations, the results of the calculations, and comparison with experiment. In section I we describe the initial conditions and the approach to thermodynamic equilibrium in the MD simulations. Section III gives our results and comparison with experiment of the heat of fusion, the melting temperature, the atomic distribution function, and the fluid phase diffusion coefficient. The anharmonic internal energy as a function of temperature and the radial distribution functions are also discussed.

II. THE MOLECULAR DYNAMICS CALCULATIONS

In this section we will describe the MD calculational cell and the initial conditions. The attainment of thermodynamic equilibrium is monitored by calculating the second and fourth order cumulants of the particle velocity distribution; these cumulants are the temperature T and kurtosis C , respectively.⁽⁴⁾

The calculational cell contained 672 particles in a rectangular volume with periodic boundary conditions on all sides. Each particle is located at a lattice site at time $t = 0$ and given a random initial velocity. The system particle velocity distribution does not correspond to a Maxwell-Boltzmann distribution and thus the system is not initially in thermodynamic equilibrium. The coupled classical equations of motion are solved numerically for increasing time in the centered finite difference approximation. The time step is chosen so that each particle's trajectory is smoothly resolved by a series of straight line segments. The size of the system is chosen to contain the potential and large enough to not affect any final result due to its finiteness.

The approach to thermodynamic equilibrium is determined by monitoring the temperature and kurtosis of the particle velocity distribution. Figure 2 is a plot of the temperature and Figure 3 is a plot of the kurtosis as a function of time. In both figures, one should notice an initially rapid change of values near $t = 0$ followed by a slower approach to the final value. The temperature plot in Figure 2 is for two different systems with an initial temperature only a few degrees apart. Upon equilibration, the higher temperature system was in the fluid phase while the lower temperature system remained in the solid crystalline phase. The approach to the final state was qualitatively different for solid and fluid systems, the temperature increasing to equilibrium for the solid and decreasing to equilibrium for the fluid.

The kurtosis, C , is shown in Figure 3. For a system in thermodynamic equilibrium, C will approach zero as the number of particles N increases. For

a finite size system C will remain slightly negative. The curves plotted are scaled by T^2/N . The kurtosis is initially large and negative and rapidly decreases its magnitude by time $t = 10 t_0$ ($t_0 = 7 \times 10^{-15}$ sec). A much slower decrease in the value of C then takes place with a time scale $t = 1000 t_0$ that corresponds to the time for the temperature to reach its final value.

The MD calculations are all performed under the constraints of constant volume and constant total energy. The constant volume condition allows the straightforward application of a central pair potential between ions from pseudopotential theory. The constant energy condition results in the MD system seeking a structure, either crystalline or fluid, that provides the most stable partitioning of the energy between kinetic and potential contributions.

III. RESULTS AND COMPARISON WITH EXPERIMENT

From the molecular dynamics simulation we have calculated several thermodynamic properties that may be directly compared with experiment. These include the heat of fusion, the melting temperature, the atomic distribution function, and the fluid phase diffusion coefficient. In addition, we can make a direct calculation of the anharmonic thermal behavior of the solid phase at high temperature. We will begin our discussion of the results with the anharmonic behavior followed by additioned comparisons with experiment.

A. The Anharmonic Thermal Energy At High Temperatures

The total internal energy U that is calculated in molecular dynamics can be written as

$$U(V,T) = U_H(V,T) + U_A(V,T) \quad , \quad (2)$$

where U_H is the harmonic contribution and U_A is the anharmonic contribution. For a classical system of particles at high temperatures the harmonic term is

$$U_H(V,T) = 3NkT + \phi_0(V) \quad , \quad (3)$$

where the first term is the kinetic energy contribution and the second is the static potential energy at $T = 0$. k = Boltzmann's constant.

In Figure 4 we show the results of the MD calculations for the total energy U at different temperatures by the dots. Each point represents the final equilibrated value of the system and the magnitude of any error bars due to the statistical fluctuation of the energy is contained in the dots. The straight line shown goes through the $T = 0$ value and has a slope of $3k$. Departures of U from this straight line are due to the anharmonicity U_A of equation (2).

The anharmonic internal energy can be obtained directly from the MD results by subtracting Eq. (3) from Eq. (2) giving

$$U_A(V,T) = U(V,T) - 3NkT - \phi_0(V) \quad (4)$$

The result for U_A is given in Figure 5 for the solid phase points of Fig. 4 where the volume per ion is $\Omega_0 = V/N$. The error bars on the MD points result primarily from the statistical fluctuations in the temperature and only secondarily from uncertainty in the value of the internal energy.

High temperature thermodynamic perturbation theory predicts a leading order T^2 temperature dependence for U_A .⁽⁵⁾ If we assume a functional form for the anharmonic Helmholtz free energy given by

$$F_A(V,T) = a_2(V) T^2 + a_3(V) T^3 + a_4(V) T^4 \quad (5)$$

the anharmonic internal energy is

$$U_A(V,T) = -a_2(V)T^2 - 2a_3(V)T^3 - 3a_4(V)T^4 \quad (6)$$

a_2 , a_3 , a_4 are coefficients that are independent of the temperature. The solid curve in Fig. 5 is the result given by Eq. (6) with the values of the coefficients listed in Table 1. For comparison are values of $a_2(V)$ as determined by a high temperature analysis of the experimental entropy⁽⁵⁾ and the high temperature limit of the anharmonic free energy in thermodynamic perturbation theory calculated to leading order T^2 for the same potential as was used in the MD calculations.⁽⁶⁾ The agreement with the experimental analysis is quite good while the perturbation results are poor.

B. The Melting Transition and the Fluid Phase

The transition from the solid crystalline phase to the fluid phase at the volume $\Omega_0 = 256a_0^3$ has been determined from MD to occur over a small temperature interval of 11K between $T = 385K$ and $T = 396K$. The identification of a solid or fluid phase for a particular molecular dynamics calculation was made by considering

the internal energy, the diffusion coefficient, and the radial distribution function. We will discuss each of these quantities and their behavior near melting separately.

In Figure 4, the MD points show a discontinuous break in the internal energy between the $T = 385\text{K}$ point and the $T = 396\text{K}$ point. At $T = 396\text{K}$ and above, the system remained in the fluid phase. The analysis of Eq. (4) for the $T = 396\text{K}$ point and above gives an increase in U_A by about an order of magnitude with a dramatic change in the slope of U_A versus l . The fit to the solid data determined in Eq. (6) is clearly inappropriate for the fluid.

Another criteria for the onset of melting was to examine the mean square particle displacement $\langle \Delta r^2 \rangle$ as a function of time. The diffusion coefficient D can be related to $\langle \Delta r^2 \rangle$ by

$$D = \langle \Delta r^2 \rangle / 6t \quad . \quad (7)$$

In Fig. 6 we plot $\langle \Delta r^2 \rangle$ versus t and hence the slopes of the curves shown are proportional to the diffusion coefficient. The $T = 390\text{K}$ line has a zero slope indicating no diffusion in the solid phase. This is the result that would be expected for a solid phase MD calculation for the length of "real" observational time available ($\sim 15\text{picosec}$). At $T = 400\text{K}$, the slope is positive and the MD result and experimental value⁽⁷⁾ are

$$D_{\text{MD}} = 4.1 \pm 0.1 \times 10^{-5} \text{ cm}^2/\text{sec at } T = 400\text{K} \quad ,$$

$$D_{\text{EXP}} = 4.2 \times 10^{-5} \text{ cm}^2/\text{sec at } T = 373\text{K} \quad .$$

Further increases in temperature give the correct qualitative behavior of particle diffusion in a fluid as illustrated by the $T = 590\text{K}$ curve.

The radial distribution function was also used to determine whether the MD system had undergone the melting transition. In Fig. 7, we show the calculated radial distribution function for bcc sodium at $T = 50\text{K}$. The bcc shell structure

is evident and only slightly broadened by thermal motion at this temperature. In Fig. 8, we have plotted the radial distribution function at $T = 385\text{K}$ (solid), 396K (fluid), and 590K (fluid). The structure on the $T = 385\text{K}$ curve is that appropriate to the bcc phase although thermal broadening is a major effect. The shoulders that are seen near the peaks are significant. At $T = 396\text{K}$, all evidence of structure of the solid phase has dissappeared and the system is in the fluid phase. Additional thermal broadening is evident on the $T = 590\text{K}$ fluid phase curve.

The experimental value of the melting temperature is $T_M = 371\text{K}$ ⁽⁸⁾ compared with the MD result of T_M between $T = 385\text{K}$ and $T = 396\text{K}$. For the present study, the melting transition is considered only at constant volume. This is not the same as the experimental conditions.

C. Additional Comparisons Between Molecular Dynamics Results and Experiment

Our MD results for the latent heat of fusion and the atomic distribution function may also be compared with experiment. An approximate estimate of the latent heat of fusion, L_H , can be made from Fig. 4 by extending the solid and fluid phase lines and calculating their difference at the assumed melting temperature of $T = 390\text{K}$. The MD and experimental values⁽⁸⁾ are

$$L_H^{\text{MD}} = 1.68 \pm 0.02 \times 10^{-3} \text{ Ry/ion} ,$$

$$L_H^{\text{EXP}} = 2.32 \times 10^{-3} \text{ Ry/ion} .$$

The atomic distribution function $a(r)$ for fluid sodium has been measured by neutron scattering by Gingrich and Heaton.⁽⁹⁾ The atomic distribution function is related to the radial distribution function $g(r)$ by

$$g(r) = a(r)/4\pi r^2 \bar{\rho} \quad ,$$

with $\bar{\rho}$ equal to the average density of the entire system. The MD result at $T = 400\text{K}$ is compared with experiment in Fig. 9. The experimental measurement was at $T = 375\text{K}$ and in the fluid state.

IV. CONCLUSION

We have used the calculational technique of molecular dynamics to examine the high temperature thermal properties of metallic sodium. MD allows the direct integration of the nonlinear, time dependent, coupled, classical equations of motion for a system of particles; the anharmonic behavior may be examined directly without additional approximation.

The noncentral potential for metallic sodium is derived from pseudopotential theory and is expressible as the sum of a strictly volume dependent potential plus a two-body interaction between all pairs of particles.

We obtain good agreement with experimental observations of the melting temperature, the latent heat of fusion, the fluid phase diffusion coefficient, and the atomic distribution function. The anharmonic contributions to the internal energy are found to not be predicted by leading order thermodynamic perturbation theory; our calculation of the anharmonic energy near the melting point is limited only by the use of classical statistical mechanics.

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Table 1. Coefficients of the Anharmonic Thermal Energy For

$$\Omega_0 = 256 a_0^3$$

	a_2 (Ryd/K ²)	a_3 (Ryd/K ³)	a_4 (Ryd/K ⁴)
Molecular Dynamics Calculation	$- 1.2726 \times 10^{-9}$	$+ 2.8273 \times 10^{-12}$	$- 6.2203 \times 10^{-15}$
Analysis of Experimental Data ^(a)	$- 0.85 \times 10^{-9}$		
Thermodynamic Perturbation Expansion from Harmonic Lattice Dynamics ^(b)	$- 10. \times 10^{-9}$		

(a) From the high temperature analysis of the experimental entropy in reference (5), pp. 368-380.

(b) From the high temperature limit of the anharmonic free energy in thermodynamic perturbation theory calculated to leading order T^2 (6).

Figures

1. Total Effective Ion-Ion pair potential for Na calculated from a modified point ion pseudopotential at a volume $\Omega_0 = 256a_0^3$. The dotted lines are multiplied by the factor indicated near the curves. The potential energy is in units of Rydbergs (Ry) and the separation is in units of Bohr radii (a_0).
2. The temperature in Kelvins (K) as a function of time for the equilibration of two different molecular dynamics calculations. The upper curve is for a system that came to final equilibrium in the fluid phase while the lower curve remained in the solid phase.
3. The kurtosis C of the particle velocity distribution versus time during the equilibration of molecular dynamics calculations at temperatures $T = 50K$ and $T = 100K$. The kurtosis is scaled by $(kT/m)^2/N$ where N and m are the number and mass of the particles in the distribution respectively. k is Boltzmann's constant.
4. The total internal energy U versus temperature T for bcc solid sodium to about 400K and fluid sodium above 400K for a fixed volume $\Omega_0 = 256a_0^3$. The straight line with slope $3k$ gives the value for a classical solid system with completely harmonic interactions and departures from this line in the solid phase give the anharmonic internal energy U_A .
5. The anharmonic contribution U_A to the total internal energy as a function of temperature for solid bcc sodium where $U_A = U - 3NkT - \Phi_0$ and Φ_0 is the static potential energy at $T = 0K$.
6. The mean square particle displacement $\langle \Delta r^2 \rangle$ vs time for solid bcc sodium at $T = 390K$, fluid sodium at $T = 400K$, and $T = 590K$ as determined from the molecular dynamics calculations.
7. The radial distribution function versus distance R for bcc sodium at $T = 50K$ as determined from the molecular dynamics calculations.

8. The radial distribution function versus distance R for molecular dynamics calculations of sodium for two fluids at $T = 590K$, $T = 396K$, and for the solid bcc structure at $T = 385K$.
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Fig. 2

Fig 3

Fig 6