

Thermodynamic properties of potassium at 160 and 308 K

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We have carried out a computer simulation of the properties of solid potassium near its melting point and at half the way to melting. In the present study we have made use of the recently derived pseudopotential of Dagens, Rasolt, and Taylor. We have calculated the elastic constants, the thermodynamic Grüneisen parameter, the pressure, the energy, and the specific heat at both 160 and 308 K, using a system composed of 250 potassium atoms of which each particle is allowed to interact with its 112 closest neighbors. Periodic boundary conditions have been invoked in order to simulate an ideal infinite system. We compare our results with those available from experimental studies and find very good agreement between the two. This indicates that the pseudopotential used in the present study is a reliable one.

I. INTRODUCTION

In the past the study of dynamic, as well as thermodynamic, properties of metals often suffered from a lack of adequate interatomic pair potentials that describe the interactions in such systems. At least for the case of nontransit ion metals, this situation has changed, since pseudopotentials have been invoked and reliable procedures have been provided for their determination.¹ In a metal, the valence electrons form a quasifree system interacting with the background positive ions. In general, the ions occupy but a small fraction of the available volume per atom ($\sim 10\%$ for nontransit ion metals), and hence it is concluded that they do not overlap. The common picture is that of an electron interacting with the core ion through a bare Coulomb potential in most regions of the unit cell. However, it is realized that in the interior of the ion core the electron's wave function undergoes rather strong oscillations. Thus, the effective interaction between the ion and the electron is considerably smaller than the bare Coulomb interaction. This decrease in the effective interaction can be thought of as originating from some effective repulsive potential in the region of the ionic core. Therefore, the common approach is to replace the true ionic potential by some pseudopotential which is constructed such as to fit some known properties. Reliable pseudopotentials for the alkali metals have been provided in recent years.^{2,3} For potassium (and also for sodium,⁴ lithium,⁵ and aluminum⁵) good agreement was thus obtained between the calculated phonon dispersion curves, using such model potentials.^{4,5} Hence in the present study we considered it worthwhile to examine the thermodynamic properties (including the elastic constants) of K, using the most recent interionic pseudopotential of Dagens, Rasolt, and Taylor.⁵ We shall use the classical computer-simulation Monte Carlo (MC) method⁶ to study the prop-

erties of K at high temperatures. Our work can be regarded as complementing that of Shukla and Taylor⁷ and Duesbery, Glyde, and Taylor.⁸ There are two reasons that make this investigation especially interesting. First, these authors used an earlier version of the pseudopotential.³ Second, the MC method affords an essentially exact calculation of ensemble averages, so that comparison with experiment should reveal directly any failure of the model potential.

Formal expressions relating the various thermodynamic properties to a suitable pair potential have been derived previously,⁹ and we shall not repeat the detailed expressions here. The starting point for such a derivation is the Wigner-Kirkwood expansion for the Helmholtz free energy F . Taking into account pairwise interactions only, the potential energy of such a system will be given by

$$\phi = \sum_{k>l=1}^N \Phi_{II}(k, l), \quad (1)$$

where $\Phi_{II}(k, l)$ is the pair potential between the particles labeled by the indices k and l . The classical internal energy E is, for example, then given by $E = \partial(\beta F)/\partial\beta$; $\beta = 1/k_B T$.

$$E = \frac{3}{2} N k_B T + \langle \phi \rangle, \quad (2)$$

where $\langle \rangle$ denotes the ensemble average, which we evaluated by a MC method⁶; also, N is the number of particles in the system, and k_B is the Boltzmann constant. The adiabatic elastic constants may now be obtained by calculating the appropriate strain derivatives of the energy E . Expressions for other quantities, such as the pressure and the Grüneisen parameter, may also be readily obtained.⁹ In Sec. II we shall, briefly, describe the method of calculation that we performed, and present our results. These are compared with available experimental data. We also comment on some of the effects and contributions not included in the ion-ion model potential. Anticipating our results we shall see that

TABLE I. K at 160 K, $a = 5.2767 \text{ \AA}$: (i) The C_{ij} constants are defined in Ref. 9; (ii) the c_{ij} constants involved in this section are the actual ones observed experimentally; (iii) the various dimensioned quantities. The MC run involved 200 000 moves.

Type of contribution	$\frac{VC_{11}^S}{Nk_B T}$	$\frac{VC_{12}^S}{Nk_B T}$	$\frac{VC_{44}}{Nk_B T}$	$\frac{pV}{Nk_B T}$	$\frac{E}{Nk_B T}$
"Kinetic" terms	2.00	...	1.00	1.00	1.50
"Born" terms:					
Φ					-10.61
Φ'	-0.60	-4.93	-4.93	10.45	
i Φ''	150.60	87.53	87.53		
"Fluctuation" terms	11.28	0.50	6.09		
Thermodynamic corrections	3.51	3.51	...		
Subtotal (MC, 4 shells)	145.43	95.47	87.37	11.45	-9.11
Subtotal (static/harmonic)	144.46	98.45	98.45	7.67	-12.13
	$(c_{11} = C_{11} - p)$	$(c_{12} = C_{12} + p)$	$(c_{44} = C_{44} - p)$		
Tail corrections	0.09	6.48	2.96	1.76	-0.12
(static or harmonic)	136.78	106.12	90.79	7.67	
ii (MC, 4 shells)	133.98	106.92	75.92	11.45	
Total (MC+tails)	134.07	113.40	78.88	13.21	-9.23
iii Dimensioned quantities	40.31 (kbar)	34.10 (kbar)	23.72 (kbar)	3.97 (kbar)	-1.23 (10^{11} erg)

the new K potential provides a good description of the experimental quantities.

II. RESULTS FOR POTASSIUM AT 160 AND 308 K

We have already mentioned that the ensemble averages occurring in the expressions for the various thermodynamic quantities have been evaluated using the standard MC computer simulation method.⁶ We have studied the bcc lattice with $N = 250$ particles and periodic boundary conditions. Since the pseudopotential features the usual long-range Friedel oscillations some care was needed in specifying the range of allowed interionic interactions. A careful study of the static properties revealed that the truncation after eight shells of neighbors gave negligible errors in the static elastic constants. That is, if each ion was allowed to interact with its $n = 112$ closest neighbors, the remaining tail correction was very small. The smallest system that can accommodate this situation is the one with $N = 250$. However, the computing time and storage requirements are proportional to $n \times N$, so studies were also carried out with 4 shells of interacting neighbors ($n = 50$). In this case it was necessary to add a correction for the tail of the oscillating potential, and this was done in a manner described elsewhere.¹⁰ We have verified that the elastic constants calculated for both systems then differ by little more than their statistical uncertainties ($\sim \pm 3\%$).

We chose to study the properties of potassium at 308 and 160 K; that is near the melting point and about half the way to melting. The lattice constants of bcc K at these temperatures were taken from Schouten and Swenson.¹¹ Our results for the various thermodynamic quantities of the solid are

given in Tables I and II. In Fig. 1, we present our results for the elastic constants together with the experimental values obtained by Marquardt and Trivisonno¹² and Fritsch and Bube.¹³ Since our calculations were carried out at temperatures in excess of the Debye temperature, corrections for quantum effects were not applied. Comparison of Tables I and II shows that, as expected, the solid at 160 K is quite harmonic (the MC values differ but a little from the static ones). Anticipating this result we therefore only considered four shells of interacting neighbors in this run. We observed in both cases a rather profound effect of anharmonicity on c_{44} . We note that our c_{44} values should rep-

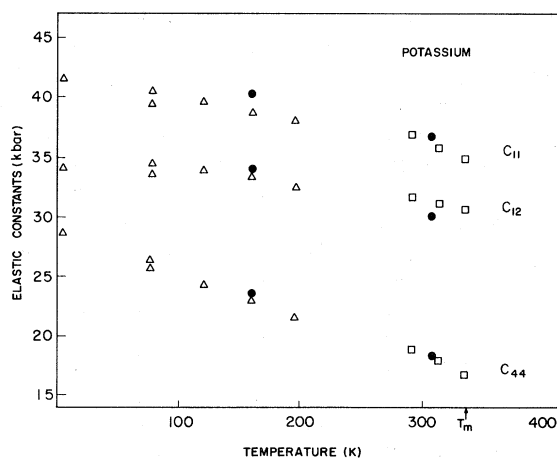


FIG. 1. Adiabatic elastic constants of potassium as a function of temperature. Triangles and squares represent data taken from Refs. 12 and 13, respectively. Full circles represent the MC results of the present study.

TABLE II. K at 308 K, $a=5.333 \text{ \AA}$. Presentation is same as in Table I.

Type of contribution	$\frac{VC_{11}^s}{Nk_B T}$	$\frac{VC_{12}^s}{Nk_B T}$	$\frac{VC_{44}^s}{Nk_B T}$	$\frac{pV}{Nk_B T}$	$\frac{E}{Nk_B T}$
"Kinetic" terms	2.00	...	1.00	1.00	1.50
"Born" terms					
Φ					-4.96
Φ'	-1.33	-2.32	-2.32	5.96	
Φ''	77.29	42.21	42.11		
"Fluctuation" terms	11.75	1.72	5.33		
Thermodynamic corrections	4.29	4.29	...		
Subtotal (MC, 8 shells)	73.16	47.00	38.90	6.96	-3.46
Subtotal (static/harmonic)	69.91	50.71	50.71	3.24	-6.54
	$(c_{11} = C_{11} - p)$	$(c_{12} = C_{12} + p)$	$(c_{44} = C_{44} - p)$		
Tail corrections	-0.67	-0.23	-0.04	-0.10	-0.77
(static or harmonic)	66.67	53.95	47.48	3.24	
(MC, 8 shells)	66.20	53.97	32.93	6.96	
Total (MC+tails)	65.53	53.74	32.89	6.86	-4.23
iii Dimensioned quantities	36.74 (kbar)	30.13 (kbar)	18.44 (kbar)	3.85 (kbar)	-1.08 (10^{11}_{erg})

resent the exact prediction for the pseudopotential, since electron-gas terms (which were not accounted for in Tables I and II) do not contribute to shear modes. We see in Fig. 1 impressive agreement with experiment. The bulk modulus derived from these elastic constants also agrees well with experiment,¹¹ even though no correction has yet been applied for the electron-gas contributions.

We have made an estimate of the electron-gas contributions to the various quantities, in the manner described in Ref. 3. Using the Bohm-Pines expression for the ground-state energy of the electron gas, we were able to calculate the contributions to the internal pressure and adiabatic bulk modulus from $PV_{\text{eg}} = -\frac{1}{3} r dE_{\text{eg}}/dr$ and $B_{\text{eg}}^s V - PV_{\text{eg}} = +\frac{1}{3} r(d/dr)(r dE_{\text{eg}}/dr)$. We found for K at 308 K, $P_{\text{eg}} = -3.8$ kbar, $B_{\text{eg}}^s = c_{11}^{\text{eg},s} = c_{12}^{\text{eg},s} = 2.84$ kbar. Apart from E_{eg} , there is another term contributing to the volume-dependent part of the potential. This comes from the shift in the energy of the electron-gas, owing to the fact that the positive charges are situated on lattice sites rather than forming a truly uniform distribution. This term is more difficult to calculate,³ and we used for it the empirical form $E_{\text{eg},1} = A/v_a$, where v_a is the atomic volume and A is a parameter chosen such that the condition for equilibrium of the lattice is fulfilled. Taking this compensatory effect into account we found that at 308 K *in total* the electron-gas terms contributes only about 0.8 kbar to B^s , c_{11} , and c_{12} . We therefore conclude that the electron-gas has only a small effect in potassium. We found a similar result for sodium.¹⁰

The pseudopotential used in the present study assumes the ion core to be unpolarizable. This is a common assumption in the study of metals which,

of course, need not be true in all cases. The K^+ ion has the same electronic configuration as Ar and hence will have only a slightly smaller polarizability. The van der Waals interaction between two K^+ ions can be approximated by $E_{12} = -C/R_{12}^6$, where C can be estimated from the work of Kim and Gordon¹⁴ to be 40.6 a.u. The contribution of such a term to the energy of a pair of nearest-neighbors K^+ ions, in the solid phase at 308 K, turns out to be -2.50 meV, compared with the pseudopotential energy of 28.2 meV. Such a contribution, while small, appears to be non-negligible. For the pressure, we then obtain a contribution equal to -0.65 kbar; also, the contribution to the bulk modulus is -1.94 kbar, and for c_{11}^s , c_{12}^s , and c_{44} we have obtained -1.97, -1.93, and -0.64 kbar as the van der Waals contributions. This effect is similar in magnitude and opposite in sign to the electron-gas terms.

Apart from the elastic constants and bulk moduli we have also calculated, in the MC run, the specific heat of the solid, the Grüneisen parameter, and the root-mean-squared displacement of an atom from its equilibrium lattice site. We find that the heat capacity at constant volume at 308 K is greater than 3R, indicating positive anharmonic contributions, as was also found by Shukla and Taylor⁷ and observed experimentally.¹¹

The Grüneisen parameter γ is found to be in very good agreement with the experimental value of Schouten and Swensson.¹¹ At 160 K we have obtained for γ the value of 1.15 ± 0.05 , and at 308 K the calculated value is 1.19 ± 0.1 compared with the experimental value of 1.23.

Finally, the calculated root-mean-squared amplitude of vibration of an atom about its equilibrium

lattice site was found to be equal to $10 \pm 1\%$ of the first-neighbor distance at 160 K and $20 \pm 2\%$ at 308 K. The value at 308 K is considerably larger than the value of $\sim 13\%$ found for rare-gas solids at their melting temperature. This seems to be due to the softer potential of the alkali metals.

In conclusion we see that the MC technique can successfully be extended to calculate properties of alkali metals near the melting temperature using realistic pseudopotentials that include the long-

range Friedel oscillations.

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¹W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

²W. M. Shyu, K. S. Singwi, and M. P. Tosi, *Phys. Rev. B* 3, 237 (1971); D. L. Price, K. S. Singwi, and M. P. Tosi, *ibid.* 2, 2983 (1970).

³M. S. Duesbery and R. Taylor, *Phys. Lett. A* 30, 496 (1969); Z. S. Basinski, M. S. Duesbery, A. P. Pogany, R. Taylor, and Y. P. Varshni, *Can. J. Phys.* 48, 1480 (1970).

⁴M. Rasolt and R. Taylor, *Phys. Rev. B* 11, 2717 (1975).

⁵L. Dagens, M. Rasolt, and R. Taylor, *Phys. Rev. B* 11, 2726 (1975).

⁶N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.* 21, 1087 (1953).

⁷R. C. Shukla and R. Taylor, *Phys. Rev. B* 9, 4116

(1974).

⁸M. S. Duesbery, R. Taylor, and H. R. Glyde, *Phys. Rev. B* 8, 1372 (1973).

⁹D. R. Squire, A. C. Holt, and W. G. Hoover, *Physica (Utrecht)* 42, 388 (1969); W. G. Hoover, A. C. Holt, and D. R. Squire, *ibid.* 44, 437 (1969).

¹⁰S. S. Cohen, M. L. Klein, M. S. Duesbery, and R. Taylor, *J. Phys. F.* (to be published).

¹¹D. R. Schouten and C. A. Swensson, *Phys. Rev. B* 6, 2175 (1974).

¹²W. R. Marquardt and J. Trivisonno, *J. Phys. Chem. Solids* 26, 273 (1965).

¹³G. Fritsch and H. Bube (unpublished).

¹⁴Y. S. Kim and R. G. Gordon, *J. Chem. Phys.* 61, 1 (1974).