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Thermodynamic properties of simple liquid metals calculated using an analytic pair potential

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An analytic pair potential proposed by Pettifor and Ward is used to calculate the thermodynamic properties of Na, Mg, and Al. The energy, pressure, and bulk-modulus values calculated using the Pettifor-Ward pair potential are in qualitative accord with calculations based on other models.

I. INTRODUCTION

Recently, Pettifor and Ward[1] (PW) derived an analytic interatomic pair potential $\phi(r)$ for simple metals from first principles using second-order pseudopotential theory. The PW pair potential is based on the density-functional local-density approximation to the dielectric function. The usual Linhard free-electron-gas response function is replaced by a rational function. This removes the weak logarithmic singularity in the slope of the Linhard function, which is responsible for the long-range Friedel oscillations. The resulting pair potential, which is given by a sum of exponentially damped terms, allows for a direct interpretation of predicted structural phase transitions of Na, Mg, and Al under pressure. The main feature of $\phi(r)$ is its short range which makes it ideal for use in a molecular-dynamics type of simulation work.

In this work, we put the proposed analytic potentials to yet another test by using them in calculating some thermodynamic properties of Na, Mg, and Al. Although the **k**-space formulation is more widely used in pseudopotential formalism of thermodynamic properties of liquid metals we use a real-space formulation since the role of interatomic forces is more transparent there. There are a number of previous calculations and experiments to compare with.[2-7] We present a short theoretical discussion on the calculated thermodynamic quantities in Sec. II.

II. FORMALISM

The total internal energy per ion U is given by

$$U=\tfrac{3}{2}k_BT+u(n_0)+2\pi\rho_0\int_0^\infty dr\,R^2\phi(R;n_0)g(R)\ , \tag{1}$$

where $g(R)$ is the pair-distribution function, $\phi(R;n_0)$ is the pair potential, $u(n_0)$ can be interpreted as the energy of a pseudoion surrounded by its neutralizing cloud of electrons of density $n_0=NZ/V$, N is the number of ions, and V is the volume. $u(n_0)$ is given by

$$\begin{aligned}u(n_0)&=Zu_{\rm el}-\frac{n_0Z}{2\Pi(0)}-\sum_q\frac{2\pi Z^2}{Vq^2}F_N(q)\\&=u_1+u_2+u_3\ ,\end{aligned}\tag{2}$$

where

$$Zu_{\rm el}=2.21r_s^{-2}-0.916r_s^{-1}-(0.115-0.031\ln r_s)\ , \tag{3}$$

is the Nozières-Pines form for the ground-state energy of the electron gas, $\Pi(0)$ is the usual polarization function, and $F_N(q)$ is the normalized energy wave-number characteristic so that

$$u_3=-\frac{2Z^2}{\pi}\int F_N(q)dq\ . \tag{4}$$

The pressure P is the volume derivative of the Helmholtz free energy as is given by[8]

$$\begin{aligned}P&=\rho_0k_BT+\rho_0n_0\frac{du(n_0)}{dn_0}\\&\quad-\tfrac{2}{3}\pi\rho_0^2\int_0^\infty dR\,R^3\frac{\partial\phi(R;n_0)}{\partial R}g(R)\\&\quad+2\pi\rho_0^2\int_0^\infty dR\,R^2n_0\frac{\partial\phi(R;n_0)}{\partial n_0}g(R)\\&=P_{\rm kin}+P_0+P_{\rm dir}+P_{\rm ind}\ .\end{aligned}\tag{5}$$

The normalized energy wave-number characteristic is given by

$$F_N(q)=\left[\frac{V_{\rm ps}(q)}{8\pi Z/q^2}\right]^2\left[1-\frac{1}{\epsilon(q)}\right]\ , \tag{6}$$

where we use Ashcroft empty-core model pseudopotential

$$V_{\rm ps}(q)=-\frac{8\pi Z}{q^2}\cos(qR_c)\ . \tag{7}$$

We use the same dielectric function as that of PW for internal consistency.

The bulk modulus is defined by

$$B=-V\left[\frac{\partial P}{\partial V}\right]_T\ , \tag{8}$$

and is related to the long-wavelength (LW) limit of the structure factor $S(q)$,

$$B_{\rm LW}=\frac{\rho_0k_BT}{S(0)}\ . \tag{9}$$

The expression for $B_{\rm LW}$ can be written as[2]

TABLE I. Input parameters.

	r_s (a.u.)	ρ_0 (a.u.)	R_c (a.u.)	T (K)
Na	3.99	0.0038	1.66	373.0
Mg	2.66	0.0063	1.39	948.0
Al	2.07	0.0090	1.12	1000.0

$$B_{\mathrm{LW}}=\rho_0 k_B T-\tfrac{4}{9}\pi\rho_0^2\int_0^\infty R^3 g(R)\frac{\partial\phi}{\partial R}dR+\tfrac{2}{9}\pi\rho_0^2\int_0^\infty R^4 g(R)\frac{\partial^2\phi}{\partial R^2}dR=B_{\mathrm{IG}}+B_1+B_2\,, \tag{10}$$

where B_{IG} is the compressibility of the ideal gas and $B_1=\frac{2}{3}P_{\mathrm{dir}}$.

III. RESULTS AND CONCLUSIONS

The input data used in our calculations are given in Table I. For the radial distribution function $g(r)$ the experimental values tabulated by Waseda[9] are used.

The graphical form of the analytical pair potential and corresponding experimental radial distribution function are shown in Fig. 1 for Na as an illustrative case. In all the cases studied there is good coincidence between the first peak of $g(r)$ and the minimum of the pair potential. One should notice that $\phi(r)$ does not extend much more than the second peak in $g(r)$.

Various contributions to self-energy $u(n_0)$ for Na, Mg, and Al are given in Table II. All values reported in this table are in qualitative agreement with previous calculations which employ different screening functions. It is already noted that the self-energy is not too sensitive to the choice of screening function. The fact that our values are close to those calculated by Kumaravadivel proves once more the insensitivity of the band-structure contribution u_3, which is the major contribution to $u(n_0)$, to variations in the model potential and screening function.

TABLE II. Various contributions to the self-energy $u(\rho_0)$, $\rho_0 du/d\rho_0$, and internal energies U for Na, Mg, and Al. U_{expt} values are calculated by Hafner (Ref. 6) using the data of Gschneider (Ref. 7). All energies are in Rydbergs.

	Na	Mg	Al
u_1	−0.163	−0.233	−0.057
u_2	−0.021	−0.183	−0.549
u_3	−0.297	−1.448	−3.892
$\rho_0 du_1/d\rho_0$	0.006	0.166	0.558
$\rho_0 du_2/d\rho_0$	−0.034	−0.180	−0.475
$\rho_0 du_3/d\rho_0$	−0.015	−0.164	−0.454
U	−0.489	−1.857	−4.450
U_{expt}	−0.464	−1.797	−4.176

The calculation of pressure and compressibility involves the quantity $n_0[du(n_0)/dn_0]$. Table II also shows various contributions to this quantity. Although the orders of magnitude of all three contributions are comparable, the first two tend to cancel each other. As expected, $n_0[du(n_0)/dn_0]$ is more sensitive to the choice of screening functions than $u(n_0)$.

The calculated internal energies U are also shown in Table II. The internal energies compare favorably well with the experimental values calculated by Hafner[6] using the data of Gschneider.[7]

Various contributions to pressure are calculated and given in Table III. We have included the values calculated by Kumaravadivel[2] in the same table for comparison. He uses the Ashcroft empty-core pseudopotential Kleinman[10] and the Vashista-Singwi[11] screening function and experimental $g(r)$ within second-order perturbation theory in the pseudopotential formalism. Comparison reveals that the agreement between two calculations is very good indeed for P_{kin}, P_0, and P_{dir}. The biggest discrepancy is found in the case of P_{ind}, where even the signs come out to be different. This is not surprising since the term

$$\frac{d}{dn_0}\left[1-\frac{1}{\epsilon(q)}\right]$$

appearing in pseudopotential calculation of P_{ind} is known to be negative for some screening functions $\epsilon(q)$ and positive for others. P_{ind} is not too sensitive to the radial distribution function, while P_{dir} is rather sensitive. The effect of $g(r)$ on the calculation is checked by using a hard-sphere value $g(r)$ instead of the experimental one.

TABLE III. Various contributions to pressure (in 10^{10} dyn/cm^2). Values calculated by Kumaravadivel (Ref. 2) are given in parentheses.

	P_{kin}	P_0	P_{dir}	P_{ind}	P
Na	0.130	−2.410	0.057	−0.250	−2.470
	(0.125)	(−2.550)	(0.210)	(0.830)	(−1.380)
Mg	0.561	−16.595	3.046	−3.152	−16.139
	(0.503)	(−13.330)	(3.630)	(2.460)	(−6.740)
Al	0.837	−48.959	10.278	−8.590	−46.433
	(0.730)	(−47.600)	(12.700)	(8.400)	(−25.800)

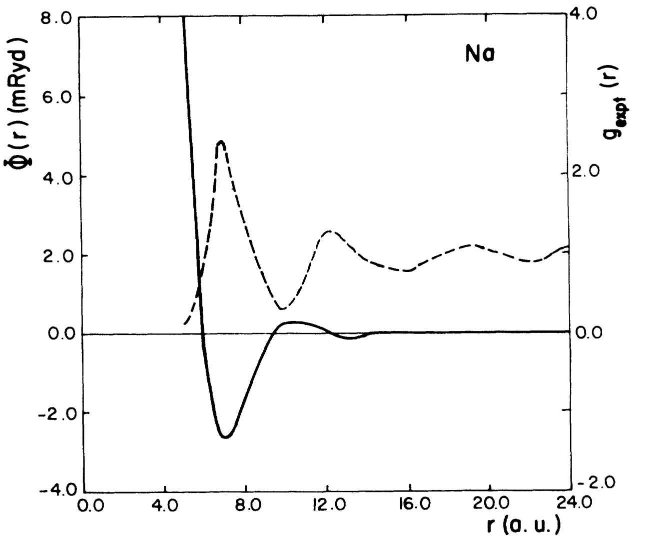

FIG. 1. The pair potential and the radial distribution function for Na. (——, pair potential; — — —, experimental radial distribution function.)

The resulting values for various contributions to pressure in Na are 0.131, −2.410, 0.680, and −0.829 in the same order as in Table III. The resulting pressure is −2.429 which is extremely close to the one calculated using the experimental value $g(r)$. The result is therefore not sensitive to the actual values of $g(r)$ but we find a sensitive dependence on the relative positions of the first peak in $g(r)$ and the minimum of $\phi(r)$. The relative positions are similar for experimental and hard-sphere $g(r)$ for Na.

TABLE IV. Various contributions to B_{LW} (in 10^{10} dyn/cm^2). B_{expt} is taken from Ref. 12.

	Na	Mg	Al
B_{IG}	0.131	0.561	0.837
B_1	0.033	2.034	6.857
B_2	4.529	31.765	50.791
B	4.692	34.360	58.484
B_{expt}	5.380	20.000	41.322

The internal energy and pressure values for Na calculated in this work compare well with the results of Ono and Yokoyama[3] who make use of the one-component plasma reference system.

Finally, the calculated values of the bulk modulus for Na, Mg, and Al are given in Table IV. The agreement with both experiment[12] and previous calculations is reasonable. B_1 and B_2 have the same sensitivity as P_{dir} on how the peak in $g(R)$ matches the minimum of $\phi(r)$.

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