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Effects of a Volume-Dependent Potential on Equilibrium Properties of Liquid Sodium*

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Calculations of cohesive energy, pressure, and compressibility have been made for liquid Na at 393 °K. They are based on the Ashcroft form for the pseudopotential and the self-consistent dielectric function recently given by Singwi *et al.*, which have been found to give good agreement with the measured phonon dispersion relations in crystalline Na, and a liquid structure derived from a recent molecular-dynamics calculation by Rahman. The theory is formulated in terms of a volume-dependent pair potential and additional volume-dependent terms. A model which considers only volume-independent pairwise interactions gives incorrect results for the cohesive energy and pressure. It also gives a different result for the compressibility from the full theory, owing to the neglect of certain three- and four-particle interactions which are considered in the full theory; this result is, however, in reasonable agreement with experiment. The full theory gives good agreement for the cohesive energy, pressure, and compressibility if and only if an adjustment is made to the Hartree energy, similar to that made in a previous calculation for the crystal.

I. INTRODUCTION

The dynamics of metals in the solid and liquid state is often treated by assuming pairwise interactions between the ions. The validity of this approach is to some extent justified by the basic theory of simple metals.[1] If (a) the adiabatic approximation, and (b) perturbation theory to second order in the electron-ion interaction, are both valid, one can indeed define an effective potential between each pair of ions. The pairwise interactions, however, do not give a complete description of the system; not only are the effective pair potentials themselves volume dependent, but also the energy of the system contains additional terms depending on the volume alone. These features have an influence on the dynamic as well as the static properties; for example, they are primarily responsible for the failure of the Cauchy relations in metal crystals, as pointed out by Mott and Jones.[2] Furthermore, third- and fourth-order terms in the electron-ion interaction are probably not negligible even in the alkali metals; such terms represent three- and four-particle interactions in real space. In the long-wavelength limit some of these terms contribute to second order,[3,4] and explicit calculations for the solid[4,5] have shown that they are relatively large.

On the other hand, the complexity of the problem of liquid dynamics is such that the assumption of pairwise interactions is almost indispensable. Models based on this assumption have been used in all molecular-dynamics[6] and many-body theory[7] calculations up to now. The principal aim of the present paper is to investigate the meaning of equilibrium properties such as cohesive energy, pressure, and compressibility for a model considering only volume-independent pairwise interactions (VIPI model). This is done by calculating both the pairwise interaction terms and the volume-dependent terms for liquid sodium. The calculations are based on a local pseudopotential and a dielectric function which give phonon dispersion relations in the crystal in very good agreement with those measured by neutron scattering, as described in an earlier paper,[5] hereafter referred to as I. An effective pair potential (EPP) derived from these (Ref. 8, hereafter referred to as II) has been used in a molecular-dynamics machine calculation,[9] and the pair distribution function (PDF) from that calculation has been used here. In this way one is able to make a completely consistent calculation with a realistic potential, avoiding the use of approximations like the hard-sphere model, which has been widely used in previous discussions of liquid metals.[10]

The second aim of the paper is to investigate the extent of the agreement between equilibrium properties of the liquid calculated on the lines described above and experimental values. Since an EPP derived from data in the crystal can only give information at discrete points corresponding to the pair separations in the lattice, liquid properties can in principle help to determine it more uniquely. Dynamical calculations for liquid Na are also in progress,[11] and should provide a further test of the EPP. In that case, however, one has to contend with the many-body aspects of liquid dynamics, whereas the properties considered here involve only the EPP and PDF and their derivatives.

II. COHESIVE ENERGY

The cohesive energy of a static metal crystal was considered in I. A simple form of pseudopotential due to Ashcroft[12] and a self-consistent dielectric function due to Singwi *et al.*[13] gave phonon dispersion relations in agreement with neutron scattering measurements in Na and were used to calculate the cohesive energy, equilibrium lattice parameter, and compressibility of the crystal. It was found that a small adjustment of the Hartree term E_H was needed to give the observed value of the lattice parameter, but that, when this was made, the calculated cohesive energy and compressibility were also brought into agreement with the observed values. The Hartree term represents the average interaction of the conduction electrons with the nonelectrostatic part of the bare potential:

$$E_H = Z \lim_{q\to 0}\left[w(q) + 4\pi Z e^2/\Omega q^2\right] , \tag{1}$$

where Z is the number of conduction electrons and $\Omega = \frac{4}{3}\pi r_s{}^3 Z$ is the average volume per ion. This term is likely to be the least accurate one in the above description since it involves the long-wavelength limit of $w(q)$, whereas the form of $w(q)$ is usually fixed by comparison with short-wavelength data such as phonon-dispersion or Fermi-surface measurements; an equivalent adjustment is made by Ashcroft and Langreth in a similar calculation.[14]

An expression analogous to Eq. (22) of I can be written down for the internal energy of the liquid, adding the kinetic energy of the ions and replacing the sums over reciprocal-lattice vectors by integrals over the static structure factor $S(\vec{q})$. The latter has been derived in a molecular-dynamics machine calculation of Rahman,[9] simulating liquid Na at 393 °K and a density of 0.927 g/cm^3, corresponding to $r_s = 4.05$. The EPP used was that which fitted the phonon dispersion measurements in the crystal, as described in II. It has the form

$$\varphi(q) = \varphi_{\text{es}}(q) + \varphi_{\text{bs}}(q) , \tag{2a}$$

$$\varphi_{\text{es}}(q) = 8\pi Z^2/\Omega q^2 , \tag{2b}$$

$$\varphi_{\text{bs}}(q) = -G(q)\,\varphi_{\text{es}}(q) , \tag{2c}$$

where the function $G(q)$ is defined for a local pseudopotential $w(q)$ and dielectric function $\epsilon(q)$ as[5]

$$G(q) = \left[\frac{w(q)}{-8\pi Z/\Omega q^2}\right]^2 \left[\frac{\epsilon(q)-1}{\epsilon(q)}\right] , \tag{2d}$$

although it can be defined more generally for a nonlocal pseudopotential. Energies are given in Ry/ion and distances in units of the Bohr radius.

The structure factor $S(\vec{q})$ and the EPP described above can be used to evaluate the cohesive energy of the liquid. This reciprocal-space calculation turns out, however, to be unsatisfactory. The factor $G(q)$ in Eq. (2c) damps out $\varphi_{\text{bs}}(q)$ at large q, leaving the long-range Coulomb part $\varphi_{\text{es}}(q)$ essentially unscreened. The integral over q has therefore to be carried to large q where $S(\vec{q})$ has to be obtained by Fourier transformation of the PDF $g(\vec{r})$, a process with large inherent errors. It is necessary instead to work in real space; since $\varphi_{\text{bs}}(r)$ and $\varphi_{\text{es}}(r)$ cancel for large r, the integral involved is short-ranged.

One must first transform the expression for the cohesive energy given in I to a real-space form. The required form is given by

$$E = E_1 + E_2 + E_3 + E_K , \tag{3a}$$

where

$$E_1 = \tfrac{1}{2}\int g(\vec{r})\,\varphi(r)\,d\vec{r} , \tag{3b}$$

$$E_2 = \tfrac{1}{2}\varphi_{\text{bs}}(r=0) , \tag{3c}$$

$$E_3 = 0.982\,\frac{Z}{r_s{}^2} + \left(\frac{0.407}{\xi} - 0.916\right)\frac{Z}{r_s} - (0.115 - 0.031\ln r_s)Z , \tag{3d}$$

E_K = the kinetic energy of the ions ,

and ξ is a constant related to the compressibility of the electron gas.[5,13] The physical meaning of the three potential terms is clear: E_1 represents the pairwise interactions, E_2 the self-energy of the band-structure part (which cannot be left out like the self-energy of the electrostatic part), and E_3 that part of the energy of the electron gas not included in the first two terms.

Calculations performed with values for $g(\vec{r})$ obtained from the molecular-dynamics computations proved satisfactory; after a certain point, the value of E_1 did not depend significantly on the cutoff of the integral. The results for the liquid are given in the third column of Table I. For comparison, analogous results for the solid are given in the second column, equivalent to the reciprocal-space calculation de-

TABLE I. Equilibrium properties of liquid Na (Ry/ion).

Term	E_s Solid, 0 °K	E_l Liquid, 393 °K	ΩP	$\Omega \bar{B}$	ΩB
1	−0.0160	−0.0114	0.0203	0.0950	0.1030
2	−0.2902	−0.2882	−0.0194		−0.0350
3	−0.1880	−0.1857	−0.0284		−0.0212
ΔE_H	0.0308	0.0280	0.0280		0.0560
Total PE	−0.4634	−0.4573	0.0005	0.0950	0.1028
KE	0.0010	0.0038	0.0025	0.0025	0.0025
Total calc	−0.4624	−0.4535	0.0030	0.0975	0.1053
		$E_l - E_s = 0.0089$			
Total obs	−0.460 ± 0.002[b]	0.008 95 ± 0.000 02[c]	0.0000	0.0973[a]	

[a] Reference 15, error not given.

[b] Heat of sublimation plus first-ionization energy (Refs. 16 and 17).

[c] Reference 17, corrected for electron contribution.

scribed in I. The rows labeled 1, 2, and 3 refer to E_1, E_2, and E_3, respectively, and the row labeled ΔE_H refers to the modification of the Hartree term mentioned above. The value of this term has been taken as 0.218 E_H, as in I. The kinetic energy is $\frac{3}{2}kT$ for the liquid, and the zero-point motion has been included for the solid, taken from a Debye model with $\Theta = 172$ °K. The calculated energy difference between liquid at 393 °K and solid at 0 °K is 0.009 Ry, agreeing well with the experimental value of 0.008 95 ± 0.000 02 Ry. (The latent heat of melting is 0.001 95 Ry, the remainder representing the energy needed to heat the solid to the melting point and the liquid from the melting point to 393 °K.)

The agreement is perhaps fortuitously good in view of the uncertainties in the calculation, in particular the adjustment to the Hartree term. Nevertheless, it is clear that the state of the theory is sufficiently advanced to make the calculations of the small energy differences between liquid and solid feasible, contrary to what has been said earlier.[18] The improvement seems to be due to two factors, first, the availability of reliable structure data from molecular dynamics, and second, the use of a real-space representation which utilizes the considerable cancellation between φ_{bs} and φ_{es}.

Comparison of the second and third columns in Table I shows that the contributions to the energy differences between solid and liquid from the volume-dependent terms E_2, E_3, and ΔE_H are as large as those from the pairwise interaction term E_1. Thus the VIPI model (considering only volume-independent pairwise interactions) is not adequate to explain the observed differences in energy.

III. PRESSURE

The pressure of a liquid can be derived by standard statistical mechanics once the interatomic potential is known.[19] In the case of a metal one must take the volume dependence of the potential into account, both because the EPP itself depends on Ω and because of the terms E_2 and E_3 which depend only on Ω. The result[20] is

$$\Omega P = \Omega P_1 + \Omega P_2 + \Omega P_3 + kT\ , \tag{4a}$$

where

$$\Omega P_1 = -\tfrac{1}{6}\int g(\vec{r})\left(r\frac{\partial\varphi}{\partial r} + r_s\frac{\partial\varphi}{\partial r_s}\right)d\vec{r}\ , \tag{4b}$$

$$\Omega P_2 = -\tfrac{1}{6} r_s \frac{\partial}{\partial r_s}[\varphi_{\mathrm{bs}}(r=0)]\ , \tag{4c}$$

$$\Omega P_3 = -\tfrac{1}{3} r_s \frac{\partial E_3}{\partial r_s}\ . \tag{4d}$$

Here $\partial/\partial r$ denotes differentiation with respect to the space coordinate at fixed r_s, and $\partial/\partial r_s$ differentiation with respect to r_s at fixed space coordinate. The integrands in Eqs. (4a) and (4b) can be evaluated from the expressions in Eq. (2a). Since the dielectric function $\epsilon(q)$ is a function of q/q_F, i.e., qr_s only,[5] the full derivative in Eq. (4b) does not involve $\epsilon(q)$ but only the pseudopotential $w(q)$; the same fact can be used to evaluate the derivative in Eq. (4c), and leads to a considerable simplification of the algebra.

The results are given in the fourth column of Table I. The potential terms give a result which is nearly zero, but the addition of the kinetic term gives a total ΩP of 0.003 Ry/ion. Since the bulk modulus ΩB is about 0.1 Ry/ion (see Sec. IV), such a pressure would require a change in r_s of about 1% to produce equilibrium, which is a reasonable result in view of the approximations made; in particular, the total ΩP is about 10% of the contribution from the adjustment to the Hartree energy.

In the VIPI model, the pressure is given by

$$\Omega \bar{P} = -\tfrac{1}{6}\int g(\vec{r})\, r\,\frac{\partial\varphi}{\partial r}\, d\vec{r} + kT\ . \tag{5}$$

For liquid sodium this gives a value of 0.011 Ry/ion, a much larger pressure than we get with the full calculation. Thus a molecular-dynamics calculation at a fixed value of Ω is simulating a system of particles under a large positive pressure. A similar situation exists for the crystal in a force-constant description, and leads to the violation of the Cauchy relation even though the force constants are axially symmetric.[2] It does not, however, follow that such a description is a bad representation of the metal; the metal is in equilibrium with respect to the ions and electrons combined, not with respect to the ions by themselves. The positive pressure of the VIPI model is merely simulating the volume-dependent effects of the electrons.

IV. COMPRESSIBILITY

The compressibility or its inverse, the bulk modulus, is an interesting property of a condensed system in that it ties together static and dynamic aspects. There is a "compressibility sum rule" which must be obeyed in a consistent theory for the system. In a crystal, for example, the static bulk modulus B, derived by double differentiation of the energy with respect to volume, must agree with the dynamic bulk modulus $\tilde{B}$ representing the appropriate combinations of elastic constants evaluated from the phonon dispersion relation by the method of long waves.[21] The latter depends on the interatomic interactions at constant volume, and not on terms in the energy which depend on volume alone. In a consistent theory, however, there must be a relation between the form of the interatomic interactions at constant volume and the derivatives of the total energy—including the volume-dependent terms—with respect to volume. This relation leads to the compressibility sum rule.

In I the compressibility sum rule was investigated for the case of crystalline sodium, and a significant violation was found. This arises because our "full theory" is actually not self-consistent, since it stops at second order in the perturbation expansion in terms of the electron-ion interaction.[3,4] There are certain terms which appear in the dynamical matrix to third and fourth order which contribute to second order in the long-wavelength limit. These are neglected in the dynamic modulus but included in the static modulus, leading to the discrepancy mentioned. Of course, it is in principle possible to set up a dynamical matrix including these extra terms[22,23]; these correspond to triplet and quadruplet interionic interactions. No such calculations have as yet been performed, however, and we neglect these terms in our theory. In that case the dynamical matrix and hence the dynamic modulus involve only the pairwise interactions at constant volume. The dynamical modulus $\tilde{B}$ therefore corresponds to the modulus calculated from the VIPI model. Since this is itself a perfectly consistent model, the static and dynamic moduli for the model are both equal to $\tilde{B}$.

For the case of crystalline sodium investigated in I, it was found that an adjustment to the Hartree energy was needed to bring the static modulus B into agreement with experiment, but that the dynamic modulus $\tilde{B}$, which agreed with experiment before the adjustment, then became too large. A possible explanation is that the third- and fourth-order terms in the dynamical matrix become more important as q becomes small, so that, if they were included, one would have to modify the pseudopotential at small q to maintain agreement with experiment; this modification would then correspond to our adjustment of the Hartree energy.

A similar sum rule applies in the case of a liquid. The static isothermal bulk modulus is derived from the differentiation of the pressure:

$$\Omega B = -\Omega^2\left(\frac{\partial P}{\partial \Omega}\right)_T , \tag{6}$$

while the dynamic isothermal bulk modulus is related to the long-wavelength limit of the structure factor $S(Q) = \int S(Q,\omega)\, d\omega$ by

$$\Omega \tilde{B} = kT/S(0) . \tag{7}$$

In a consistent theory the two moduli must agree. If however we use second-order perturbation theory and derive $\Omega\tilde{B}$ from $S(0)$ through a calculation with the VIPI model—such as the molecular-dynamics calculation described above—we may expect a discrepancy similar to that obtained for the crystal.

The explicit expressions are as follows:

$$\Omega B = \Omega B_1 + \Omega B_2 + \Omega B_3 + kT , \tag{8a}$$

$$\Omega B_1 = \tfrac{1}{18}\int D g(\vec{\mathrm{r}}) D\varphi(r)\, d\vec{\mathrm{r}} + \tfrac{1}{18}\int g(\vec{\mathrm{r}}) D^2\varphi(r)\, d\vec{\mathrm{r}} , \tag{8b}$$

where

$$D \equiv r\frac{\partial}{\partial r} + r_s \frac{\partial}{\partial r_s}$$

and the derivatives have the sense described after Eq. (4a), and

$$\Omega B_2 = \tfrac{1}{18}\, r_s \frac{\partial}{\partial r_s}\, r_s \frac{\partial}{\partial r_s}\left[\varphi_{\mathrm{bs}}(r=0)\right] + \Omega P_2 , \tag{8c}$$

$$\Omega B_3 = \tfrac{1}{9} r_s \frac{\partial}{\partial r_s}\, r_s \frac{\partial E_3}{\partial r_s} + \Omega P_3 . \tag{8d}$$

A similar expression can be written for the dynamic modulus $\tilde{B}$ since this can be calculated with the VIPI model, which, as we said, is a consistent model and therefore gives the same result for static and dynamic compressibilities. (Wallace[4] establishes this fact for the crystal in the reciprocal-space representation, but the result is much more transparent in the real-space representation.) The required expression is

$$\Omega\tilde{B}=\Omega\tilde{B}_1+kT\ , \tag{9a}$$

$$\Omega\tilde{B}_1=\tfrac{1}{18}\int Dg(\vec{\mathrm{r}})\,\frac{r\partial\varphi(r)}{\partial r}\,d\vec{\mathrm{r}} + \tfrac{1}{18}\int g(\vec{\mathrm{r}})\frac{r\partial}{\partial r}\frac{r\partial}{\partial r}\,\varphi(r)\,d\vec{\mathrm{r}}\ . \tag{9b}$$

Of course Eq. (7) gives a much simpler expression for $\Omega\tilde{B}$. The equivalence of Eqs. (7) and (9a) is in fact a special case of the consistency condition[24] between the (n)- and $(n+1)$-particle distribution functions. However, Eq. (9a) has the merit of giving us some indication of how to evaluate Eq. (8a) for the static compressibility, for which we do not have an equivalent simple form. There are in fact two problems in evaluating Eq. (8b):

(a) We should, strictly, use a $g(\vec{\mathrm{r}})$ that is consistent with the full theory, i.e., that gives $S(0) \equiv 1+\int[g(\vec{\mathrm{r}})-1/\Omega]\,d\vec{\mathrm{r}}$ equal to the correct value of $kT/\Omega B$. This however would require a calculation which took account of the third- and fourth-order terms for small q. Since such terms correspond to effective interactions between three and four ions, this is practically impossible. We will therefore assume that the $g(\vec{\mathrm{r}})$ calculated with molecular dynamics using an EPP at fixed Ω will not be seriously in error except in the long-wavelength limit, and will therefore use this $g(\vec{\mathrm{r}})$ both in Eqs. (8) and (9).

(b) Both Eqs. (8) and (9) require the volume derivative of $g(\vec{\mathrm{r}})$, which could only be obtained from molecular-dynamics calculations at different volumes, a rather tedious task. For the present purpose we make the approximation

$$g(\vec{\mathrm{r}},\ r_s,\ T)=(1/\Omega)\times\text{function}\,(\vec{\mathrm{r}}/r_s,\ T)\ . \tag{10}$$

This is taking the structure to scale uniformly with volume at constant temperature, which is true for the static crystal lattice but not necessarily for the liquid. From this approximation it follows that

$$Dg(\vec{\mathrm{r}})\equiv\frac{r\partial g}{\partial r}+r_s\,\frac{\partial g}{\partial r_s}=-\,3g(\vec{\mathrm{r}})\ . \tag{11}$$

With these assumptions, Eq. (8b) becomes

$$\Omega B_1=\tfrac{1}{18}\int g(\vec{\mathrm{r}})\,(D^2-3D)\,\varphi(r)\,d\vec{\mathrm{r}} \tag{8b$'$}$$

and Eq. (9b) becomes

$$\Omega\tilde{B}_1=\tfrac{1}{18}\int g(\vec{\mathrm{r}})\left[\left(\frac{r\partial}{\partial r}\right)^2-\frac{3r\partial}{\partial r}\right]\varphi(r)\,d\vec{\mathrm{r}}\ . \tag{9b$'$}$$

Results for the dynamic modulus $\Omega\tilde{B}$ are given in the fifth column of Table I. The value 0.097 derived *without* the adjustment of the Hartree energy agrees well with the experimental value of 0.0973, just as was found in the case of the crystal in I. The value of $S(0)$ from the molecular-dynamics calculations[9] is 0.032 ± 0.002, giving $\Omega\tilde{B}=0.078\pm0.005$. Now the approximation Eq. (10) implies that the modulus obtained using Eq. (9b$'$) is an "instantaneous" bulk modulus, which Schofield[24] shows is an upper limit to the adiabatic bulk modulus, the latter being about 10% higher than the isothermal bulk modulus in liquid Na. Our result is consistent with this, but shows that the difference is not very large, and therefore that Eq. (11) is a reasonable approximation for the present purposes.

We may therefore proceed to evaluate ΩB with the same approximation, using Eq. (8b$'$). The results are shown in the last column of Table I. Including now the adjustment to the Hartree energy, we get a final result of 0.105, which again is in reasonable agreement with experiment, considering that we are calculating an upper limit to the actual compressibility. As in the case of the crystal, the adjustment to the Hartree term gives a large contribution and is essential to obtain agreement.

On the other hand the dynamic modulus $\tilde{B}$, which is identical with that obtained from a model considering only volume-independent pairwise interactions, then becomes too large. The entire situation is exactly analogous with that found in the crystal[5] and must be explained in the same way. One possible explanation, in terms of a modification of the pseudopotential at small q, has been mentioned above; a definitive statement, however, must await a calculation of the third- and fourth-order terms for larger q, i.e., of the effective triplet and quadruplet interactions.

V. CONCLUSIONS

The principal aim of this work was to investigate the meaning which can be attached to values of equilibrium properties based on a model which considers only volume-independent pairwise interactions. The conclusions may now be summarized. The calculated energies, even the small energy difference involved in melting, are incorrect. The pressure is meaningless, since the model is simulating a system of particles under a large positive pressure. The matter of the compressibility is less straightforward, because of the uncertainty about the higher-order terms in the electron-ion interaction. The instantaneous bulk modulus calculated from the pairwise interaction model, which is identical with the dynamic modulus calculated from the full theory taken to second order, is significantly different from the static modulus calculated from the second-order theory. The former is in good agreement with the experimental isothermal modulus, while the latter is only brought into agreement by adjusting the Hartree energy. This is the same situation as that found with the crystal in I. A possible explanation is that the modification of the pseudopotential represented by the adjustment of the Hartree term and the significant higher-order terms in the electron-ion interaction are both negligible except at long wavelengths, where they balance each other out. Without further calculations, it is impossible, of course, to know how far out in the zone this long-wavelength region extends.

As regards the second aim, the agreement between theory and experiment for the equilibrium properties of liquid sodium, the results are satisfactory. It is essential to include the adjustment to the Hartree energy, but the same adjustment gives good agreement for cohesive energy, pressure, and static compressibility. These results are also similar to those found for crystalline sodium.

Finally, it should be mentioned that the resistivity and thermoelectric power of liquid sodium have also been calculated with the formalism described in the previous sections. Good agreement with the experimental values was obtained. However, not too much importance can be ascribed to this result since in lithium, for example, the value of the core-radius parameter which fits the phonon dispersion relation[5] is very different from either of the two values which give the correct resistivity for the liquid.[25] The resistivity and more especially the thermoelectric power are sensitive to the behavior of the pseudopotential around $2k_F$, while the dynamical and equilibrium properties are sensitive to the values at shorter wave vectors.

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