Pair potentials for liquid sodium near freezing from electron theory and from inversion of the measured structure factor

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An effective pair potential for liquid sodium near freezing has been calculated from electron theory using the density-functional method. The main features of the potential extracted by Reatto, Levesque, and Weis [Phys. Rev. A **33**, 3451 (1986)] by inverting the measured structure factor of Greenfield, Wellendorf, and Wiser [Phys. Rev. A **4**, 1607 (1971)] are faithfully reflected by electron theory. To obtain precise agreement between the two methods will evidently require further progress in setting up nonlocal exchange and correlation functionals.

The proposal of Johnson and March[1] to invert the measured structure factor $S(k)$ of liquid metals to extract a pair potential $\phi(r)$ has recently been brought to full fruition for a particular thermodynamic state of liquid Na. Specifically, the x-ray diffraction data of Greenfield, Wellendorf, and Wiser[2] at $T = 100\,°C$ and density equal to 0.929 g cm^{-3} have been inverted by Reatto, Levesque, and Weis[3] to obtain $\phi(r)$ for this state. These workers employed an iterative predictor-corrector method in which the predictor was the modified hypernetted-chain approximation of liquid state structural theory, while the corrector was simulation. Reatto, Levesque, and Weis[3] verified the convergence of their method for a Lennard-Jones fluid and for a model potential for Al.

In parallel with this progress in extracting a pair force from structural data has been the development of methods for obtaining $\phi(r)$ based on electron theory. While work was carried out on the lightest alkali metal some time ago, both for a single Li ion embedded in a electron liquid of appropriate metallic density by Dagens, Rasolt, and Taylor[4] as well as for crystalline bcc Li by Perrin and co-workers,[5,6] which was of first-principles character, heavier alkali metals have hitherto been tackled using pseudopotentials, as in the work of Price, Singwi, and Tosi[7] on Rb.

In the case of Na, a detailed analysis of the charge density was reported by Rasolt and Taylor. These authors compared the density displaced by a Na ion in an electron gas, as obtained using nonlocal model potentials[8] or in a full nonlinear density-functional calculation done by Dagens.[9] Excellent agreement between these two methods was noticed when the parameters of the model potential were conveniently chosen.

The present calculations on liquid Na were based on a first-principles approach known as the neutral pseudo atom method.[9] The details will be published elsewhere.[10] Briefly, the calculations reported here consist of two distinct parts. First, a Kohn-Sham density functional calculation was performed for a Na nucleus, charge $11e$, em-

bedded in the center of a cavity in a jellium background, of mean conduction electron density $\bar{n}$ corresponding to the mass density of 0.929 g cm^{-3}. Naturally, an approximate form $V_{xc}(\mathbf{r})$ of the exchange-correlation contribution to the one-body potential $V(\mathbf{r})$, given by

$$V(\mathbf{r}) = V_{\text{Hartree}}(\mathbf{r}) + V_{xc}(\mathbf{r}) , \qquad (1)$$

must be adopted at the outset. Two such forms of $V_{xc}(\mathbf{r})$ were used in the present calculation, the first due to

TABLE I. Self-consistent density-functional calculation of the density displaced by an Na atom embedded in a cavity in jellium at electron density $\bar{n} = 0.003\,604\,6$ a.u. The radius R_a of the cavity is such that $\frac{4}{3}\pi R_a^3 \bar{n} = Z^* = 1$.

| | Exchange correlation | |
	Ichimaru[a]	Hedin-Lundqvist[b]
Eigenvalues (Ry)		
E_{1s}	−74.9628	−74.9314
E_{2s}	−3.6336	−3.6293
E_{2p}	−1.6281	−1.6244
Average of r: $\langle r \rangle$ (a.u.)		
$1s$	0.1439	0.1439
$2s$	0.7916	0.7919
$2p$	0.8090	0.8096
Average of r^2: $\langle r^2 \rangle$ (a.u.)		
$1s$	0.0279	0.0279
$2s$	0.7600	0.7609
$2p$	0.8578	0.8591
Total energy of embedding (Ry)		
ΔE	−322.8526	−322.8237
Friedel sum		
Z_F	−0.000495	−0.000488
Total displaced charge (integrated in r space)		
Q	10.000508	10.000512

[a] Reference 11.
[b] Reference 12.

TABLE II. Characteristics of diffraction potential compared with electron theory form.

Positions of turning points and nodes (Å)	Principal minimum	First maximum	Second minimum	First node
Diffraction[a] $\phi(r)$	3.9	5.76	7.44	3.3
Electron theory $\phi(r)$	3.73	5.67	7.37	3.20

[a]Reference 13.

Ichimaru[11] and the second, the older form, due to Hedin and Lundqvist.[12]

Denoting the displaced charge around the Na nucleus in the jellium background with cavity by $\Delta n(r)$, Fig. 1 shows the radial density $D(r) = 4\pi r^2 \Delta n(r)$ for the two choices of V_{xc} in Eq. (1.1). Table I shows relevant data for one-electron eigenvalues, etc., in the two cases.

The second stage of the calculations involves the construction of the appropriate q space quantities $\overline{\Delta n}(q)$ and $w(q)$ needed to insert in the usual second-order perturbation formula for the pair interaction

$$\phi(r) = \frac{(Z^*e)^2}{r} + \int w(q)\overline{\Delta n}(q)\exp(-i\mathbf{q}\cdot\mathbf{r})d\mathbf{q} . \quad (2)$$

One of us describes elsewhere[10] in full detail the way $\overline{\Delta n}(q)$ is to be calculated from $\Delta n(r)$: care is needed to ensure that $\overline{\Delta n}(q)$ normalizes to the valence Z^*, which is unity for Na, to ensure precise cancellation with the Coulomb term in Eq. (1.2) at sufficiently large r. Given $\overline{\Delta n}(q)$, the (weak) potential $w(q)$ is calculated, by linear response theory,

$$w(q) = \frac{1}{\chi(q)}\overline{\Delta n}(q) , \quad (3)$$

$$\frac{1}{\chi(q)} = \frac{1}{\pi_0(q)} + \left[\frac{4\pi}{q^2} + X\right] , \quad (4)$$

where π_0 is the random-phase approximation (RPA) density response function and X the local field correction in the local density approximation for exchange and correlation effects. X is q independent and given by

$$X = \frac{dV_{xc}(\bar{n})}{d\bar{n}} . \quad (5)$$

The calculations reported here differ from those of Ref. 9 for the following reasons.

(i) We have used the Ichimaru (or Hedin-Lundqvist) exchange and correlation functional, instead of a pure Kohn-Sham exchange,

(ii) The density is that of the liquid ($\rho = 0.929$ g cm^{-3}) instead of the solid density ($\rho = 1.0067$ g cm^{-3}).

Nevertheless, our pair potential and those of Rasolt and Taylor are in qualitative agreement. The position of the first minimum is approximately the same in both theories. The main difference resides in the depth of the well: $\beta\phi$ ranges between -0.72 and -0.87 in Ref. 8 (depending on which model potential is used), and ours is $\beta\phi = -1.22$.

With the simplest nontrivial form of $\chi(q)$ involving $dV_{xc}(\bar{n})/d\bar{n}$, curve 1 of Fig. 2 was obtained. The choice of V_{xc} did not affect this curve to graphical accuracy. Table II records the characteristic features of this potential, where it is compared with the same features of the potential extracted by inverting the measured structure factor $S(k)$. All the trends of the potential obtained from the diffraction measurements are clear in the potential
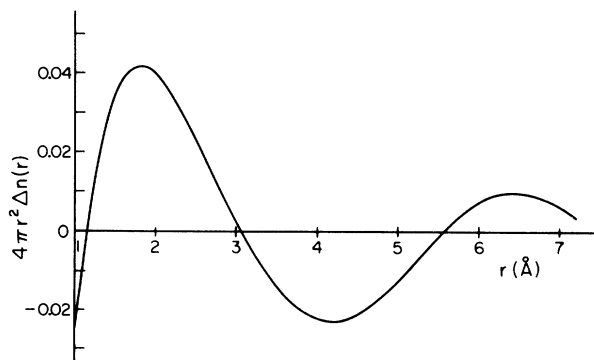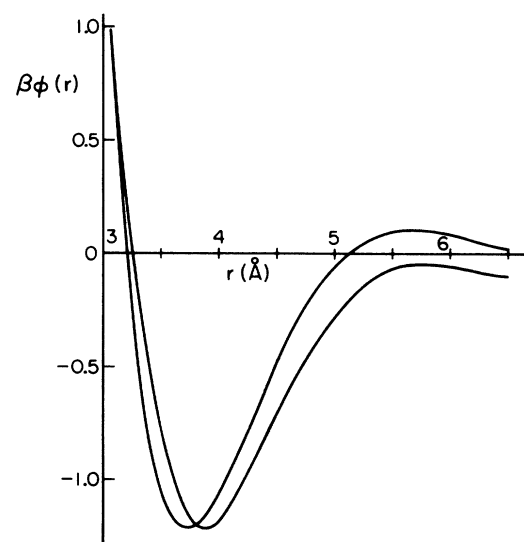

FIG. 1. Radial valence density $4\pi r^2 \Delta n(r)$ for Na nucleus embedded in the center of a cavity in originally uniform electron liquid. For graphical accuracy, this is the same for either choice of $V_{xc}(r)$ in Eq. (1.1) for Ref. 11 or 12.

FIG. 2. Pair potentials for liquid Na at $T = 100\,°C$ and density of 0.929 g cm^{-3}. Electron theory: upper curve for large r. Inversion of liquid structure factor, taken from Refs. 3 and 13: lower curve for larger r.

$\phi(r)$ calculated here from electron theory.

In conclusion, without any adjustable parameters electron theory gives a pair potential $\phi(r)$ at freezing for liquid Na in quite good general agreement with that extracted from the diffraction data of Greenfield, Wellendorf, and Wiser,[2] and by Reatto, Levesque, and Weis.[3] As for detailed comparison, the depth of $\phi(r)$ at the principal minimum is almost the same for the two potentials, though, as Table II shows, the theoretical $\phi(r)$ has its minimum a few tenths of an angstrom inside the diffraction form.[13] But the maxima and minima are practically at the same positions, though the diffraction $\phi(r)$ remains negative at larger r while the electron theory $\phi(r)$ just crosses the axis. On this latter point, we have checked that a modified $\chi(q)$ with a Hubbard-type correction would lead to a negative $\phi(r)$ at larger r, but at the expense of substantially deepening the principal minimum, this moving now to a position slightly outside the diffraction potential minimum. Thus the $\phi(r)$ extracted from $S(k)$ for liquid Na, while not fully quantitatively reproduced in detail by electron theory, nevertheless reflects all the trends predicted by that theory. Evidently, increasing effort to measure the structure factor $S(k)$ for liquid metals over the widest possible range of momentum transfer is now a matter of considerable importance.

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