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## LETTER

### The Deviation of the Pair Potential from the Potential of Mean Force in Molten Na Near Freezing

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The difference between the pair potential  $\phi(r)$  and the potential of mean force  $U(r)$  is studied carefully in molten Na near freezing. Beyond some 4–5 Å the three-body term strongly cancels with  $U(r)$ , leaving  $\phi(r)$  pretty small. Current approximate theories of liquid structure do not handle this cancellation well. Some improvements are therefore proposed.

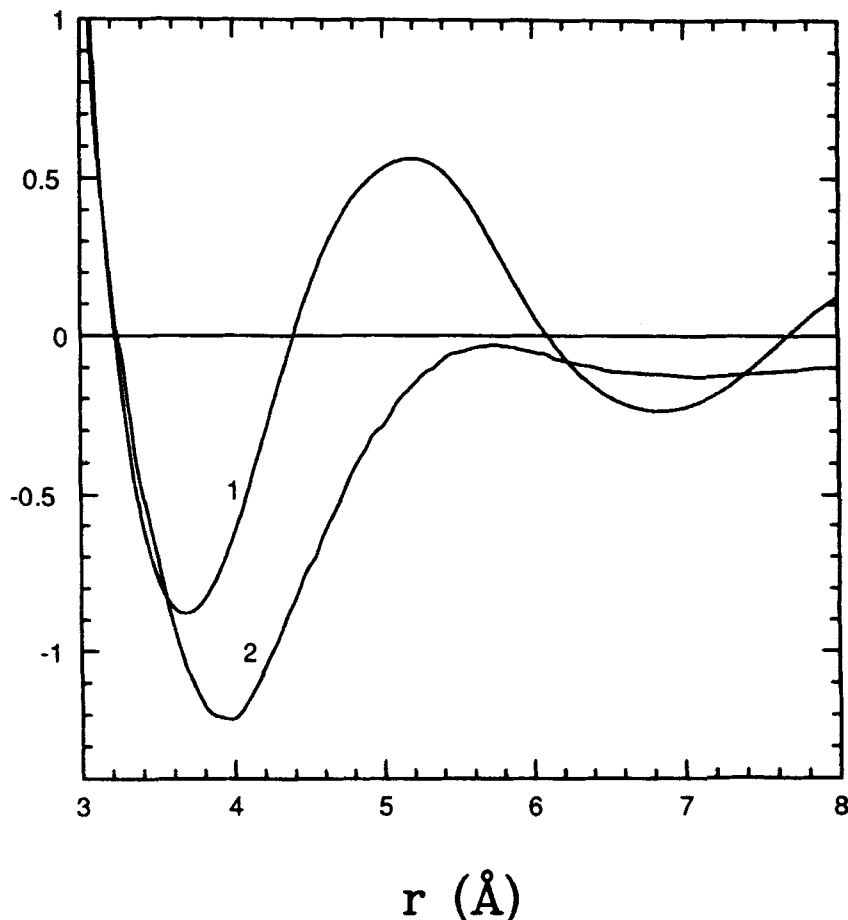
KEY WORDS: Inverse problem, diffraction potential, force correlation function

The proposal of Johnson and March<sup>1</sup> to invert the liquid structure factor  $S(k)$  obtained by diffraction experiments to obtain a pair potential  $\phi(r)$  for liquid metals has been brought to fruition by Reatto and coworkers<sup>2</sup> for Na. It is then very encouraging that all the main features of this “diffraction” potential are found in electron theory study of Perrot and March<sup>3</sup>. However, it remains of interest to see whether the diffraction potential could be extracted from largely analytical liquid structural theories, thereby by-passing the still lengthy computer simulation studies required in the inversion procedure of Reatto *et al.* The present letter is aimed at this aspect of the pair potential inverse problem.

From the diffraction study of Greenfield *et al.*<sup>4</sup>, we have plotted in curve 1 of Figure 1 the potential of mean force  $U(r)$ , in units of thermal energy  $k_B T$ , near the freezing point of liquid metallic Na.  $U(r)$  is simply related to pair correlation function  $g(r) = h(r) + 1$ , with  $h(r)$  the so-called total correlation function, by

$$g(r) = \exp(-U(r)\beta): \beta = (k_B T)^{-1}. \quad (1)$$

Curve 2 shows the pair potential  $\phi(r)$  of Reatto *et al.*<sup>2</sup>. The point we wish to emphasize at the outset is the smallness of  $\phi(r)$  in the tail. There is plainly strong cancellation between the three-body term in the force equation<sup>5</sup> and  $U(r)$ , in arriving at



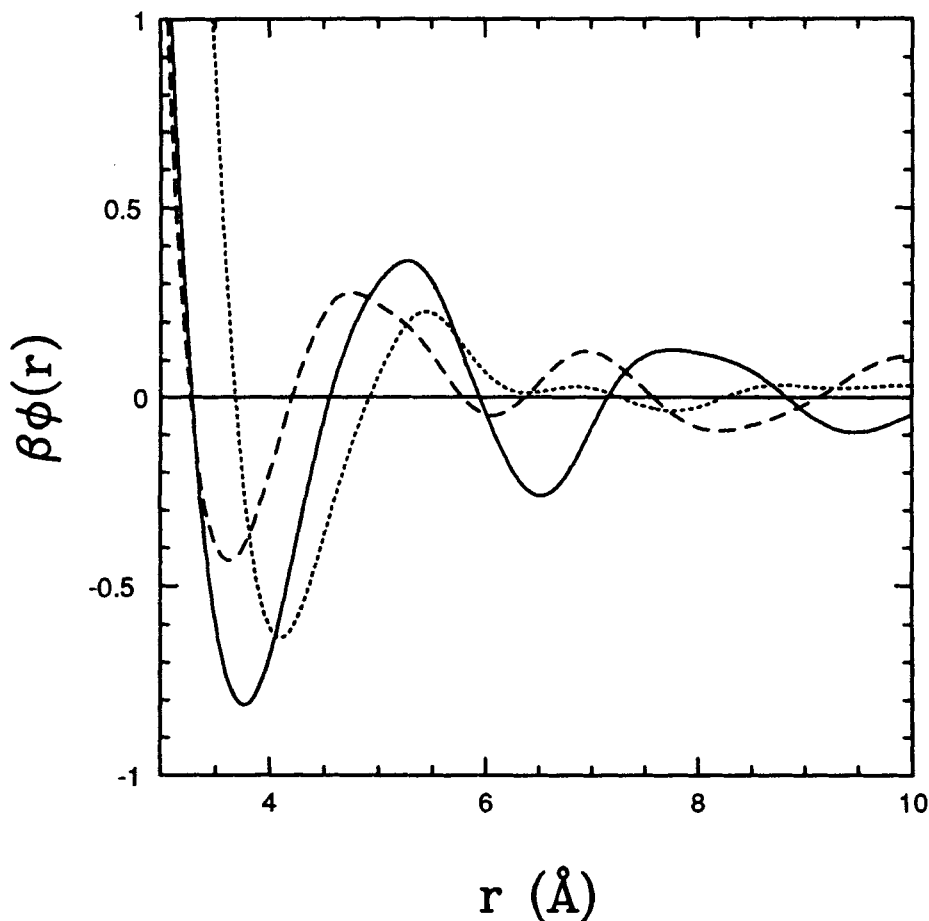
**Figure 1** Curve 1: Potential of mean force  $U(r)$  in units of  $\beta = (k_B T)^{-1}$  for liquid Na near its freezing point. Curve 2: pair potential  $\phi(r)$  of Reatto *et al.*<sup>2</sup>.

this form of  $\phi(r)$ . Thus the use of approximate structural theories, in which  $g_3$  is inevitably approximated, is delicate in this region.

To make this point quite clear, we show in Figure 2 a variety of such theories, and in particular their predictions of  $\phi(r)$  when  $U(r)$  from experiment shown in curve 1 of Figure 1 is used as input data. The dashed curve in Figure 2 is the result of approximate treatment proposed by Angelis and March<sup>6</sup>, where  $\phi(r)$  is given by

$$\beta\phi(r) = \beta U(r) + (8\pi^3\rho)^{-1} \int (S(k) - 1)^2 \exp(ik \cdot r) dk. \quad (2)$$

The potential is a poor quantitative representation of that in curve 2 of Figure 1, and in particular, as stressed above, the approximation is too crude to annul in  $\phi(r)$  the oscillation in  $U(r)$  at large  $r$ . We have investigated possible improvements of



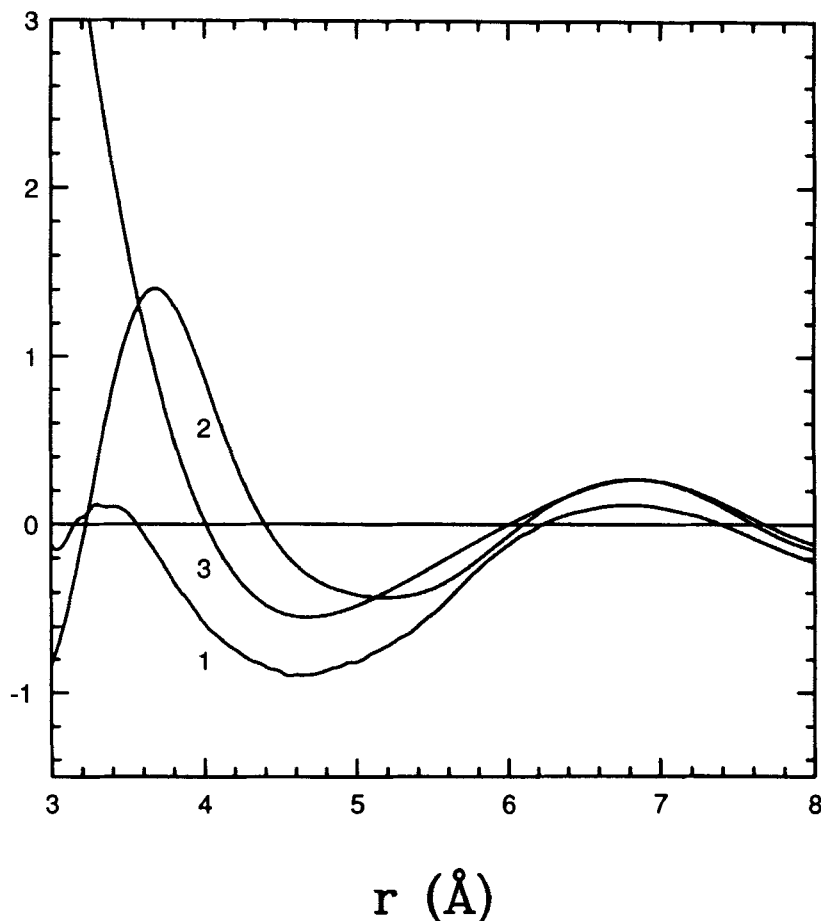
**Figure 2** Effective pair potential  $\phi(r)$  for liquid Na. Full, dashed and dotted curves are the results obtained from Eqs. (3), (2) and (4), respectively.

Eq. (2). One of these is that in which the Kirkwood approximation for  $g_3$  in terms of  $g(r)$  is combined in the force equation with the replacement in the three-body term of  $\phi(r)$  by the “effective potential”  $-k_B T c(r)$ , where  $c(r)$  is the Ornstein-Zernike direct correlation function. With neglect of term involving  $c(r)dg(r)/dr$ , one then finds

$$\beta\phi(r) = \beta U(r) + (8\pi^3 \rho)^{-1} \int FT(g(r)c(r))(S(k) - 1) \exp(-ik \cdot r) dk \quad (3)$$

with

$$FT(g(r)c(r)) = \rho \int g(r)c(r) \exp(ik \cdot r) dr.$$



**Figure 3** Curve 1:  $\beta[\phi(r) - U(r)]$  obtained using data from Figure 1. Curve 2:  $h(r)$ . Curve 3:  $h(r) - c(r)$ .

The result of Eq. (3) is shown by full curve in Figure 2. Finally in Figure 2 the dotted curve shows the hypernetted chain (HNC) results:

$$\phi(r) = U(r) + k_B T(h - c). \quad (4)$$

As anticipated above, none of these three approximate structural theories is sufficiently refined to exhibit the cancellation between  $U(r)$  and the three-body term revealed at large  $r$  in Figure 1.

Turning to possible refinements, we note that when  $U(r)/k_B T$  is substantially less than unity, then Eq. (1) yields  $h(r) = -U(r)/k_B T$ . Thus after some 5 Å one can write from Figure 1 the result

$$\phi(r) - U(r) = h(r)k_B T \quad (5)$$

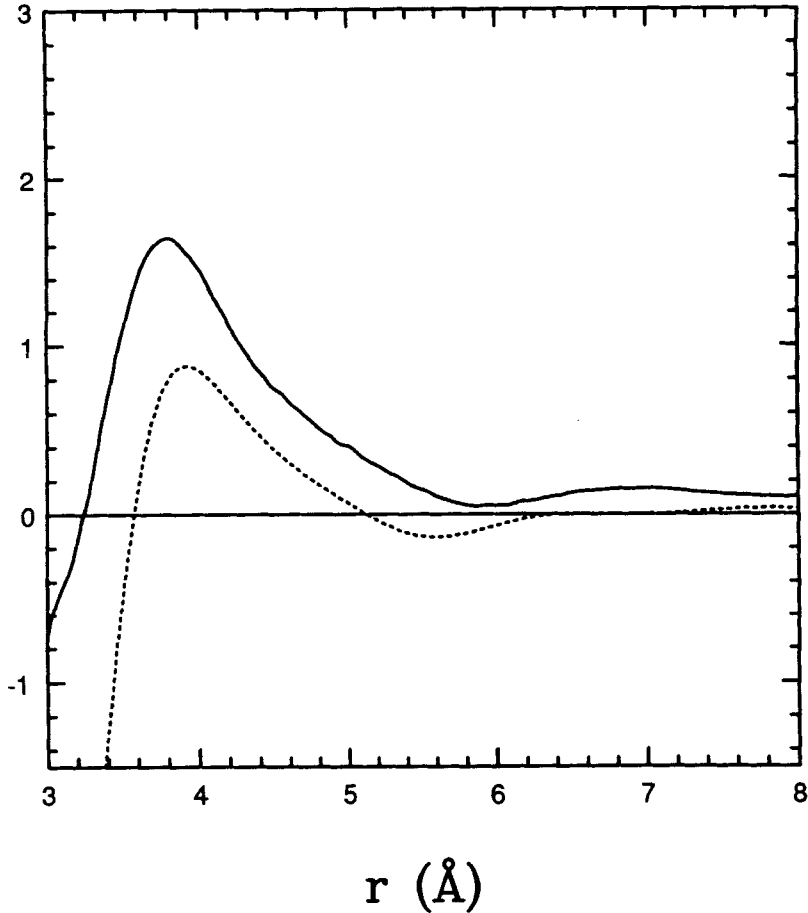


Figure 4 Full curve is  $f(r)$  obtained from Eq. (7). Dashed curve represents direct correlation function  $c(r)$ .

which immediately builds in the large  $r$  cancellation emphasized above. Thus, in Figure 3, we plot the difference  $\beta[\phi(r) - U(r)]$  obtained from Figure 1, in curve 1, while curve 2 shows  $h(r)$ . Curve 3 shows the HNC result  $h-c$  for comparison. For  $r$  greater than  $4 \text{ \AA}$ , curves 1 and 3 have the similar shapes. Therefore,  $\phi(r) - U(r) = h(r) - c(r) - B(r)$ , where  $B(r)$  is slow decaying function of  $r$ , may be the right modification. On the other hand for small  $r$ , it might be necessary to make an admixture of  $h(r) - \nu c(r)$ , where  $\nu$  is a constant hopefully very much less than unity.

In summary, while Eqs. (2), (3) and (4) lead to general shapes which are appropriate for pair potentials in conducting liquid like molten Na near freezing, they are far from quantitative at the first minimum, severely underestimating the depth of potential; Eq. (2) gives magnitude 0.43 for  $\beta\phi(r)$ , Eq. (3) 0.80, Eq. (4) 0.63 while the value of Perrot and March is 1.2, quite near to that of Reatto *et al.*<sup>2</sup>. Even more significant, the cancellation between  $U(r)$  and the three-body term at large  $r$  is not

adequate in any of Eqs. 2–4. In this respect, Eq. (5) is a definite improvement, though presently without fundamental status. However, it is tempting, in conclusion, to return to an observation made long ago by one of us<sup>7</sup> that a class of simple theories has the shape:

$$\phi(r) - U(r) = k_B T \rho \int G(\mathbf{r} - \mathbf{r}') h(\mathbf{r}') d\mathbf{r}' \quad (6)$$

Of course, if one retained the convolution from Eq. (6) for the deviation of  $\phi(r)$  from  $U(r)$ , then Eq. (5) is regained by choice of the so-called force correlation function  $G(r)$  as a  $\delta$  function. Obviously this is too primitive, but it does suggest that  $G(k)$ , the FT of  $G(r)$ , is long-ranged in  $k$  space. Of course, an alternative is to give up the convolution from Eq. (6) and write

$$\beta[\phi(r) - U(r)] = h(r) - f(r) \quad (7)$$

To get an admittedly rough estimate of  $f(r)$ , we have taken  $\phi(r) - U(r)$  from Figure 1 and the experimental  $h(r)$ . Then from Eq. (7), we have plotted  $f(r)$  as curve 1 in Figure 4. For comparison, the HNC  $c(r)$  is also shown as curve 2. It is found that  $f(r)$  is always larger than  $c(r)$ .

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