Relation between Principal Peak Height, Position and Width of Structure Factor in Dense Monatomic Liquids

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Letter

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In monatomic dense liquids, the condition that the pair function $g(r)$ vanishes at $r = 0$ is shown to lead to the approximate relation

$$S(q_m) = \text{constant} \, \frac{q_m}{\Delta q} \; ; \text{constant} \simeq 0.3, \tag{I}$$

for the principal peak height, at position q_m, of the structure factor $S(q)$ in terms of the peak width Δq. In (I), $2\Delta q$ is defined precisely as the distance between the two adjacent nodes of $S(q) - 1$ which embrace the peak position q_m. Examples for liquid argon, sodium and potassium using measured diffraction data confirm the form (I), with constant $\simeq 3/8$.

First principles theory by which the pair function $g(r)$, or the structure factor $S(q)$, of a dense monatomic liquid, related by

$$g(r) - 1 = \frac{1}{(2\pi)^3 \rho} \int [S(q) - 1] e^{i\mathbf{q} \cdot \mathbf{r}} d^3 q \tag{1}$$

can be calculated from a specified force law continues to prove somewhat intractable. Therefore, it remains of interest to examine what regularities are

exhibited by structure factors $S(q)$ which are available for a variety of dense liquids from diffraction experiments. Here, we shall concern ourselves exclusively with data on argon at 85 K, and on liquid metallic sodium and potassium, each in two thermodynamic states.

In classical liquids, the pair function must satisfy $g(0) = 0$, which then yields according to eqn. (1)

$$-2\pi^2 \frac{N}{V} \equiv -2\pi^2\rho = \int_0^\infty [S(q) - 1]q^2 dq, \qquad (2)$$

with N atoms in volume V. An approximate evaluation of the integral (2) in such dense liquids as cited above can be carried out as follows. Let q_m denote the position of the principal peak of $S(q)$. Suppose the peak width, $2\Delta q$ say, is to be measured by the distance between the two adjacent nodes of $S(q) - 1$ which embrace q_m, and that any asymmetry of the peak about q_m is neglected. If we now write eqn. (2) as

$$-2\pi^2\rho = \int_0^{q_m - \Delta q} [S(q) - 1]q^2 dq + \int_{q_m - \Delta q}^{q_m + \Delta q} [S(q) - 1]q^2 dq$$

$$+ \int_{q_m + \Delta q}^\infty [S(q) - 1]q^2 dq, \qquad (3)$$

then for an $S(q)$ appropriate to dense fluids, such as argon near the triple point, or Na and K near the melting point, the following approximations are reasonable:

(i) To replace $S(q) - 1$ by -1 over the range of the first integral in eqn. (3).

(ii) To neglect the third integral in eqn. (3), because of the oscillations about zero of $S(q) - 1$.

(iii) To estimate the second integral by the triangular area

$$[S(q_m) - 1]q_m^2 \Delta q.$$

Using these simplifications and introducing the mean interatomic separation R_A through $\rho = 3/4\pi R_A^3$ it is readily shown that

$$S(q_m)q_m^2 \Delta q \doteqdot \frac{1}{3} q_m^3 \left(1 - \frac{9\pi}{2} \frac{1}{(R_A q_m)^3}\right). \qquad (4)$$

Empirically, in dense liquids, $R_A q_M \simeq 4.4$ and the second term in the round bracket in eqn. (4) contributes 0.15 compared with unity. Thus, one is left with the result

$$S(q_m) \sim 0.3 \frac{q_m}{\Delta q}. \qquad (5)$$

When we confront the approximate prediction (5) with the accurate diffraction data of Yarnell et al[1] on liquid argon at 85 K we find $S(q_m) = 2.70$, $q_m = 2.00$ and $\Delta q = 0.275$ (all q_m, Δq in $A^{\circ -1}$), yielding $S(q_m)/(q_m/\Delta q) = 0.37$, which is nearer to 3/8 than the predicted 0.3 in eqn. (5). It is satisfying that the data of Greenfield et al[2] on liquid potassium at 65 C yields $S(q_m) = 2.73$, $q_m = 1.62$, $\Delta q = 0.225$ and hence a constant of 0.38, while for the experiment at 135 C, $S(q_m) = 2.51$, $q_m = 1.62$, $\Delta q = 0.24$, and the constant in eqn. (5) is 0.37. For Na at 100 C, $S(q_m) = 2.80$, $q_m = 2.02$, $\Delta q = 0.27$, the constant being 0.37 while at 200 C, $S(q_m) = 2.46$, $q_m = 2.00$, $\Delta q = 0.29$, and the constant is 0.36. Thus, for the five experiments we find eqn. (5) to be quantitative when 0.3 is replaced by 3/8. The fact $3/8 > 0.3$ seems to indicate that the third integral actually has a non-zero negative value.

Turning to $g(r)$, it is worth noting that an argument in which $S(0)$ is evaluated via $\int_0^\infty [g(r) - 1]r^2 \, dr$ can be carried out with assumptions made paralleling (i) to (iii) above for calculating $g(0)$. We merely record here the result:

$$g(r_m)r_m^2 \Delta r = \tfrac{1}{3}r_m^3 - \tfrac{1}{3}R_A^3(1 - S(0)), \tag{6}$$

with definitions paralleling precisely those for $S(q)$. Since $g(r)$ is less readily accessible, we shall not comment further on eqn. (6) as it stands. However, for the data of Yarnell et al on liquid argon at 85 K, we find

$$g(r_m) = 3.05, \Delta r = 0.545 \, A^\circ, r_m = 3.68 \, A^\circ \tag{7}$$

and if we form $r_m/\Delta r$ we find 6.7, to be compared with $q_m/\Delta q = 7.2$. Thus very approximately

$$\frac{q_m}{\Delta q} \simeq \frac{r_m}{\Delta r}. \tag{8}$$

Though the main aim of this letter has now been achieved, eqns. (5) and (8) together prompt us finally to comment on the criterion, which it seems was first pointed out by Verlet, that simple liquids like argon freeze when $S(q_m) \simeq 2.8$. Ferraz and March,[3] using the one-component plasma model as starting point, drew attention to the fact that simple liquid metals, and in particular Na and K, also freeze when $S(q_m) \simeq 2.7$. In the cases of Ar, Na and K where freezing involves only minor changes in local coordination, then, at the melting temperature T_m, use of $S(q_m)|_{T_m} = 2.8$ yields from eqns. (5) and (8) the estimate $(\Delta r/r_m)_{T_m} \sim 0.11$. But Lindemann's law of melting, according to Faber,[4] gives $(\Delta r/R_A)_{T_m} \sim 0.2$ if we identify here Δr as the root mean square displacement of the atoms. Since $r_m \sim 1.8 \, R_A$ these results are seen to be roughly consistent. Thus, there is no conflict between freezing criteria based on $S(q_m)|_{T_m} = 2.8$ on the one hand and Lindemann's law on the other, even though the latter is sometimes interpreted, for simple liquid

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metals say, in terms of $S(0)|_{T_m} = $ constant. Somewhat more generally, any acceptable microscopic theory of dense fluids, not far from the triple point, will have to be in accord with the above approximate relation between peak height, position and width of the structure factor $S(q)$.

Acknowledgement

References

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