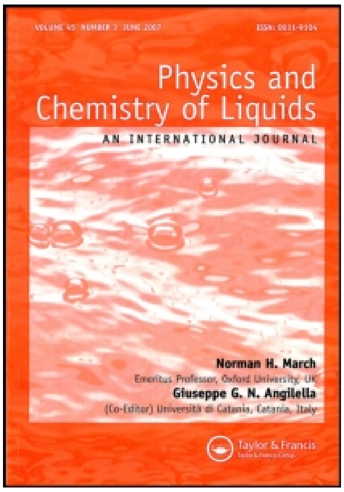

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Specific heats of liquids and phonon theory

P. Bratby[a]; T. Gaskell[a]; N. H. March[a]
[a] Department of Physics, The University Sheffield,

To cite this Article Bratby, P. , Gaskell, T. and March, N. H.(1970) 'Specific heats of liquids and phonon theory', Physics and Chemistry of Liquids, 2: 1, 53 — 66

To link to this Article: DOI: 10.1080/00319107008084079

URL: http://dx.doi.org/10.1080/00319107008084079

Physics and Chemistry of Liquids. 1970. Vol. 2, pp. 53–66
Copyright © 1970 Gordon and Breach Science Publishers
Printed in Great Britain

Specific Heats of Liquids and Phonon Theory

P. BRATBY, T. GASKELL and N. H. MARCH

Department of Physics
The University
Sheffield

Abstract—The measured ratio of the specific heats γ for liquid metals near the melting point and for the liquid insulator argon just above its melting point differ considerably. For metals, $\gamma \sim 1.2$ or 1.3 while for argon $\gamma \sim 2.2$. Furthermore, the measured specific heat at constant volume, per atom, is near to $3k_B$ and always slightly greater, for metals, in contrast to argon for which $C_v \simeq 2.3\, k_B$ near the melting point.

These observations suggest that a phonon model should be good in liquid metals, but that a very 'anharmonic' situation exists in liquid argon. That the softer core and longer range potentials characteristic of metals will lead to γ values near to unity is confirmed by using an inequality due to Schofield to obtain an upper bound for γ. In a model of liquid Na, using the long-range oscillatory potential of Paskin and Rahman which fits the neutron structure factor, we obtain $\gamma \leq 1.2$. The same inequality for argon yields $\gamma \leq 3.5$. The main contribution for argon comes from the region inside 4*A*°, whereas the long-range contribution is large for Na.

For liquid metals, the phonon picture yields for C_v corrections to $3k_B$ which are small, but always positive, the magnitude of the corrections being related to the structure factor. But for argon the phonon picture is clearly bad as evidenced by $\gamma \sim 2.2$ and attempts are made instead to estimate $C_p - C_v$ and C_v from exact equations which unfortunately involve the 3 and 4 particle correlation functions. The value of $C_p - C_v$ is shown to depend very sensitively on the approximation made for g_3; the superposition approximation being unsuitable for this purpose.

1. Introduction

The measured values of γ, the ratio of specific heats, are all around 1.2 or 1.3 near the melting points of liquid metals. In marked contrast, γ for liquid argon just above its melting point (at 84°K) is 2.2. Additionally, C_v for metals at the melting point is found experimentally to be near, and generally slightly in excess of, $3k_B$.

These facts suggest that a phonon theory should be a good starting point for liquid metals, in contrast to the situation in liquid argon. For a phonon theory, the zeroth order values are $\gamma = 1$ and $C_v = 3k_B$ which are already very reasonable estimates for metals.

A variety of evidence is now available which demonstrates that the forces in liquid metals have softer cores and are longer range than in argon, which is usefully described by a relatively hard sphere-like model, with the addition of a van der Waals tail. We might anticipate that it is in the very different character of these force laws that the differences in the specific heats arise and the object of this paper is to turn the above qualitative ideas into a numerical calculation.

A precise quantitative calculation of γ can, in principle, be made (see Eqs. (2.2) and (2.10) below) but in practice we shall content ourselves with obtaining upper bounds. The point here is that an upper bound can be calculated in terms of the radial distribution function $g(r)$ and the pair potential $\phi(r)$, whereas a precise calculation involves the three and four particle correlation functions g_3 and g_4.

2. Theory of Specific Heats in Terms of Static Correlation Functions

We summarize briefly below the chief tools we shall use to discuss the specific heats of liquids.

Two results due to Schofield (1966) will be used. The first is an inequality for the ratio of the specific heats γ which we shall write in the form

$$\frac{\gamma}{S(o)} \leqslant \tfrac{5}{3} + \frac{2\pi\rho}{9k_BT}\int g(r)\left[r^2\frac{\partial^2\phi}{\partial r^2} - 2r\frac{\partial\phi}{\partial r}\right]r^2\,dr \tag{2.1}$$

where $S(o)$ is the long wavelength limit of the liquid structure factor $S(k)$ and ρ is the number density. The second result is for the specific heat at constant volume C_v in terms of g_3 and g_4, namely

$$\begin{aligned} C_v = \tfrac{3}{2}k_B + \frac{1}{k_BT^2}\Bigg[\tfrac{1}{2}\rho\int g(r)\,\phi^2(\mathrm{r})\,d\mathbf{r} + \rho^2\int g_3(\mathbf{rs})\phi\,(r)\,\phi(s)\,d\mathbf{r}\,ds \\ + \tfrac{1}{4}\rho^3\int\Big\{g_4(\mathbf{rst}) - g(r)\,g(\,|\,\mathbf{t}-\mathbf{s}\,|\,)\Big\}\,\phi(r)\,\phi(\,|\,\mathbf{t}-\mathbf{s}\,|\,)\,d\mathbf{r}\,ds\,dt \\ - \frac{[\rho\int g(r)\,\phi(r)\,d\mathbf{r} + \tfrac{1}{2}\rho^2\int\{g_3(\mathbf{rs}) - g(r)\}\,\phi(\mathrm{r})\,d\mathbf{r}\,ds]^2}{S(o)} \end{aligned} \tag{2.2}$$

We shall also develop a method for calculating $C_p - C_v$ from the usual thermodynamic relation

$$C_p - C_v = -\frac{T}{N}\left(\frac{\partial P}{\partial T}\right)_V^2\left(\frac{\partial V}{\partial P}\right)_T \tag{2.3}$$

This can be rewritten in the form

$$C_p - C_v = \frac{1}{\rho^2 k_B}\left(\frac{\partial P}{\partial T}\right)_V^2 \left[-\rho k_B T \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\right] \tag{2.4}$$

and using the well known result

$$S(o) = -\rho k_B T \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{2.5}$$

and the thermodynamic equation (Zemansky, 1951)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P, \tag{2.6}$$

we find

$$C_p - C_v = S(o)\left\{\frac{P}{\rho k_B T} + \frac{1}{\rho k_B T}\left(\frac{\partial U}{\partial V}\right)_T\right\}^2 k_B \tag{2.7}$$

where P is the pressure and U is the internal energy.‡

A useful form of $(\partial U/\partial V)_T$ may be obtained from liquid state theory when the pair potential $\phi(r)$ is independent of density:

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{\rho^2}{2}\int \frac{\partial}{\partial \rho}\Big[\rho g(r)\Big]\phi(r)\,d\mathbf{r}. \tag{2.8}$$

Using the relation of Schofield for the density dependence of the radial distribution function in terms of g_3 we obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{\rho^2}{2S(o)}\left[\int g(r)\,\phi(r)\,d\mathbf{r} + \rho\int \{g_3(\mathbf{rs}) - g(r)\,g(s)\}\,\phi(r)\,d\mathbf{r}\,d\mathbf{s}\right]. \tag{2.9}$$

Combining Eqs. (2.7) and (2.9) we can write

$$\frac{C_p - C_v}{S(0)} = \left\{1 - \frac{2\pi\rho}{3k_B T}\int g(r)\,r^3\frac{\partial\phi}{\partial r}\,dr - \frac{\rho}{2k_B T\,S(o)}\right.$$
$$\left.\times\left[\int g(r)\,\phi(r)\,d\mathbf{r} + \rho\int\{g_3(\mathbf{rs}) - g(r)\,g(s)\}\,\phi(r)\,d\mathbf{r}\,d\mathbf{s}\right]\right\}, \tag{2.10}$$

‡ It is perhaps worth mentioning that (2.7) yields an exact result for hard spheres when we put $(\partial U/\partial V)_T = 0$. Estimating the pressure P from machine calculations (Alder and Wainwright, 1960) and $S(o)$ from the Percus-Yevick solution for hard spheres at a density appropriate to fluid argon near the melting point leads to a value for γ of 2.6. Though this is quite near to the measured value of 2.2 for argon, this seems largely accidental for the term $(\partial U/\partial V)_T$ in (2.7) is really the dominant one.

where we have employed the usual expression for the pressure P from liquid state theory.

3. Numerical Estimates of Specific Heats for Argon near Triple Point

In writing down the inequality (2.1), it has, of course, been assumed that the total potential energy Φ of the fluid can be decomposed into pair potentials $\phi(r_{ij})$ via

$$\Phi = \sum_{i<j} \phi(r_{ij}). \tag{3.1}$$

For argon, this is certainly a useful starting point, and the potential $\phi(r)$ is known to have the form shown in Fig. 1(a). For this interaction, Rahman (1964) has used the method of molecular dynamics to obtain the radial distribution function $g(r)$, which is plotted in Fig. 1(b). These results, obtained for a number density $\rho = 2.05 \times 10^{22}\ \mathrm{cm}^{-3}$ and

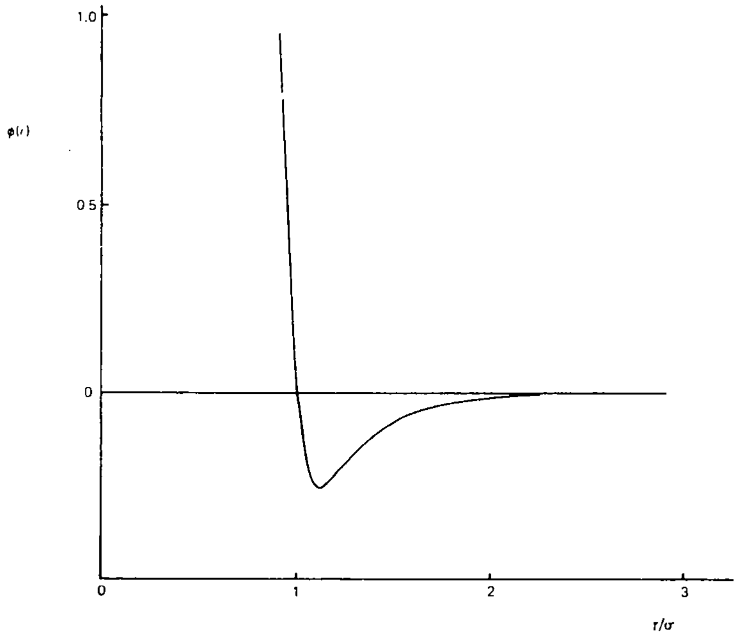

Fig. 1(a). Pair potential $\phi(r)$ for argon. Hard core diameter σ is taken as 3.4 $A°$.

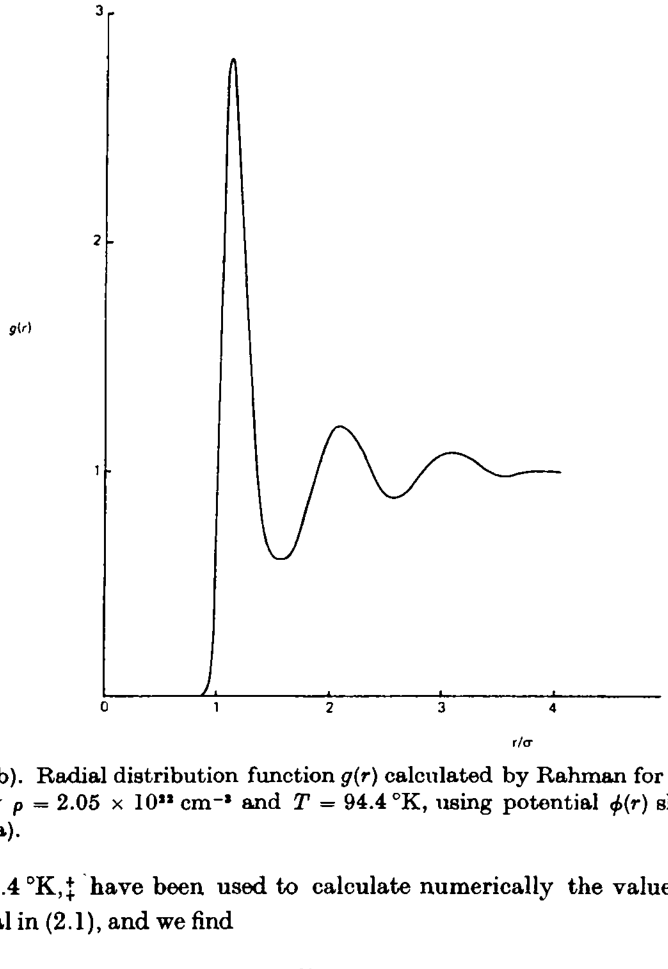

Fig. 1(b). Radial distribution function $g(r)$ calculated by Rahman for number density $\rho = 2.05 \times 10^{22}\,\mathrm{cm}^{-3}$ and $T = 94.4\,°\mathrm{K}$, using potential $\phi(r)$ shown in Fig. 1(a).

$T = 94.4\,°\mathrm{K}$,[‡] have been used to calculate numerically the value of the integral in (2.1), and we find

$$\frac{\gamma}{S(o)} \leqslant 58. \tag{3.2}$$

The calculation of $S(k)$ for small k is difficult for the small system considered by Rahman, but since his method appears to be giving an essentially exact $g(r)$ for the realistic potential shown in Fig. 1, it seems quite consistent to use the experimental value $S(o) = 0.06$ in (2.1). We then find

$$\gamma \leqslant 3.5 \pm 0.3, \tag{3.3}$$

[‡] These values are chosen because they correspond to Rahman's molecular dynamics calculations. The temperature is somewhat higher than the triple point temperature.

the error shown arising from the errors in using the graph of $g(r)$ given by Rahman.

More interesting than the numerical bound is the fact that the integrand in (2.1) is quite short-range, as shown in Fig. 2. This indicates strongly that the main contribution to γ is coming from a region inside 4A°, the atomic diameter being 3.4A°. Though a knowledge only of the upper bound (3.3) cannot be quite conclusive, the value of γ appears to be dominated by the short-range properties of $g(r)$ and $\phi(r)$. This is in marked contrast to Na, which we shall discuss below.

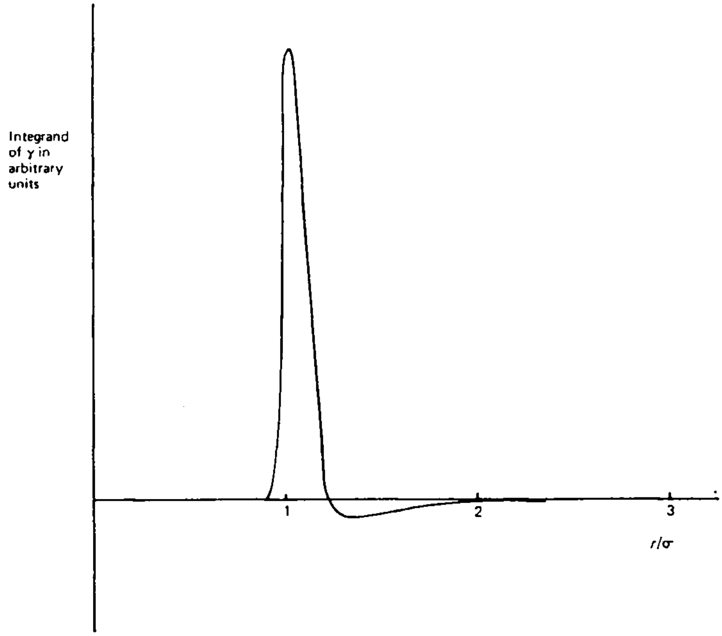

Fig. 2. Integrand of γ for argon (see Eq. (2.1)) versus distance r.

3.1. SUPERPOSITION APPROXIMATION FOR g_3

To make progress with the evaluation of $(\partial U/\partial V)_T$ in (2.9), we shall first rewrite this in a form which is similar to the term in g_3 involved in equation (2.2) for C_v. This yields

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{\rho}{2S(o)}\left[\rho\int g(r)\,\phi(r)\,d\mathbf{r}+\rho^2\int\{g_3(\mathbf{rs})-g(r)\}\,\phi(r)\,d\mathbf{r}\,d\mathbf{s}\right.$$
$$\left.-\rho^2\int g(r)\,\phi(r)\,d\mathbf{r}\int h(s)\,d\mathbf{s}\right]$$
$$= -\frac{\rho}{2S(o)}\left[2\rho\int g(r)\,\phi(r)\,d\mathbf{r}+\rho^2\int\{g_3(\mathbf{r},\mathbf{s})-g(r)\}\,\phi(r)\,d\mathbf{r}\,d\mathbf{s}\right.$$
$$\left.-S(0)\,\rho\int g(r)\,\phi(r)\,d\mathbf{r}.\right] \quad (3.4)$$

At this stage, we shall use the Kirkwood approximation for g_3, namely

$$g_3(\mathbf{rs}) \simeq g(r)\,g(s)\,g(\,|\,\mathbf{s}-\mathbf{r}\,|\,). \quad (3.5)$$

Then we may write for the term in g_3 in the brackets in (3.4)

$$\rho^2\int[g_3(\mathbf{rs})-g(\mathrm{r})]\,\phi(r)\,d\mathbf{r}\,d\mathbf{s} =$$
$$\rho^2\int g(r)[1+h(s)+h(\,|\,\mathbf{s}-\mathbf{r}\,|\,)+h(s)\,h(\,|\,\mathbf{s}-\mathbf{r}\,|\,)-1]\,\phi(r)\,d\mathbf{r}\,d\mathbf{s} \quad (3.6)$$

where $h(r) = g(r)-1$. Using the fact that

$$\rho\int h(s)\,d\mathbf{s} = S(o)-1 \quad (3.7)$$

(3.6) becomes

$$2[S(o)-1]\,\rho\int g(r)\,\phi(r)\,d\mathbf{r}+\frac{1}{8\pi^3}\int g(r)\,\phi(r)\,d\mathbf{r}\int h^2(k)\,e^{i\mathbf{k}\cdot\mathbf{r}}\,d\mathbf{k}. \quad (3.8)$$

Thus, from (3.4) we have

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{\rho}{2S(o)}\left[S(o)\,\rho\int g(r)\,\phi(r)\,d\mathbf{r}\right.$$
$$\left.+\frac{1}{8\pi^3}\int g(r)\,\phi(r)\,d\mathbf{r}\int h^2(k)\,e^{i\mathbf{k}\cdot\mathbf{r}}\,d\mathbf{k}\right]. \quad (3.9)$$

The appearance of the factor $S(o)$ in the first term in the brackets is significant in what follows. If we use Rahman's results to estimate this term, we find

$$\frac{\rho}{k_BT}\int g(r)\,\phi(r)\,d\mathbf{r} = -14.3. \quad (3.10)$$

Assuming this dominates the value of $(\partial U/\partial V)_T$, we obtain from (2.7), after noting that the pressure term is very small compared with $(\partial U/\partial V)_T$, that $C_p - C_v \sim 3k_B$, in good agreement with the measured value at the triple point of $2.8k_B$. However, when we estimate the second term in (3.9) from the results of Verlet (1968)‡ for the same density and temperature that Rahman used, it is far too large in absolute value, the second term in the square bracket being

$$-1.2k_BT.$$

Thus the superposition approximation is bad for calculating $C_p - C_v$. On the other hand, if we return to (2.9) and make the alternative assumption

$$g_3(\mathbf{rs}) - g(r)g(s) = g(r)h(|\mathbf{s}-\mathbf{r}|) \tag{3.11}$$

inside the integral in (2.9), which is equivalent to assuming in (2.8) that $\rho(\partial g/\partial \rho)$ is small compared with g, then (3.9) without the second term follows. Thus, in this particular case, (3.11) is a more useful approximation than the Kirkwood form. It is the fact that $S(o)$ cancels when we include only the first term in (3.9) that is the essential point.

This line of argument also suggests an alternative inequality for γ to that of Schofield. Dividing both sides of (2.7) by C_v we get the result

$$\gamma = 1 + \frac{S(o)}{C_v}\left\{\frac{P}{\rho k_BT} + \frac{1}{\rho k_BT}\left(\frac{\partial U}{\partial V}\right)_T\right\}^2 k_B. \tag{3.12}$$

Since C_v is always greater than $\frac{3}{2}k_B$, (3.12) can be replaced by the inequality

$$\gamma \leqslant 1 + \tfrac{2}{3}S(o)\left\{\frac{P}{\rho k_BT} + \frac{1}{\rho k_BT}\left(\frac{\partial U}{\partial V}\right)_T\right\}^2. \tag{3.13}$$

Using the estimate for $(\partial U/\partial V)_T$ based on (3.11), we find $\gamma \leqslant 3$, which is a slightly better bound than that given previously.

Finally, we have attempted to calculate C_v from (2.2). However, neglecting the term in g_4 and using the integrals recorded above plus

$$\frac{\rho}{2(k_BT)^2}\int g(r)\,\phi^2(r)\,d\mathbf{r} = 5.9$$

and

$$\frac{\rho^2}{(k_BT)^2}\int g_3(\mathbf{rs})\,\phi(r)\,\phi(s)\,d\mathbf{r}\,d\mathbf{s} = 157,$$

---

‡ Since $h(k)$ is given by Verlet, but not by Rahman.

it is clear that massive cancellation must occur between the various terms in (2.2). Therefore, this formula is very sensitive to the approximations made for the higher order correlation functions and while this might be useful later as a test of more refined theories, it is clearly not, at present, a practical way to calculate C_v.

4. Specific Heats for Liquid Sodium and Phonon Theory

However, for the liquid metals a method which closely resembles the harmonic approximation in the solid phase should be more appropriate. Such an approach has been discussed in earlier work by Eisenschitz and Wilford (1962; see also Toombs, 1965). In this work the Hamiltonian of the system is written in terms of a set of collective coordinates which are the Fourier components of the particle density, $\rho_{\mathbf{q}}$, and the conjugate momenta $b_{\mathbf{q}}$ given by $\rho_{\mathbf{q}} = \sum_j \exp(-i\mathbf{q}\cdot r_j)$ and $\mathbf{p}_j = -i\sum_{\mathbf{q}} \mathbf{q} b_{\mathbf{q}} \exp(-i\mathbf{q}\cdot\mathbf{r}_j)$ respectively. In order to maintain the correct number of degrees of freedom, the values of the wave vector $\mathbf{q}$ are restricted to the $3N$ within a sphere of radius q_c given by $q_c = (18\pi^2 N/V)^{1/3}$, N being the number of atoms and V the volume of the system.

Their result for C_v is

$$C_v = k_B\left[3 + \tfrac{1}{2}\sum_{\mathbf{q},\mathbf{l}(\mathbf{q}\neq l)} \frac{(\mathbf{q}\cdot\mathbf{l})^2}{\beta N^3 q^2 l^2 U(|\mathbf{q}-\mathbf{l}|)}\right] \tag{4.1}$$

where $U(q)$ is the Fourier component of the effective ion-ion interaction and $\beta = (k_B T)^{-1}$. The harmonic result $C_v = 3k_B$ arises within an approximation which treats the collective coordinates $\rho_{\mathbf{q}}$ as a set of independent oscillators (in the isotropic solid they vibrate harmonically with the frequency of the longitudinal normal modes), while the second term estimates the correction to this harmonic approximation due to the coupling of the oscillators. Unfortunately this term involves a knowledge of $U(q)$ which at present is somewhat uncertain. However, the theory also relates the Fourier components $U(q)$ to the structure factor of the liquid $S(q)$ and the relationship, given by Toombs, is

$$S(q) = \frac{1}{\beta N U(q)}. \tag{4.2}$$

We therefore suggest that we rewrite the expression for C_v in terms of $S(q)$ and use the experimentally determined structure factors to obtain an estimate of the size of the correction to the harmonic result. Since $S(q)$ is, by definition, positive definite, the correction always increases the value of C_v. An upper bound is immediately obtained by replacing $S(\,|\,\mathbf{q}-\mathbf{l}\,|\,)$ by its maximum value within the range $0 \leqslant q \leqslant q_c$ and hence

$$\begin{aligned} C_v &\leqslant k_B\left[3 + S_m\,\tfrac{1}{2}\sum_{\mathbf{q},\mathbf{l}} \frac{(\mathbf{q}\cdot\mathbf{l})^2}{q^2 l^2 N^2}\right] \\ &\leqslant k_B[3 + 1.5\ S_m]. \end{aligned} \tag{4.3}$$

For Na close to the melting point $(N/V) = 0.0243$ atoms Å^{-3} and $q_c = 1.63$ Å^{-1}. Using the data of Gingrich and Heaton (1961) the maximum value of $S(q)$ is its value at q_c which is approximately 0.4 so that $C_v \leqslant 3.6k_B$. This must overestimate somewhat the specific heat as given by (4.1), since over a substantial part of the range, $0 \leqslant q \leqslant q_c$, $S(q)$ is small (considerably less than 0.4) and only increases when q approaches q_c as it begins to rise towards the first peak. It seems worth noting that the connection between C_v and the structure proposed here is born out in one case where specific heat and structure data are available. C_v for K as given by Eisenschitz and Wilford is $3.62k_B$, larger than the specific heat of Na, and correspondingly the measured structure factor appears to be larger over the relevant range of q values. If the inequality above is used in this case ($q_c = 1.33$, $S_m \simeq 0.65$) we obtain the result for K that $C_v \leqslant 4$.

4.1. ESTIMATE OF RATIO OF SPECIFIC HEATS FOR MODEL OF LIQUID SODIUM

Finally we discuss the ratio of the specific heats γ for a model of liquid sodium. In the case of a liquid metal, a proper calculation of the electronic energy will eventually be required. This, at present, does not seem to be a practical approach to calculate γ, and we shall adopt as a model to simulate the properties of liquid Na, a pair potential which generates the liquid structure factor as measured by neutrons. Such a potential, due to Paskin and Rahman is shown in Fig. 3(a), together with the corresponding $g(r)$ in Fig. 3(b). The neutron structure data is also shown in curve 3 of Fig. 3(b) for comparison.

We stress that in the present model all the effects of the electrons are assumed to be built into the pair potential in Fig. 3(a). The results we obtain below suggest that correction terms to be included in the theory, when a first principles calculation is made which starts from the system of electrons and ions, are small.

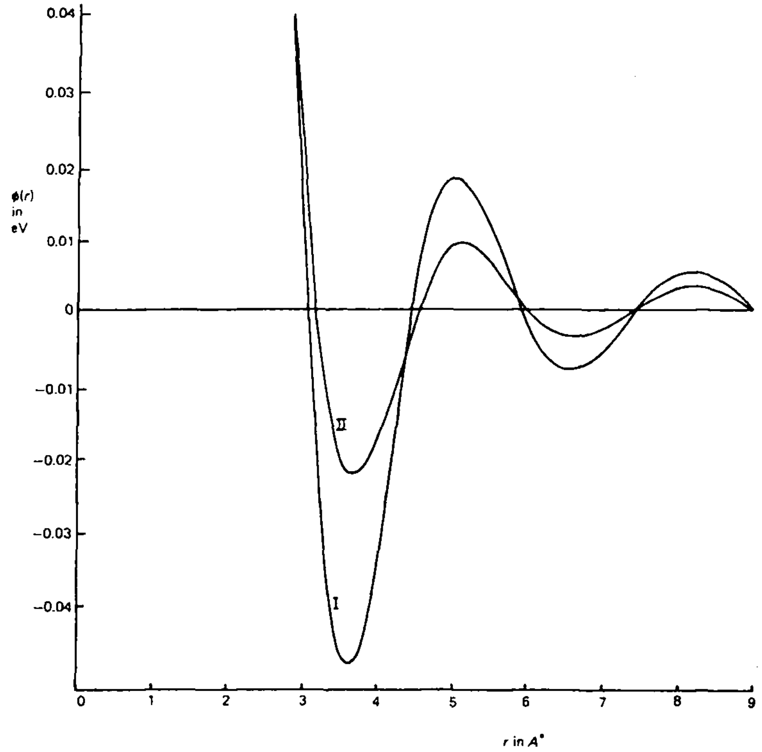

Fig. 3(a). Long-range oscillatory potentials LRO I and II used by Paskin and Rahman for liquid Na.

With the Paskin–Rahman potential of the form

$$\phi(r) = -A\left(\frac{r_0}{r}\right)^3 \cos\left\{7.81\left[\frac{r}{r_0}+\beta\right]\right\} + 0.78\exp\left(5.072 - \frac{10.786r}{r_0}\right) \qquad (4.5)$$

it is essential to include carefully an asymptotic contribution, the integrand in (2.1) stretching out to distances ~ 12 Å (cf. Fig. 4). The result we obtain is

$$\frac{\gamma}{S(o)} \leqslant 43 \qquad (4.6)$$

and using the measured value $S(o) = 0.028$ we find

$$\gamma \leqslant 1.2 \qquad (4.7)$$

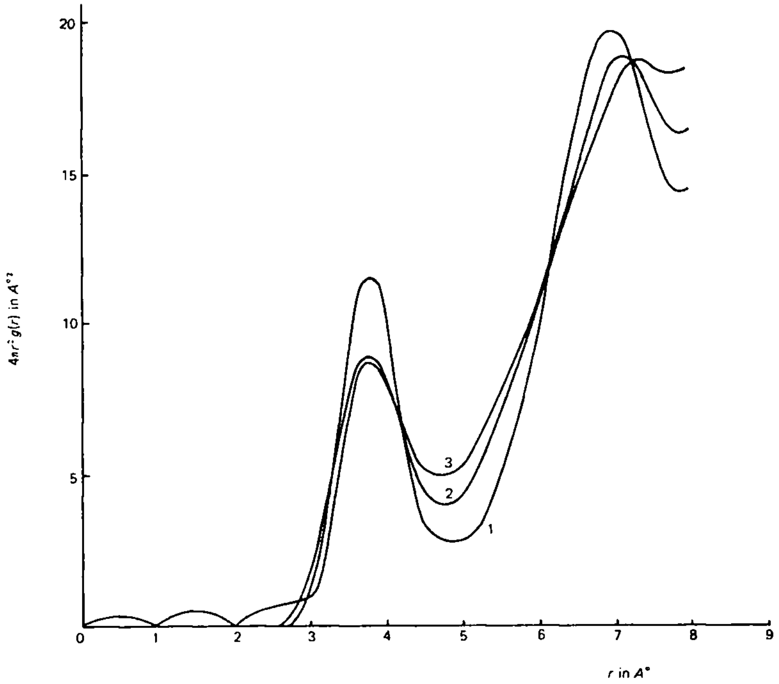

Fig. 3(b). $g(r)$'s calculated from potentials LRO I and II of Fig. 3(a) by Paskin and Rahman (curves 2 and 1 respectively). Neutron measurements of structure are shown in curve 3.

It is interesting that the inequality already allows us in this model to write $\gamma = 1.1 \pm 0.1$ which settles the matter for this potential.

However, this result is sensitive to the form of the potential, and if we use the deeper potential shown in curve 1 of Fig. 3(a) we obtain a larger value of the upper bound for γ, though still only half of the upper bound (3.3) for argon. This deeper potential is less realistic, however, being in disagreement with the measured neutron structure factor.

5. Summary

The starting point suggested by experiment for liquid metals: namely that the nature of the forces (softer cores plus long-range parts) is leading to an independent phonon picture as a useful zero order model, is confirmed by the present calculations, though more work must be done to

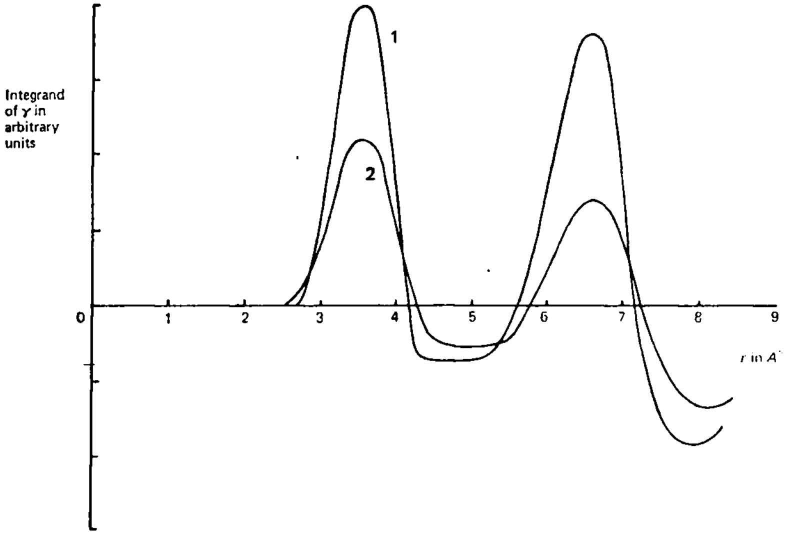

Fig. 4. Integrand of γ for sodium (see Eq. (2.1)) at melting point versus distance r. Curve 1 corresponds to $g(r)$ given in curve 1 of Fig. 3(b).

incorporate the effect of the electrons directly into the theory. The specific heat C_v is generally expected to be somewhat larger than $3k_B$ for metals.

In contrast, the value of C_v for argon, substantially less than $3k_B$, cannot possibly be obtained from such a picture, and the value of γ is dominated by the core region.

Acknowledgement

One of us (P.B.) wishes to acknowledge financial support from a Science Research Council Postgraduate Studentship, during the course of this work.

REFERENCES

Alder, B. J. and Wainwright, T. E., *J. Chem. Phys.* **33**, 1439 (1960).
Eisenschitz and Wilford, *Proc. Phys. Soc.* **80**, 1078 (1962).
Gingrich, N. S. and Heaton, L., *J. Chem. Phys.* **34**, 873 (1961).
Paskin, A. and Rahman, A., *Phys. Rev. Letters* **16**, 300 (1966).
Rahman, A., *Phys. Rev.* **136**, 405 (1964).
Schofield, P., *Proc. Phys. Soc.* **88**, 149 (1966).

Toombs, G., *Proc. Phys. Soc.* **86**, 273 (1965).
Verlet, L., *Phys. Rev.* **165**, 201 (1968).
Zemansky, M. W., *Heat and Thermodynamics*, McGraw Hill, New York, 3rd Edition, p. 251 (1951).