Dynamical structure of undercooled liquid potassium

1998 J. Phys.: Condens. Matter 10 533

(http://iopscience.iop.org/0953-8984/10/3/007)

J. Phys.: Condens. Matter **10** (1998) 533–544. Printed in the UK PII: S0953-8984(98)87166-X

Dynamical structure of undercooled liquid potassium

O Akinlade† and B R Ijaduola

International Centre for Theoretical Physics (ICTP), Trieste, Italy, and Department of Physics, University of Agriculture, Abeokuta, Nigeria

Received 28 August 1997

Abstract. We perform a quite detailed theoretical investigation of the temperature dependence of the static and dynamical structure factors for undercooled potassium. The static structure factors are calculated from the hybridized mean-spherical approximation (HMSA) form of the integral approximation using pair potentials constructed from a non-local pseudopotential and the dynamical structure factors $S(q,\omega)$ within the viscoelastic approximation. We show that the characteristic features of the static structure factors as obtained from molecular dynamics simulation are reproduced within the present framework and that, essentially, the general features of $S(q,\omega)$ at the melting points are still preserved in the undercooled region.

1. Introduction

The study of the static and dynamical structure of liquid metals has attracted the attention of a considerable number of researchers over a long period of time [1–3]; the result has been considerable advancement in both the theoretical and experimental methods required for such investigations. From the experimental side, technological advancement has made it possible to study liquid-metallic systems under conditions of high temperature and pressure, especially expanded systems [4]. The undercooled region has not been studied so much, although its study could offer more insight into the mechanism of metallic glass formation.

From the theoretical perspective, static structure factors have been studied with increasingly elegant techniques of liquid-state theory such as computer simulation [5, 6], integral equations [7, 8] and perturbation calculations [9]. The main result has been that with the advance in the level of sophistication involved in the theory, the methods have tended to give excellent results for static structure. The major limitation has always been as regards how well the pseudopotential used describes the electron–ion interaction via the pair potential for the system being studied.

In quite recent times, Lai and co-workers [5, 6] have made various attempts using molecular dynamics (MD) and Monte Carlo (MC) simulations to study the undercooled region for liquid Na and K using pair potentials obtained from the generalized non-local pseudopotential of Li *et al* [10]. One of the major points elucidated by Lai *et al* [5, 6] in their papers is a recipe for determining the variation of the atomic volume Ω with temperature; this is useful since Ω is usually obtainable only from experiment. It is noteworthy that Ω is an important parameter for determining reliable interatomic potentials.

Motivated by the availability of Ω versus T curves for liquid K in the undercooled region [6] and also—very newly—data on the dynamical structure factors of K [11, 12], we

---

† Regular Associate of ICTP.

0953-8984/98/030533+12$19.50

present in this paper preliminary results for the static structure factor $S(q)$ and the dynamical structure factor $S(q,\omega)$ for K in the undercooled region.

The static structural properties $S(q)$ and the pair distribution function $g(r)$ used in the present calculations are obtained from the solution to the HMSA integral equation of Zerah and Hansen [13] using the same generalized non-local model potential (GNMP) as was used in the calculations of Lai *et al* [6]. This makes it possible for us to make a direct comparison between the results for static properties obtained using the HMSA and those from computer simulations.

The main aim of this paper is thus to present theoretical results for the liquid dynamics of undercooled K, from hydrodynamic through viscoelastic to free-particle motion.

The present paper is organized as follows. In section 2, we present the relevant formulae required for the present calculations. In section 3, we discuss the computed values of the static and dynamical structure factors as well as the longitudinal current fluctuations. We end the paper with a brief summary of our conclusions.

2. Theory

2.1. Pair potentials

Given a system of particles in a volume Ω and at a given density $\rho = N/\Omega$ assumed to be interacting via a pairwise potential $\phi(r)$, the pair potential is constructed using the GNMP of Li *et al* [10] as

$$\phi(r) = \frac{Z_{eff}^2}{r}\left[1 - \frac{2}{\pi}\int_0^\infty F_N(q)\frac{\sin qr}{q}\,\mathrm{d}q\right] \tag{1}$$

where $F_N(q)$ is the normalized energy–wavenumber characteristic and $Z_{eff}^2 = Z^2 - \rho_d^2$, Z being the valence and ρ_d the depletion charge. The calculation of $F_N(q)$ involves a local field factor and, for this, we use the Ichimaru–Utsumi [14] form.

2.2. Integral equation theory

The pair distribution function $g(r)$ used in the present calculations is obtained from that proposed by Zerah and Hansen [13] as an extension of the Rogers–Young approximation [15] to deal with attractive potentials. It is determined from the solution of the Ornstein–Zernicke (OZ) equations

$$h(r) = c(r) + \rho\int c(r')h(|\boldsymbol{r} - \boldsymbol{r}'|)\,\mathrm{d}\boldsymbol{r}' \tag{2}$$

and reads

$$g(r) = \exp[-\beta\phi_r(r)]\left(1 + \frac{\exp\{f(r)[h(r) - c(r) - \beta\phi_a(r)]\} - 1}{f(r)}\right) \tag{3}$$

where ρ is the number density, $\beta = (k_BT)^{-1}$ is the inverse temperature in units of the Boltzmann constant, $h(r) = g(r) - 1$ and $c(r)$ is the direct correlation function. $\phi_a(r)$ and $\phi_r(r)$ are the attractive and repulsive parts of the pair potential. In equation (3), $f(r) = 1 - \exp(-\alpha r)$ is the mixing function and it smoothly interpolates between the soft mean-spherical approximation (SMSA) at $\alpha = 0$ and the hypernetted-chain (HNC) closure at large values of α. The mixing parameter α is used to impose thermodynamic self-consistency of the viral and fluctuation routes to the equation of state. For a practical determination of α, we follow the suggestion of reference [13], which is that α is assumed to be locally constant with respect to density when taking the isothermal density derivative of the viral pressure. The numerical derivative is then equated to the isothermal compressibility as obtained from the fluctuation-dissipation theorem.

This closure called the HMSA was solved using the Newton–Raphson numerical algorithm designed by Abernethy and Gillan [16, 17] using a mesh with 2049 points and a grid size $\Delta r = 0.025a$, where $a = (3/4\pi\rho)^{1/3}$.

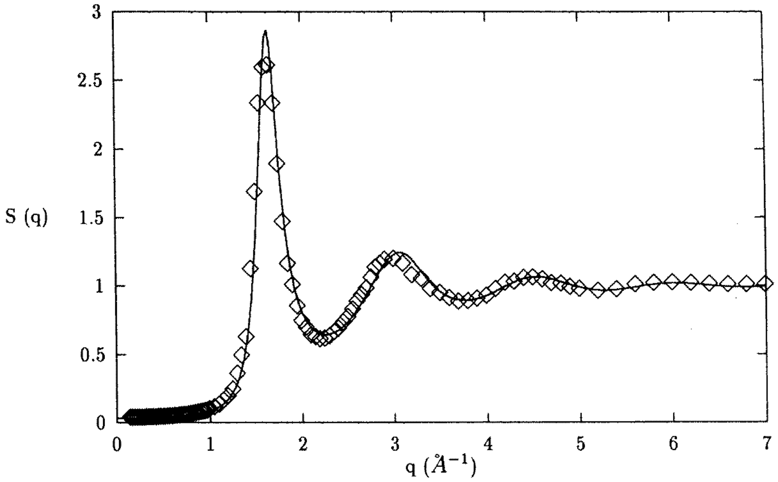


Figure 1. The static structure factor $S(q)$ for K at 343 K; (◇) experimental results from [22]) and (——) theoretical values.

2.3. The dynamical structure factor obtained from the viscoelastic approximation

In the viscoelastic approximation, the dynamical structure factor $S(q, \omega)$ is given by the expression [18]

$$S(q,\omega) = \frac{1}{\pi}\frac{\tau(q)\omega_0^2(q)[\omega_l^2(q) - \omega_0^2(q)/S(q)]}{[\omega\tau(q)\{\omega^2 - \omega_l^2(q)\}^2 + [\omega^2 - \omega_0^2(q)/S(q)]^2]} \tag{4}$$

where

$$\omega_0^2(q) = \int_{-\infty}^{\infty} \omega^2 S(q,\omega)\,\mathrm{d}\omega = V_{th}^2 q^2 \tag{5}$$

and $\tau(q)$ is a relaxation time, given in the approximation of Lovesey [19] by

$$\tau(q) = \frac{\sqrt{\pi}}{2}[\omega_l^2(q) - \omega_0^2(q)/S(q)]^{-1/2}. \tag{6}$$

$V_{th} = \sqrt{K_B T/M}$ is the thermal velocity and M is the mass of the ions.

$$\omega_l^2 = 3\omega_0^2 + \omega_E^2\left[1 - \frac{3\sin q\sigma}{q\sigma} - \frac{6\cos q\sigma}{(q\sigma)^2} + \frac{6\sin q\sigma}{(q\sigma)^3}\right] \tag{7}$$

where ω_E is the Einstein frequency, and is given by

$$\omega_E = \left[\frac{4\pi\rho}{3M}\int_0^{\infty} r^2 g(r)\frac{\mathrm{d}^2\phi(r)}{\mathrm{d}r^2}\,\mathrm{d}r\right]^{1/2} \tag{8}$$

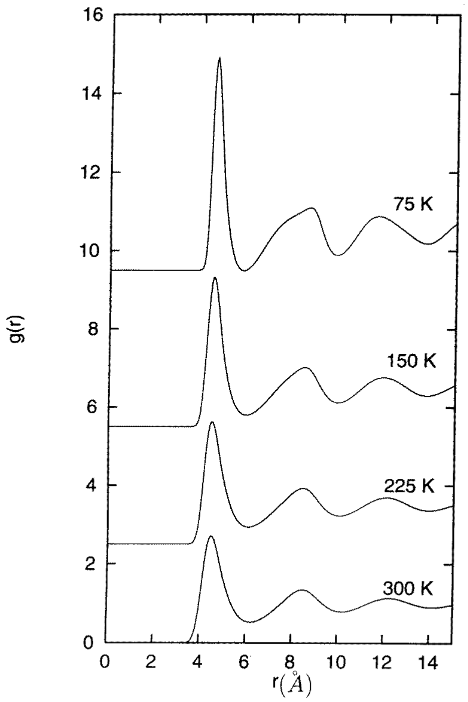


Figure 2. The temperature variation of the pair distribution function $g(r)$ for undercooled K at the temperatures indicated on the figure.

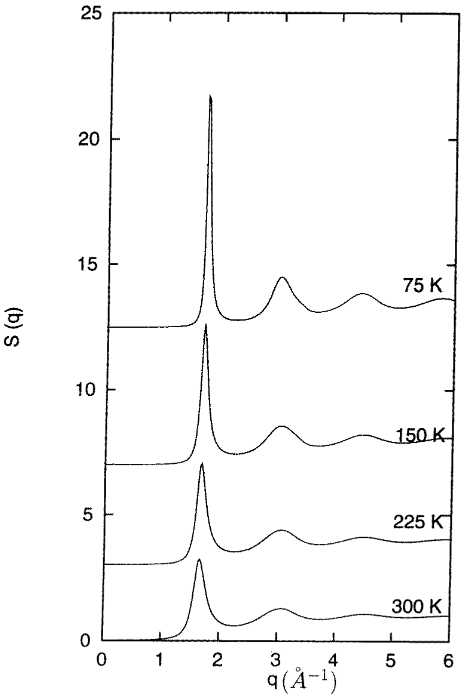


Figure 3. The static structure factor $S(q)$ for undercooled K at the temperatures indicated on the graphs.

with σ being the value of r at which $g(r)$ is a maximum. From the dynamic structure factor, we calculated the longitudinal current correlation function $J_l(q, \omega)$ through the equation

$$J_l(q, \omega) = \frac{\omega^2}{q^2} S(q, \omega). \tag{9}$$

3. Results and discussion

3.1. The static structure factor S(q)

Using the HMSA integral equations presented in section 2.2, we investigated the variation of $S(q)$ with temperature for five values of the temperature varying from 343 K (the melting point of K, and quite close to the value 340 K for which experimental results for dynamic properties are available [11, 12]) and 75 K which was about the lowest temperature at which we could obtain thermodynamic self-consistency (TSC) within our integral equation closure.

The atomic volume at 343 K was taken from [20] while those for other temperatures were taken from the estimates derived by Lai *et al* [6] on the basis of their MD simulations.

As for the practical implementation of the HMSA for the present calculations, the most important observation is that, with the decrease in temperature and atomic volume, it takes more computational time to obtain the consistency parameter α. We infer that this could be due to the possibility that, at such low temperatures, we are getting close to some sort of glass transition point. This behaviour is similar to that obtained using the modified

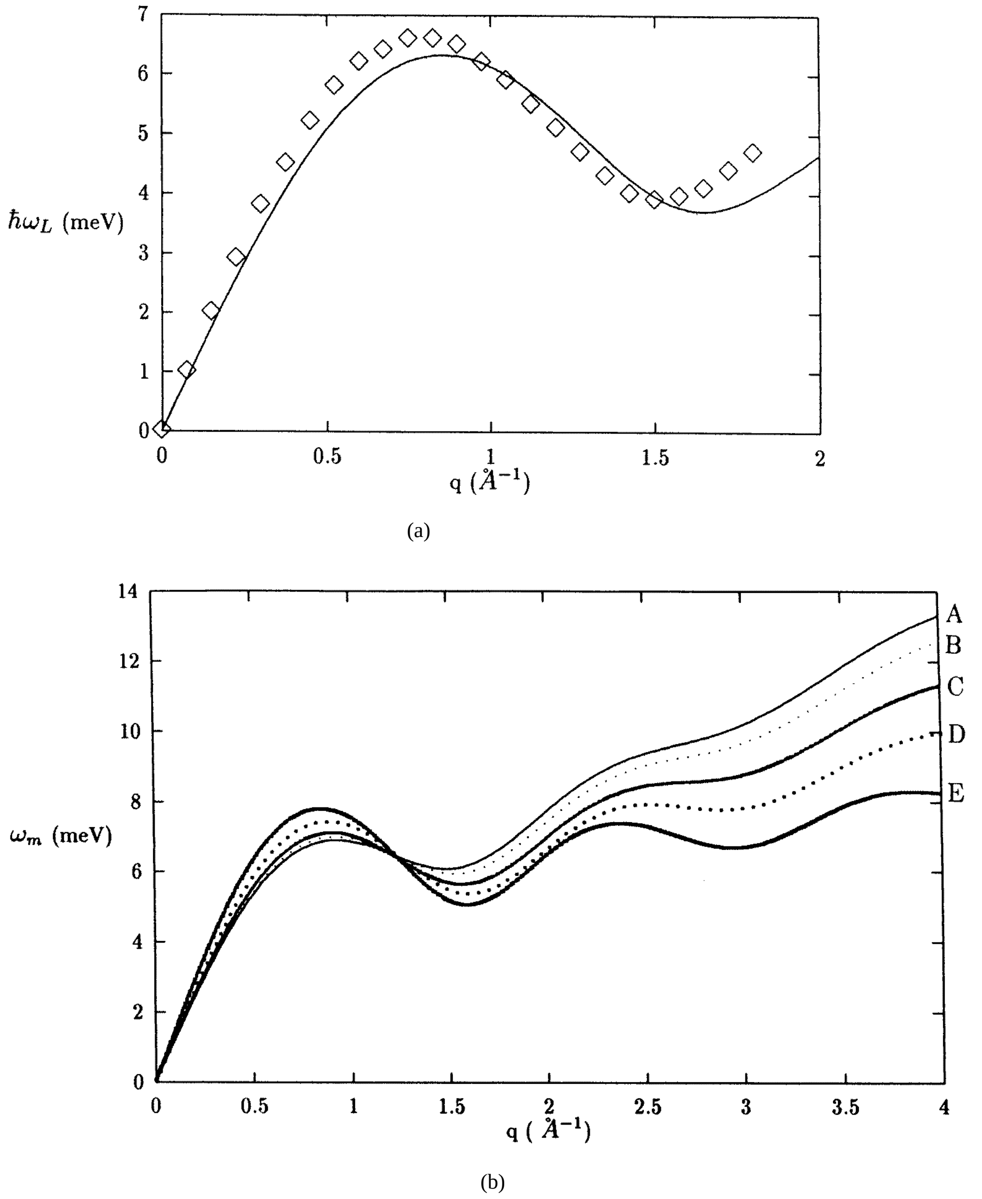


Figure 4. (a) Dispersion curves of the collective modes in potassium at 343 K. (b) The dispersion relation $\omega_m(q)$ for potassium as obtained from the maximum of the longitudinal current-density correlation function, at (A) 343 K, (B) 300 K, (C) 225 K, (D) 150 K and (E) 75 K.

hypernetted-chain closure (MHNC) [21] at temperatures very close to the freezing points for dense fluids. Moreover, the calculations had to be terminated at a temperature of 75 K because, for temperatures a little below this value, the calculations tend to the SMSA (i.e. the $\alpha = 0$) limit of the HMSA, which is definitely not thermodynamically self-consistent.

From our results for liquid K at the melting point, which are given in figure 1, we observe that the HMSA coupled with pair potentials calculated from the GNMP gives a

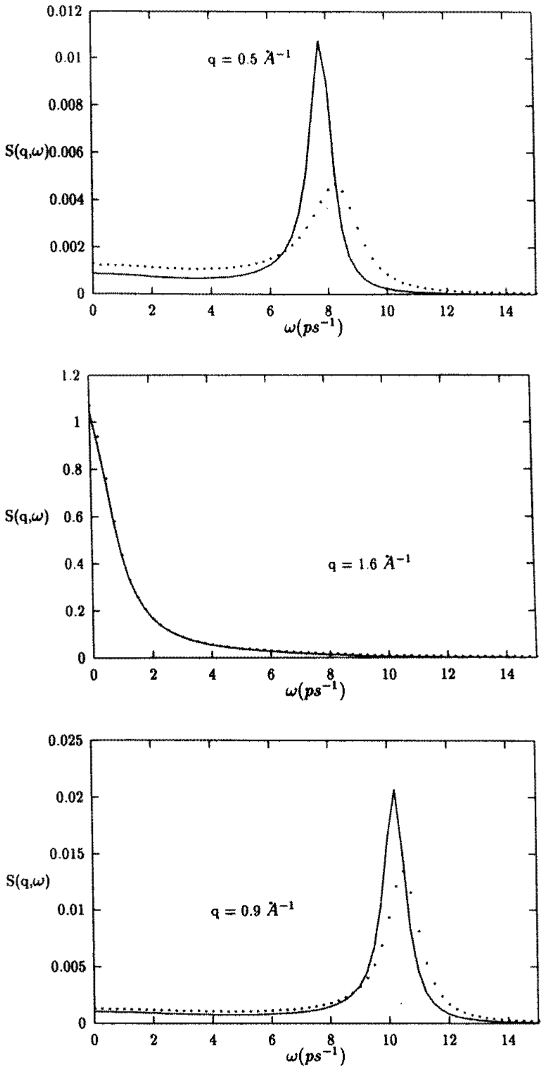


Figure 5. The variation of the dynamical structure factor $S(q, \omega)$ (ps) with ω (ps^{-1}) at different values of q; (——) theoretical values, (······) experiment.

very good description of $S(q)$ for liquid K. Apart from a slight overestimation of the first peak height, the oscillations in $S(q)$ are duplicated well by our calculations. This deduction, coupled with previous calculations in [7] for liquid potassium at temperatures higher than the melting point, gives us enough confidence to proceed with the calculations for lower temperatures. In this paper, the experimental value of $S(q)$ at the melting point (figure 1) has been taken from [22].

As to the temperature dependence of $g(r)$ in the undercooled region, there are no experimental data available to compare with; however, we observe that the general effects of a reduction in temperature such as a flattening of the second maxima in $g(r)$ with temperature and enhanced oscillations at large r are reasonably well indicated by our calculations, in agreement with computer simulation [6]. However, as a result of not

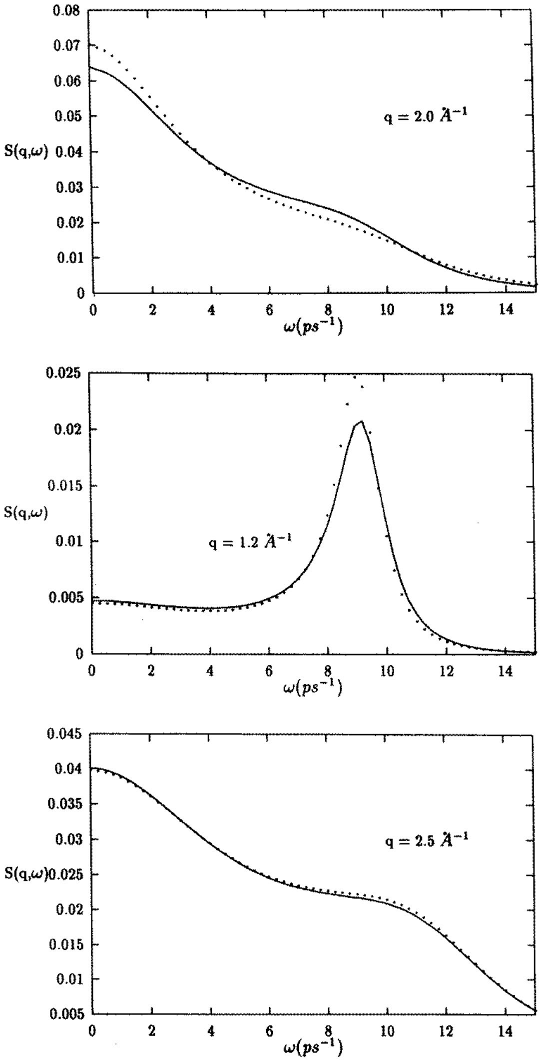


Figure 5. (Continued)

achieving TSC at low enough temperatures, our calculations do not show very distinctly the development of a twin peak structure which Lai *et al* [6] obtained at a temperature of 66 K for undercooled potassium using computer simulation. A perusal of our calculated $g(r)$ at 75 K in figure 2 shows features for the second maximum which are at variance with those for higher temperature and could be the precursors of the splitting. We also illustrate in figure 3 the resulting $S(q)$ for the same temperatures as the $g(r)$ curves are presented for. One observes a rapid enhancement in the peak heights due to increased correlations, and a narrowing of the first peak in $S(q)$ with decrease in temperature. However, the enhancements in the heights of the other peaks are not as significant as what obtains for the first one.

Using the static structure obtained from the HMSA integral equations with a large degree of confidence, we then proceeded to compute the dynamical structure factors.

Table 1. The atomic volume (Ω), σ, thermal velocity V_{th} and Einstein frequencies ω_E obtained for K at the temperatures listed in the table.

System	Temperature (K)	Ω (au)	σ (Å)	V_{th} (10^4 m s^{-1})	ω_E (meV)
K	343	530.17	4.52	2.7002	4.789
	300	513.75	4.48	2.5084	4.927
	225	495.00	4.47	2.1773	5.105
	150	480.00	4.50	1.7797	5.454
	75	470.00	4.60	1.2457	5.823

3.2. The dynamical structure factors $S(q, \omega)$

In order to calculate the dynamical properties, we proceed in our calculations as follows. Using the $S(q)$ and $g(r)$ obtained from the HMSA, we obtain σ (in equation (7)) as the value of r for which $g(r)$ is a maximum. The Einstein frequency ω_E is obtained from equation (8) using the second derivative of the pair potential obtained in equation (1). The calculations were done in a fully consistent way in the sense that all of the parameters are obtained from the same GNMP potential and there is no fitting of any form. The implication of this is that one expects the results to be as good as the GNMP is at modelling the interionic interactions within the systems. One might note that the potential is one which incorporates higher (i.e. above second-order) pseudopotential perturbation corrections. A table of the relevant parameters used for the present calculations is given in table 1.

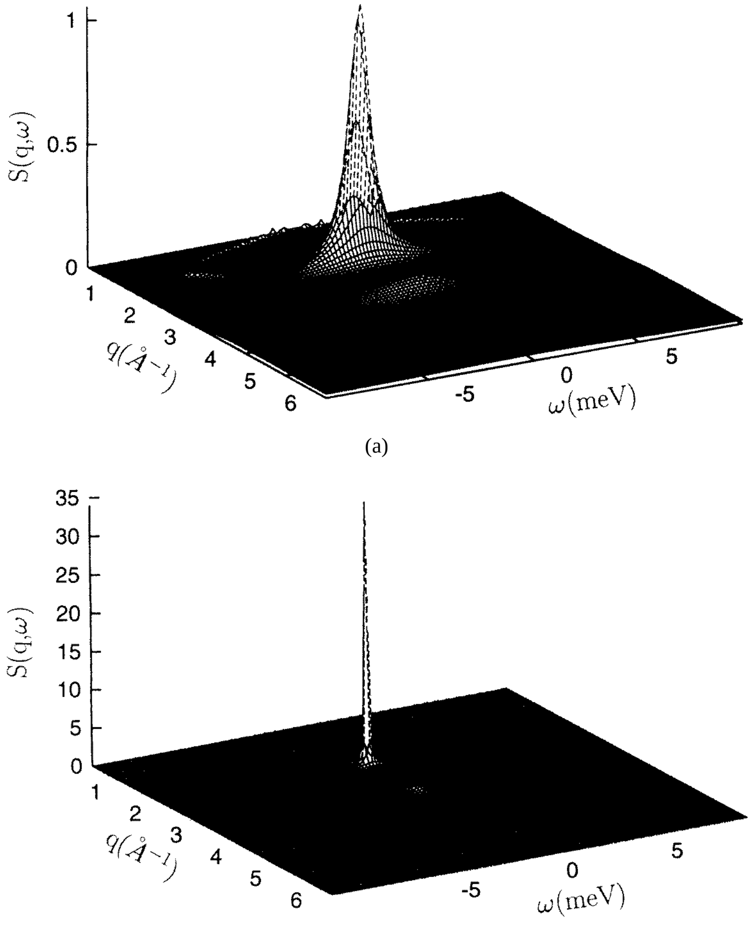
We start by comparing our results for the dispersion curves at 343 K with the limited experimental data given in [11, 12]. The results are presented in figure 4. A perusal of the curves shows that the agreement between our calculated results (without any fitting) and the experimental results is quite good. In order to obtain additional experimental points in the diagram, what we did was to use the value of ω_E given in the papers and experimental values of $S(q)$ to obtain the dispersion curves within viscoelastic theory. The dispersion curves obtained using this technique gave values which were in excellent agreement with experiments. The same procedure was used to obtain $S(q, \omega)$, which we compared with our calculations for various values of q (between 0.5 and 2.5 Å^{-1}) as indicated in the graphs in figure 5.

From a comparison of experiment and theory, it is quite clear that our calculated results are reasonably good. The general features of the dynamic structure factor are quite similar to what is observed experimentally for Cs [23] and Rb [24], namely that there are collective excitations in liquid K at the melting point for $q \leqslant 1.6$ Å^{-1}. The peak disappears at about $q = 1.6$ Å^{-1} but reappears at $q = 2.0$ Å^{-1} with a shoulder. This effect could be related to the possible existence of a dispersion gap in the range $1.6 \leqslant q \leqslant 2.0$ Å^{-1}.

In order to study the effect of a reduction in temperature on $S(q, \omega)$ over a large range of q and ω, we present in figure 6 a three-dimensional plot of the dynamical structure factor at the melting point (343 K) and that for undercooled potassium at 75 K.

We make the following observations from the figures. At this point, one should note that there are no significant deviations from the trend presented below in our calculations during the gradual reduction in temperature from 343 K to 75 K.

Firstly, we observe that $S(q, \omega = 0)$ has a temperature dependence of the peak heights that could easily be related to the variation in the peak height of $S(q)$. In addition we note that for all of the temperatures investigated, our calculations indicate that the width of the first diffraction peak (which occurs typically close to $q = 2.0$ Å^{-1}) in the spectrum of $S(q, \omega)$ narrows considerably; this effect is the well known de Gennes narrowing [26].



(a)

(b)

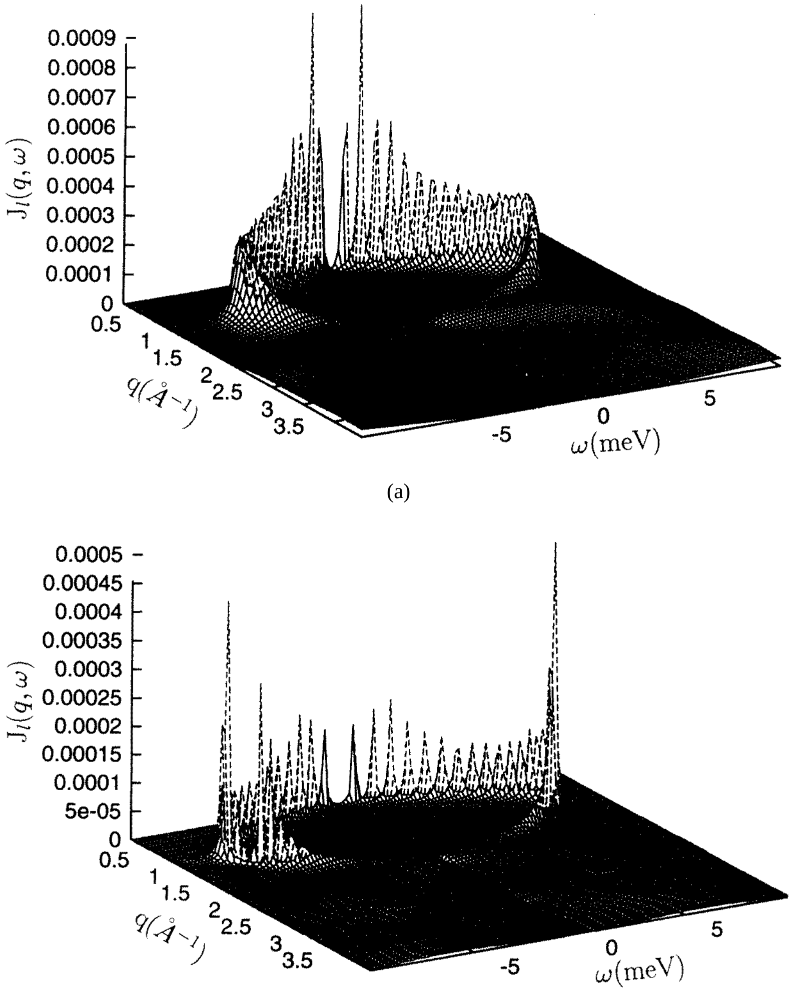
Figure 6. Three-dimensional plots of the dynamical structure factor $S(q,\omega)$ (ps) versus ω (meV) and q (Å^{-1}), (a) at 343 K and (b) at 75 K.

An obvious point is that there are collective excitations propagating in liquid K even in the undercooled region; this is evident from the peaks in $S(q,\omega)$ both in planes of constant q and those of constant ω. Lastly, the calculations indicate that within a certain range, e.g. $2.25 \leqslant q \leqslant 3.5$ Å^{-1}, $S(q,\omega)$ is structureless. For more sophisticated calculations using mode-coupling theory, this effect lends credence to the use of two-relaxation-time memory functions for dense fluids [25].

Our calculations indicate that in general, apart from enhancements in peak heights, there are no major structural changes in dynamical structure that occur in taking potassium from its melting point to quite low temperatures within the undercooled region.

3.3. The longitudinal current correlation function $J_l(q,\omega)$

The last quantity that we investigated was the longitudinal current correlation function $J_l(q,\omega)$. Firstly, we present in figure 4(b) the dispersion relation $\omega_m(q)$ obtained from the maximum of $J_l(q,\omega)$. It is observed to show the following interesting features.



(a)

(b)

Figure 7. Three-dimensional plots of the spectral function $J_l(q,\omega)$ of the longitudinal current correlation function for liquid K at (a) 343 K and (b) 75 K.

With decrease in temperature, the first peak in $\omega_m(q)$ shows an increase which, apart from its magnitude, is typical of the effect of reduced temperature on $S(q)$ in the low-q region. Secondly, $\omega_m(q)$ has a phonon-like mode for small q, a peak at intermediate q-values and a local minimum at the position corresponding to the location of the maximum in $S(q)$; in addition, one observes that the lowest first minimum occurs for the lowest temperature. Furthermore, one notes that, for large q-values, there is an increase in $\omega_m(q)$ which is proportional to $\sqrt{T}$ and obviously comes from the dependence of $\omega_0(q)$ on $\sqrt{T}$ via the thermal velocity V_{th}.

We present in figures 7(a) and 7(b) three-dimensional plots of $J_l(q,\omega)$ as functions of ω and q for liquid potassium at the melting point and at $T = 75$ K for the undercooled liquid.

From a perusal of the two figures, we observe that $J_l(q,\omega)$ has a maximum at a certain frequency as determined from equation (9). Its essential feature at the melting point is that, at low energies, there is a sharp sound peak, split by electronic effects. At higher energies, the two sub-peaks are observed to merge gradually into a broader peak that shifts to smaller wavenumbers and meets the sound-wave peaks at the highest frequencies.

We note that the longitudinal current correlation function, has more changes in its structural features than are observed for the dynamical structure. In particular, one observes that, with increase in temperature, there is a gradual change in gross features such that for the lowest value of temperature at which our calculations were performed (figure 7(b)), one observes that the sound peaks have drifted a little to higher frequencies; their magnitudes are also reduced by a factor of 2. Moreover one also observes what looks like a reduction in the extent of the sound peaks.

4. Conclusion

In the present paper, we have presented preliminary (due to the limited validity of the viscoelastic approximation) results for the static and dynamical properties of undercooled liquid potassium. A summary of our main deductions is as follows.

(i) With decreasing temperature, there is a pronounced enhancement in the magnitude of the peaks of $S(q)$; this effect is more significant for the first peaks than subsequent ones.

(ii) There exist collective excitations in liquid K, even in the undercooled region where they are in fact more pronounced.

(iii) A reduction in temperature has a more noticeable effect on the longitudinal current correlations than what obtains for dynamical structure factors.

(iv) As for $S(q, \omega)$, the gross features at the melting point are still preserved in the undercooled region.

Acknowledgments

This work was done within the framework of the Associateship Scheme of the International Centre for Theoretical Physics, Trieste, Italy. Financial support from the Swedish International Development Cooperation Agency is acknowledged.

References

[1] Copley J R D and Lovesey S W 1975 *Rep. Prog. Phys.* **38** 461
[2] Chushak Y, Hafner J and Kahl G 1995 *Phys. Chem. Liq.* **29** 159
[3] Sharma R K and Tankeshwar K 1997 *Phys. Rev.* E **55** 564
[4] Pilgrim C, Winter R and Hensel F 1993 *J. Phys.: Condens. Matter* **5** B183
[5] Lai S K and Chen H C 1993 *J. Phys.: Condens. Matter* **5** 4325
[6] Lai S K, Chou M H and Chen H C 1993 *Phys. Rev.* E **48** 214
[7] Lai S K, Li W and Tosi M P 1990 *Phys. Rev.* A **42** 7289
[8] Matsuda J, Mori H, Hoshino K and Watabe M 1991 *J. Phys.: Condens. Matter* **3** 827
[9] Badirkhan Z, Akinlade O, Pastore G and Tosi M P 1992 *J. Phys.: Condens. Matter* **4** 6173
[10] Li D H, Li X R and Wang S 1986 *J. Phys. F: Met. Phys.* **16** 309
[11] Arkady G N, Vadim V S, Alexander L S, Rena M Y and Timur R Y 1996 *Physica* B **228** 312
[12] Novikov A G, Savostin V V, Shimkevich A L and Zaezjev M V 1997 *Physica* B **234–236** 359
[13] Zerah G and Hansen J-P 1986 *J. Chem. Phys.* **84** 2336
[14] Ichimaru S and Utsumi K 1981 *Phys. Rev.* B **24** 7385
[15] Rogers F J and Young D A 1984 *Phys. Rev.* A **30** 999
[16] Gillan M J 1979 *Mol. Phys.* **38** 1781
[17] Abernethy G M and Gillan M J 1980 *Mol. Phys.* **39** 839

[18] Hansen J-P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)
[19] Lovesey S W 1971 *J. Phys. C: Solid State Phys.* **4** 3057
[20] Waseda W 1980 *The Structure of Non-Crystalline Materials* (New York: McGraw-Hill)
[21] Rosenfeld Y and Ashcroft N W 1979 *Phys. Rev.* A **20** 1208
[22] van der Lugt W and Alblas B P 1985 *Handbook of Thermodynamics and Transport Properties of Liquid Metals* ed R W Ohse (New York: McGraw-Hill)
[23] Bodensteiner T, Morke C, Glaser W and Dorner B 1992 *Phys. Rev.* A **45** 5709
[24] Copley J R D and Rowe J M 1974 *Phys. Rev. Lett.* **32** 49
Copley J R D and Rowe J M 1976 *Phys. Rev.* A **14** 408
[25] Kathol P K, Bansal R and Pathak K N 1976 *Phys. Rev.* A **14** 408
[26] de Gennes P-G 1959 *Physica* **25** 825