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Temperature dependence of mode-coupling effects in liquid sodium

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For small wave numbers, the half-width and the maximum value of the incoherent scattering function obtained from neutron scattering experiments on liquid sodium at 403, 602, and 803 K approach their hydrodynamic limits in a manner as predicted by the mode-coupling theory.

It has been shown recently[1] for hydrogen at a pressure $p=730$ bars and a temperature $T=120$ K that the dependence on frequency ω of the incoherent scattering function $S_s(k,\omega)$ obtained from neutron scattering experiments is well described by the predictions of the mode-coupling theory[2–4] for wave numbers k as high as about 1 Å^{-1}. This is remarkable because the theory was thought to be restricted to "small" wave numbers $k<k_0$ with k_0 of the order of the inverse range of the intermolecular potential in the liquid. However, the actual range of validity of the limiting expressions is not known *a priori*. Thus in Ref. 1 experimental evidence was obtained for the validity of the mode-coupling theory[5,6] for values of k large enough to be accessible in present neutron scattering experiments.

Here we consider the half-width $\omega_H^s(k)$ and the maximum value $S_s(k,0)$ of $S_s(k,\omega)$ obtained in the recent neutron scattering experiments by Gläser and Morkel[7,8] on liquid sodium at saturated vapor pressures and $T=403$, 602, and 803 K. In this paper we show that the considerable differences observed in $\omega_H^s(k)$ and $S_s(k,0)$ for small k at the three temperatures can be understood on the basis of mode-coupling theory.

According to the mode-coupling theory, $S_s(k,\omega)$ of a monoatomic classical fluid in equilibrium is for small k given by[2–4]

$$S_s(k,\omega)=\frac{1}{\pi}\frac{Dk^2}{\omega^2+(Dk^2)^2}+\frac{1}{\pi}\frac{1}{Dkk^*}\times\mathrm{Re}\,G\left[\frac{i\omega+Dk^2}{\delta Dk^2}\right]+O(k^{-1/2}f(\omega/k^2))\;, \tag{1}$$

where D is the coefficient of self-diffusion, $k^*=16\pi\beta mnD^2$ with $\beta=(k_BT)^{-1}$, k_B Boltzmann's constant, m the particle mass, n the number density, $\delta=D/(D+\nu)$ with $\nu=\eta/(mn)$ the kinematic viscosity, η the shear viscosity, and the complex function $G(z)$ is

$$\begin{aligned}G(z)&=\tan^{-1}[(z-1)^{-1/2}]-(z-2)(z-1)^{1/2}z^{-2}\\&=2.667z^{-3/2}[1-0.3z^{-1}-0.05357z^{-2}+O(z^{-3})]\;.\end{aligned} \tag{2}$$

The first term on the right-hand side of Eq. (1) reflects Fick's diffusion law and the second term is due to the coupling of the diffusion mode with the shear mode of the fluid. For the reduced top value $k^2S_s(k,0)$ and the reduced half-width $\omega_H^s(k)/k^2$ one finds[1,9] from Eqs. (1) and (2),

$$k^2S_s(k,0)=\frac{1}{\pi D}[1+ak+O(k^{3/2})]\;, \tag{3a}$$

$$\omega_H^s(k)/k^2=D[1-bk+O(k^{3/2})]\;, \tag{3b}$$

where

$$a=G(\delta^{-1})/k^*\;,\quad b=H(\delta)/k^*\;, \tag{4}$$

with

$$H(\delta)=1.4531\delta^{3/2}[1-0.7276\delta-0.1523\delta^2-O(\delta^3)]\;. \tag{5}$$

Since in Eqs. (3), a and b are positive, $k^2S_s(k,0)$ approaches its hydrodynamic limit $(\pi D)^{-1}$ from *above* and $\omega_H^s(k)/k^2$ approaches its hydrodynamic limit D from *below*, when $k\rightarrow 0$. For liquid sodium at $T=403$, 602, and 803 K we use the values of D given in Refs. 8 and 10 and the values of η given in Ref. 11. The results for δ, k^*, a, and b are summarized in Table I. We observe that for sodium the mode-coupling parameters a and b in Eqs. (3) change by more than a factor 3 when T increases

TABLE I. Thermodynamic and transport properties of liquid sodium at saturated vapor pressure.

T	(K)	403	602	803
n	(Å^{-3})	0.024 09	0.022 85	0.021 63
D	(Å^2/ps)	0.484	1.28	2.10
ν	(Å^2/ps)	66.3	36.6	27.7
k^*	(Å^{-1})	0.0196	0.0872	0.167
δ		0.007 25	0.0338	0.0705
a	(Å)	0.084	0.19	0.29
b	(Å)	0.045	0.10	0.15

from 403 to 803 K and that for all T,a is about twice as large as b. We show the mode-coupling predictions for sodium at $T=403$, 602, and 803 K in Fig. 1 for $S_s(k,0)k^2$ and in Fig. 2 for $\omega_H^s(k)/k^2$ [cf. Eqs. (3) and (4) and Table I]. We also show the experimental results for both quantities as given in Refs. 7 and 8.

For all three thermodynamic states of liquid sodium the measured values of $S_s(k,0)k^2$ approach the hydrodynamic limit from *above* (cf. Fig. 1) and the measured values of $\omega_H^s(k)/k^2$ tend to this limit from *below* (cf. Fig. 2). Also, the relative deviations of the experimental $S_s(k,0)k^2$ from the hydrodynamic limit are for small k larger than those of $\omega_H^s(k)/k^2$ at the same temperature. Furthermore, for small but fixed values of k, the deviations of both $S_s(k,0)k^2$ and ω_H^s/k^2 from their corresponding hydrodynamic limits strongly increase with increasing temperature (cf. Figs. 1 and 2). Since these observations are consistent with the mode-coupling expression Eq. (1) up to about $k \simeq 1.5$ Å^{-1} (cf. Figs. 1 and 2) we conclude that the mode-coupling theory[12] might well be relevant for the description of $S_s(k,\omega)$ for $0<k<1.5$ Å^{-1}.

We note that in liquid sodium we find more direct ex-

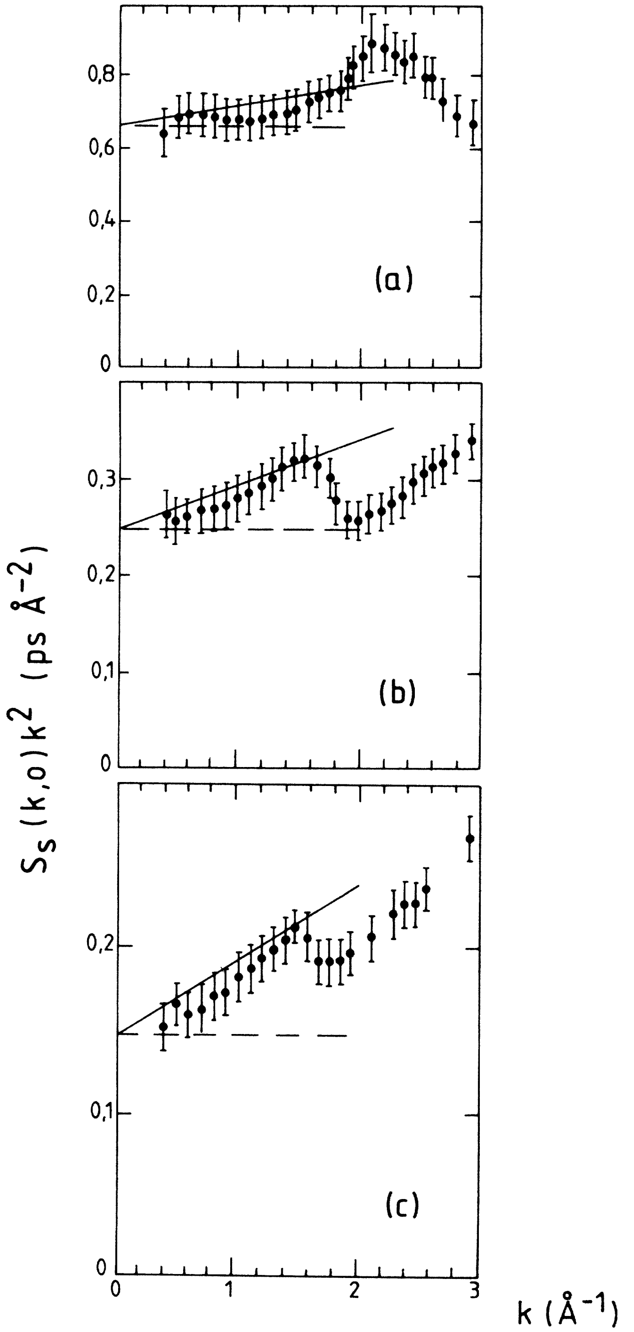

FIG. 1. The reduced top value $S_s(k,0)k^2$ as a function of k for liquid sodium at (a) 403 K, (b) 602 K, and (c) 803 K, obtained from neutron scattering experiments (cf. Refs. 7 and 8) (dots with representative error bars), Fick's diffusion law (dashed curves), and the mode-coupling theory (full curves).

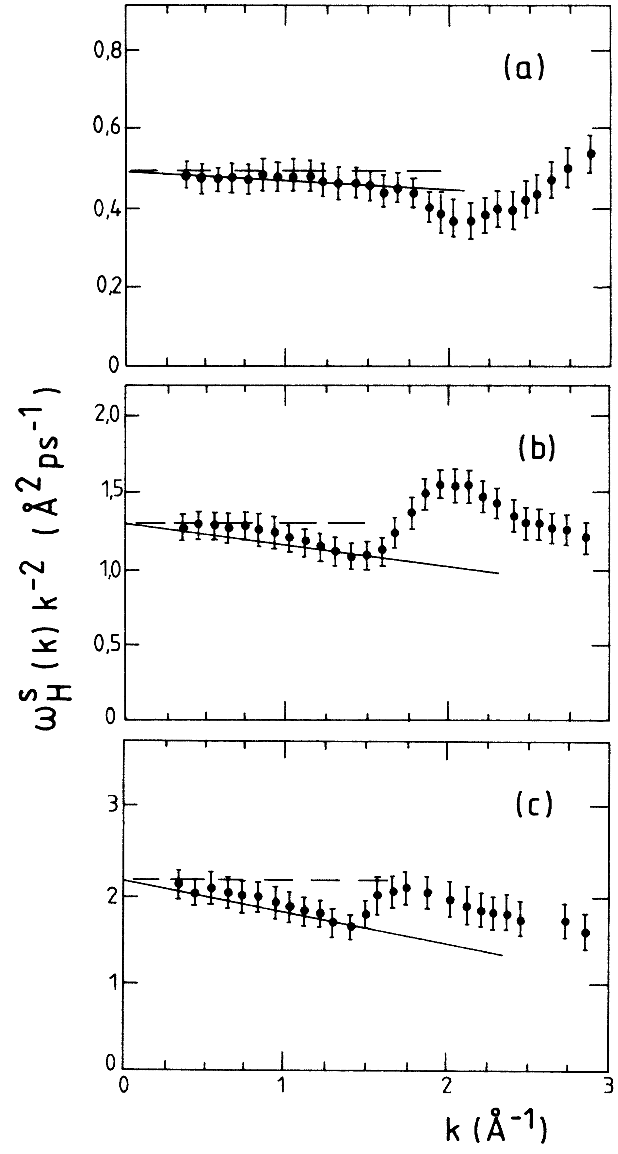

FIG 2. The reduced half-width $\omega_H^s(k)/k^2$ as a function of k for liquid sodium at (a) 403 K, (b) 602 K, and (c) 803 K, obtained from neutron scattering experiments (cf. Refs. 7 and 8) (dots with representative error bars), Fick's diffusion law (dashed curves), and the mode-coupling theory (full curves).

perimental evidence of the existence of mode-coupling effects than in liquid argon, where these effects were demonstrated in an indirect way.[13–15] [In the latter investigation the coherent structure factor $S(k,\omega)$ was decomposed into three extented hydrodynamic modes through a least-squares-fitting procedure, yielding an anomalous dispersion in the frequency of sound.]

The observation reported here is also consistent with the prediction[16] of a more pronounced influence of mode-coupling effects in a liquid metal as compared to liquid argon. Finally, we note that our result, Eq. (3b), which shows a deviation linear in k from Fick's law in the half-width, contradicts an earlier calculation[17] of this quantity which leads to a deviation quadratic in k [see Eq. (4.1) of Ref. 17]. Inserting our asymptotes, Eqs. (3), into Figs. 1 and 4 of Ref. 17 shows agreement with computer-simulation results of the half-width of argon[18] up to $K \lesssim 0.7$ Å^{-1} and of rubidium[19] up to $k \lesssim 1.3$ Å^{-1}.

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[1] P. Verkerk, J. H. Builtjes, and I. M. de Schepper, Phys. Rev. A **31**, 1731(1985).

[2] D. Bedeaux and P. Mazur, Physica **73**, 431 (1974).

[3] I. M. de Schepper, H. van Beÿeren, and M. H. Ernst, Physica **75**, 1 (1974).

[4] I. M. de Schepper and M. H. Ernst, Physica **98A**, 189 (1979).

[5] M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, Phys. Rev. Lett. **25**, 1254 (1970); Phys. Rev. A **4**, 2055 (1971); J. Stat. Phys. **15**, 7 (1976).

[6] J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Lett. **25**, 1257 (1970); Phys. Rev. A **6**, 776 (1972).

[7] W. Gläser and Ch. Morkel, J. Non-Cryst. Solids **61**, 309 (1984).

[8] Ch. Morkel, Ph.D. thesis, Technische Universität München, 1984 (unpublished).

[9] J. Bosse (unpublished).

[10] J. J. van Loef, Physica **75**, 115 (1974).

[11] A. V. Grosse, Science **147**, 1438 (1865); J. Inorg. Nucl. Chem. **28**, 795 (1966); C. C. Hsu and H. Eyring, Proc. Nat. Acad. Sci. U.S.A. **69**, 1342 (1972).

[12] M. H. Ernst and J. R. Dorfman, J. Stat. Phys. **12**, 311 (1975).

[13] I. M. de Schepper, P. Verkerk, A. A. van Well, and L. A. de Graaf, Phys. Lett. **104A**, 29 (1984).

[14] I. M. de Schepper, P. Verkerk, A. A. van Well, and L. A. de Graaf, Phys. Rev. Lett. **50**, 974 (1983).

[15] E. G. D. Cohen, I. M. de Schepper, and M. J. Zuilhof, Physica **127B**, 282 (1984).

[16] J. Bosse, W. Götze, and M. Lücke, Phys. Rev. A **20**, 1603 (1979).

[17] G. Wahnström and L. Sjögren, J. Phys. C **15**, 401 (1982).

[18] D. Levesque and L. Verlet, Phys. Rev. A **2**, 2514 (1970).

[19] A. Rahman (unpublished).