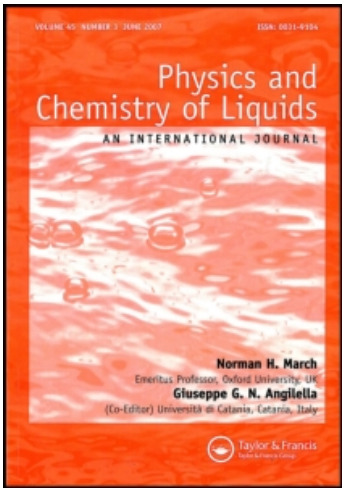

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Frequency spectra of disordered metals: especially liquid Rb

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Frequency spectra of disordered metals: especially liquid Rb

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The phonon frequency spectrum $g(\omega)$ of a crystal, such as body centred cubic (bcc) Rb, is known to be characterized by the Van Hove singularities at $\omega \neq 0$. However, for a liquid metal like Rb, $g(\omega)$ has a single, hydrodynamic-like singularity, namely a cusp $\propto \omega^{(1/2)}$, at $\omega = 0$. Here, we note first that computer simulation on liquid Rb near freezing has revealed a rather well-defined Debye frequency ω_D. Therefore, we propose here a zeroth-order model $g_0(\omega)$ of $g(\omega)$ for Rb, which combines the Debye model with the 'hydrodynamic' $\omega^{(1/2)}$ cusp. The corresponding velocity autocorrelation function $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$ has correctly a long-time tail $\propto t^{-(3/2)}$. The terms from $g_0(\omega)$ involving ω_D are then damped by weak exponential factors $\exp(-\alpha_i t)$, and the resulting first-order approximation, $g_1(\omega)$ say, to the frequency spectrum is found to have features in common with the molecular dynamics (MD) simulation form. Thus ω_D is fixed, as well as transport coefficients for the known thermodynamic state. The article concludes with a more qualitative discussion on supercooled liquids, and on metallic glasses such as Fe, for which MD simulations exist.

Keywords: Disordered metals; Liquid rubidium

1. Introduction

Given a suitable force field, built from central pair potentials appropriate in *sp* electron metals like the monovalent alkalis or the divalent metal Be, one can readily compute the phonon dispersion relations and hence the frequency spectrum $g(\omega)$. In body-centred cubic (bcc) crystalline Rb, or hexagonal close-packed (hcp) Be, the Van Hove singularities characteristic of these two different lattices are prominent features of $g(\omega)$ [1].

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When we turn from the long-range order (LRO) of crystals to the short-range order (SRO) say in liquid Rb just above its freezing point, it is known from the theory [2,3], that $g(\omega)$ is a well-behaved function of ω, except at $\omega = 0$ [4], where there is a cusp-like behaviour due to the well-established long-time tail in the velocity autocorrelation function $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$, which is related precisely to $g(\omega)$ in the Fourier transform defined in equation (4). Since computer simulations exist on liquid Rb near freezing (see the review by Copley and Lovesey [5]), it is natural to take this example as the main focal point of the present study of $g(\omega)$ in disordered metals.

However, we also explore, but now not quantitatively, how $g(\omega)$ can be expected to change in (a) a supercooled liquid metal and (b) a 'glassy' monatomic metal mimicking Fe, though the only available data is from the molecular dynamics (MD) simulations using a so-called 'glue model' force field constructed by Johnson [6].

The outline of this article is then as follows. In section 2, we summarize the low-frequency expansion of $g(\omega)$ in a liquid like Rb, following Gaskell and March [4]. This expansion is then made as the basis of a simple model $g_0(\omega)$ in which the requirements of hydrodynamics characterized by self-diffusion coefficient D and shear viscosity η are combined with the Debye model well known for modelling $g(\omega)$ in crystals. The velocity autocorrelation function $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle_0$ obtained from $g_0(\omega)$ is then compared immediately with the computer simulations of Schommers [7,8] for liquid Rb. Damping of other than the $t^{-(3/2)}$ tail in $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle_0$ is then carried out to obtain a first approximation $g_1(\omega)$ which is found to accord fairly well with the results of Schommers [7,8]. This allows ω_D to be fixed for Rb, and in the final model for $g(\omega)$ the value at $\omega = 0$ is put equal to the 'hydrodynamic' value D/π for the thermodynamic state under consideration. Furthermore, the shear viscosity η, plus number density ρ and D again, determine the 'strength' of the cusp term in $g(\omega)$ proportional to $\omega^{(1/2)}$.

Turning to supercooled liquids, section 3 summarizes work of Schenk *et al.* [9] on transition elements, and then treats the 'metallic glass' Fe studied by Tomida and Egami [10] using MD computer simulations. Finally, section 4 constitutes a summary together with some proposals for future directions which appear to us to offer promise.

2. Exact low-frequency expansion of $g(\omega)$ and its modelling in liquid Rb

Gaskell and March [4] gave the exact series expansion of the frequency spectrum $g(\omega)$ in a monatomic liquid metal like Rb as

$$g(\omega) = a_0 + a_1\omega^{(1/2)} + a_2\omega + a_3\omega^{(3/2)} + a_4\omega^2 + \cdots \tag{1}$$

Here $g(\omega)$ is defined by

$$g(\omega) = \omega^2 \lim_{k \to 0} \frac{S_S(k, \omega)}{k^2}, \tag{2}$$

where $S_S(k,\omega)$ is the Fourier transform with respect to $\mathbf{r}$ and t of the self-correlation function $G_S(\mathbf{r},t)$ [11]. It is well known that the Green–Kubo formula

$$\frac{D}{\pi} = \lim_{\omega\to 0}\omega^2 \lim_{k\to 0}\frac{S_S(k,\omega)}{k^2}, \tag{3}$$

where D denotes the self-diffusion coefficient, means that $\lim_{\omega\to 0} g(\omega) = D/\pi = g(0)$.

The term $\omega^{(1/2)}$ in the expansion equation (1) means that $g(\omega)$ has a cusp at the origin, with a negatively infinite slope at $\omega = 0$. As Gaskell and March emphasized in obtaining the series equation (1), the origin of such an $\omega^{(1/2)}$ term resides in the long-time behaviour of the velocity autocorrelation function $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$, which is related to $g(\omega)$ by

$$g(\omega) = \frac{k_B T}{m\pi}\int_0^\infty \frac{\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle}{\langle v^2(0)\rangle}\cos\omega t\,\mathrm{d}t, \tag{4}$$

where $k_B T$ is the thermal energy, while m is the atomic mass. Then, as found initially by Adler and Wainwright [2] for hard spheres, and elaborated quantitatively by [3], $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$ at sufficiently long times is given by

$$\frac{\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle}{\langle v^2(0)\rangle} \simeq \frac{2}{3\rho}\left[4\pi\left(D+\frac{\eta}{m\rho}\right)t\right]^{-(3/2)}, \tag{5}$$

where ρ is the number density and η denotes the shear viscosity. Using equations (4) and (5), it is a straightforward matter to verify that a_1 in equation (1) is given by [4]

$$a_1 = -\frac{2\sqrt{2\pi}}{3\rho}\frac{k_B T}{m\pi}\left[4\pi\left(D+\frac{\eta}{m\rho}\right)\right]^{-(3/2)}. \tag{6}$$

Because this is determined by the transport coefficients D and η, it is appropriate to refer to the cusp at $\omega = 0$ in $g(\omega)$ as having 'hydrodynamic' character.

2.1. *Zeroth-order model of g(ω) in liquid Rb*

Fortified by the above knowledge of the hydrodynamic cusp, we now return to the point already made that incoherent neutron scattering or MD simulation on liquid Rb near freezing reveals a rather well defined high frequency edge, which we take therefore to be characterized by a Debye frequency ω_D. Then, by analogy with the Debye model of a crystalline solid, we propose to form a 'zeroth-order' model of $g(\omega)$ for liquid Rb which we denote below by $g_0(\omega)$.

It is then natural to retain the $\omega^{(1/2)}$ and ω^2 terms in equation (1) and to write therefore

$$g_0(\omega) = \begin{cases} a_0 + a_1\omega^{(1/2)} + a_4\omega^2, & \text{if } \omega \le \omega_D, \\ 0, & \text{if } \omega > \omega_D. \end{cases} \tag{7}$$

In the 'final' form of the model developed below, we know a_0 and a_1 as discussed above, but, we shall not impose these values on the zeroth-order model.

Inverting the Fourier transform relation equation (4) with $g(\omega)$ replaced by $g_0(\omega)$ in equation (7), we can calculate the normalized velocity autocorrelation function, again of course in zeroth-order, and denoted again by subscript zero, as

$$\frac{k_B T}{2m\omega_D}\frac{\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle_0}{\langle v^2(0)\rangle} = \left(a_0 + a_1\omega_D^{(1/2)}\right) j_0(\tau) + a_4\omega_D^2\left[\frac{j_1(\tau)}{\tau} - j_2(\tau)\right] - a_1\left(\frac{\pi\omega_D}{2}\right)^{(1/2)}\frac{S(\tau)}{\tau^{(3/2)}}, \tag{8}$$

where $\tau = \omega_D t$, $j_n(\tau)$ is the spherical Bessel function of first kind and order n, and $S(\tau)$ is the sine-Fresnel integral, with $S(\tau) = (1/2) - (1/\tau\sqrt{2\pi})\cos\tau^2 + O(\tau^{-2})$ as $\tau \to \infty$ [12]. The result of the model equation (8) yields, as $\tau \to 0$,

$$\frac{k_B T}{2m\omega_D} = a_0 + \frac{2}{3}a_1\omega_D^{(1/2)} + \frac{1}{3}a_4\omega_D^2. \tag{9}$$

This equation (9) relates the parameters recorded in table 1.

Figure 1 [line (a)] shows $g_0(\omega)$, equation (7), for the values of the parameters listed in table 1, where use has been made of the values for D, ρ, ω_D and $g_0(0)$ in Ref. [8], and of the value for η in Ref. [13]. Correspondingly, figure 2 [line (a)] shows the normalized velocity autocorrelation function.

2.2. *First-order model of g(ω) in liquid Rb*

A first-order model for the frequency spectrum $g(\omega)$, $g_1(\omega)$ say, is defined from equation (8) by attaching separate exponential damping factors to the coefficients a_i $(i = 0, 1, 4)$, as

$$a_i \mapsto \tilde{a}_i \equiv a_i e^{-\alpha_i \tau} \tag{10}$$

(see table 1), while retaining undamped the leading asymptotic behaviour $\sim\tau^{-(3/2)}$ as $\tau \to \infty$. Specifically, we assume

$$\begin{aligned}\frac{k_B T}{2m\omega_D}\frac{\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle_1}{\langle v^2(0)\rangle} = {} & \left(\tilde{a}_0 + \tilde{a}_1\omega_D^{(1/2)}\right) j_0(\tau) + \tilde{a}_4\omega_D^2\left[\frac{j_1(\tau)}{\tau} - j_2(\tau)\right] \\ & - \left(\frac{\pi\omega_D}{2}\right)^{(1/2)}\left[\tilde{a}_1\frac{S(\tau) - (1/2)}{\tau^{(3/2)}} + a_1\frac{1}{2\tau^{(3/2)}}\right].\end{aligned} \tag{11}$$

One then Fourier transforms equation (11) back into the frequency domain, to obtain $g_1(\omega)$ [14]. Equation (10) thus provides a first-order approximation of the velocity autocorrelation function, which is displayed in figure 2 [lines (b) and (c)], along with the first-order frequency spectrum $g_1(\omega)$ in figure 1 [lines (b) and (c)]. We note that until the coefficient a_1 in equation (7) is substantially increased [line (c) in figure 1], the hydrodynamic cusp is not very pronounced in $g(\omega)$, though it does, of course, in contrast to Schommers results with a pair potential simulation, at first decrease

Table 1. Values of the parameters used to model $g(\omega)$ in zeroth-order, equation (7), and first-order approximation. Labels (a), (b) and (c) in the first columns refer to labels of lines in figures 1 and 2.

	ω_D ($\times 10^{12}$ s^{-1})	a_0 ($\times 10^{-6}$ cm^2/s^{-1})	$a_1\omega_D^{(1/2)}$ ($\times 10^{-6}$ cm^2/s^{-1})	$a_4\omega_D^2$ ($\times 10^{-5}$ cm^2/s^{-1})
(a, b)	$9.7 \cdot 10^{12}$	$9.2 \cdot 10^{-6}$	$-4.8 \cdot 10^{-6}$	$2.9 \cdot 10^{-5}$
(c)	$9.7 \cdot 10^{12}$	$9.2 \cdot 10^{-6}$	$-9.7 \cdot 10^{-6}$	$2.9 \cdot 10^{-5}$
		α_0	α_1	α_4
	(a)	0.0	0.0	0.0
	(b, c)	0.1	0.01	0.1

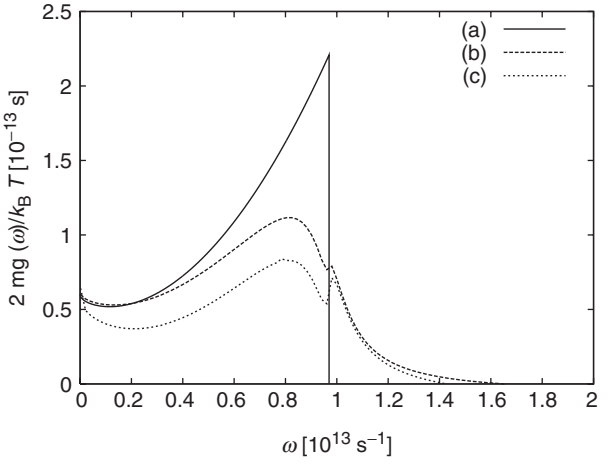

Figure 1. Frequency spectra $g(\omega)$ in zeroth-order approximation, $g_0(\omega)$, equation (7) [line (a)], and first-order approximation, equation (11) [lines (b) and (c)]. Values of the parameters are as in table 1.

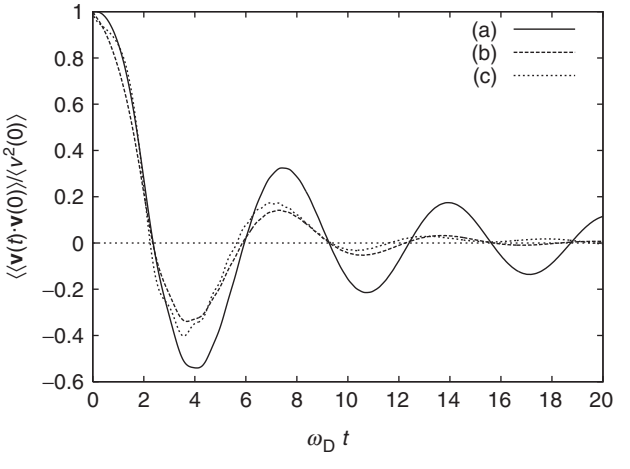

Figure 2. Velocity autocorrelation function, $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle v^2(0) \rangle$, defined in terms of the Fourier transform of the frequency spectrum $g(\omega)$ as in equation (4). Line (a) refers to the zeroth-order approximation of equation (7), while lines (b) and (c) refer to the first-order approximation of equation (11). Table 1 provides a list of the values of the parameters employed here.

from $\omega = 0$. No attempt has been made to preserve normalization between the three curves of $g(\omega)$ in figure 1: it will be a simple matter to deal with that when incoherent neutron scattering data becomes available for liquid Rb near freezing.

In the first-order approximation, the less oscillatory form of the velocity autocorrelation function already bears some resemblance to that given by Schommers [8].

3. Short-range ordering of icosahedra in supercooled liquids and metallic glasses

Having given a semi-quantitative modelling of the frequency spectrum $g(\omega)$ in liquid Rb, we turn to a qualitative discussion of $g(\omega)$ in disordered metals in two other phases, namely (i) supercooled liquids and (ii) metallic glasses.

First, we summarize the findings of Schenk *et al.* [9], who have validated early ideas of Frank [15] on the existence of icosahedral units in supercooled liquids in the specific cases of supercooled Fe, Ni and Zr.

3.1. *Some experimental facts on undercooled metallic melts*

Here, our object is to summarize some experimental evidence obtained by Schenk *et al.* [9] on stable and deeply undercooled melts of pure metallic elements. The combination of electromagnetic levitation with neutron scattering measurements enabled the conclusions summarized below to be reached.

The metallic elements chosen by Schenk *et al.* [9] were such that they form bcc and face-centred cubic (fcc) structures in the solid state. This was done, using Fe and Zr for the bcc case and Ni for fcc in order to test whether the structure of the crystalline solid might influence the liquid SRO. Table 1 of Schenk *et al.* [9] gives nearest and next-nearest neighbour distances and local coordination numbers for the above three transition elements for a variety of undercooled liquid states. Their major conclusion is that, from their experimental data, icosahedral SRR in the melt, first postulated by Frank [15], is in evidence in their undercooled melts, independently of the structure of the nucleating solid phases.

We shall below, after summarizing the computer simulation results on a model of metallic glass Fe, comment on the possible relevance of the above findings to vibrational dynamics in supercooled liquids. While on this subject of undercooled metallic melts, also it is relevant to refer the study of Page *et al.* [16] on liquid Ga.

3.2. *Vibrational structure in metallic glasses*

While experimentally a lot of metallic glasses exist on alloying, e.g. $Pd_{40}Ni_{40}P_{20}$ (for other examples, see figure 1 of Ref. [17]), to our knowledge no monatomic metallic glass has, as yet, been produced in the laboratory.

Therefore, in this section we shall take as our 'experimental' basis the MD computer simulations of a 'model Fe glass' [10], using the so-called 'glue model' force field of Johnson [6] (see also [18]).

Duval *et al.* [19] have constructed a model which assumes a non-continuous structure of glasses to interpret experiments on glasses using both inelastic neutron scattering and Raman scattering. They consider specifically As_2S_3 and also SiO_2 glasses, whereas our interest here is in monatomic metallic glasses. To date, no such metallic glass

is available for experimentation, so we must use computer simulation to make any progress.

Tomida and Egami [10] describe the structure of their assembly in terms of spherical harmonic representations of topology of local clusters of 'Fe atoms', and the orientational correlation among these. They clearly demonstrate that the variation of the averaged topology of the nearest-neighbour clusters displays an anomalous behaviour at temperatures lying between the glass transition temperature T_g and a temperature well above this value. They show from their MD studies, that this anomalous nature resides in the aggregation of the clusters with icosahedral topology, in accordance with the early ideas of Frank [15].

In the 'model Fe' glass discussed by Tomida and Egami [10], our conclusion is that in all probability $g(\omega)$ will exhibit much structure, with prominent peaks around the 'discrete' normal mode frequencies of an icosahedron obtained using again a 'Johnson-like' force field. Some of this structure, we feel, is likely to disappear as we go to the bcc Fe crystal, with its characteristic Van Hove singularities.

4. Summary and future directions

The main result of the present study is the construction of a semiquantitative model for the frequency spectrum $g(\omega)$ of liquid Rb near freezing. The pair potential simulations of Schommers [7,8] (see also Ref. [5]) provides our starting point. However, while this is very useful at frequency $\sim\omega_D$, it does not contain the 'hydrodynamic' cusp emphasized in the early study of Gaskell and March [4]. Therefore, we have combined a Debye-like elastic continuum model with this hydrodynamic feature to obtain a zeroth-order approximation to the normalized velocity autocorrelation function, which already contains a long-time tail proportional to $t^{-(3/2)}$. By damping all terms in $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle_0$ except this tail with appropriately chosen exponential factors, Schommer's $g(\omega)$ for $\omega \simeq \omega_D$ is reasonably well accounted for.

The remainder of this article is qualitative, dealing with two other phases of disordered metals, namely (i) supercooled liquids and (ii) metallic glasses. In both areas, we have emphasized, in admittedly specific cases such as those studied by Schenk *et al.* [9], the importance of icosahedral units. We turn immediately below to raise two 'unconventional' areas related to the present context which may be worthy for future study.

4.1. *Future directions*

We believe it may be important in the area covered in this article to study further: (i) The possible relevance of the hydrodynamic cusp even in supercooled metallic liquids and in monatomic metallic glasses. Increase in shear viscosity η might enhance the initial 'plunge' in $g(\omega)$ away from D/π at $\omega = 0$; (ii) The question of whether, especially in monatomic metallic glasses, the normal mode vibrational spectra of a single 'Frank' icosahedron is a useful 'building block' for vibrational dynamics. Obviously, the force field used for the icosahedron discrete frequencies must reflect its metallic environment, through a force field related to that of Johnson [6] for metallic Fe. Then, SRO of the icosahedra, both positional and orientational, will clearly broaden the discrete frequencies into a (possibly peaky) vibrational spectra of the metallic glass.

Finally, the role of frustration in glassy structures has been reviewed recently [20], and this area is right for future work.

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