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Stochastic dynamics in liquid potassium as explored by polarized neutron scattering

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Abstract

The coherent $S_c(Q,\omega)$ and single particle $S_s(Q,\omega)$ dynamic structure factors which contribute to the low-energy spectrum of molten potassium are separated by means of neutron polarization analysis. The linewidth and amplitude of the single-particle spectra follow an apparent Fickian behavior with a diffusion coefficient well below the value found by macroscopic means. Once this is accounted for, the results are found to conform with predictions made from kinetic theory. In contrast, the available theoretical recipes to account for the coherent quasielastic intensity are seen to be semiquantitative, at best.

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1. Introduction

The nature of low-frequency excitations that give rise to the quasielastic part of the spectrum of density fluctuations $S_c(Q,\omega)$ in liquid metals still remains to be understood on a quantitative basis. In the hydrodynamic limit ($Q \to 0$, $\omega \to 0$) the $S_c(Q,\omega)$ spectrum can be calculated analytically in terms of linearized hydrodynamics, including first-order corrections [1]. The basic quantities are here hydrodynamic variables for particle, longitudinal current and energy densities that are connected with the corresponding conserved quantities. In the simplest case, the spectrum is composed of two finite-frequency peaks corresponding to propagating excitations plus a central, relaxing thermodiffusive mode that shows a linewidth given up to first order by $D_T Q^2$ where D_T stands for the thermal diffusion coefficient. In contrast and also within this limit, the $S_S(Q,\omega)$ single-particle counterpart is known to follow an exponential relaxation process, as dictated by the Fick's law with a decay constant given in terms of the D_s self-diffusion coefficient as $D_s Q^2$. Beyond the hydrodynamic realm the behavior of $S_S(Q,\omega)$ is now beginning to be understood on a quantitative basis [2,3], mostly as a consequence of developments of kinetic theories of the mode-coupling family. These have provided us with prediction capabilities able to account for the shape and characteristic parameters (i.e. wavevector dependence of its linewidth and amplitude) of the $S_S(Q,\omega)$ spectrum. The picture that emerges from these studies, mostly concerning molten sodium, portrays motions within the kinetic regime that is for time-length scales comparable with inter-particle separations and characteristic times as mediated by collective modes. Close to melting, coupling to a longitudinal mode results in a

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retardation of diffusive motions if compared to the hydrodynamic prescription [3]. The state of our knowledge concerning the low-frequency part of $S_c(Q,\omega)$ is however on a far more primitive stage. Guidance from kinetic theory [4] tells that close to Q_p, that is where the static $S(Q)$ shows its maximum, its linewidth may be approximated by [4]

$$\Delta\varpi_c = \frac{D_E Q^2}{S(Q)[1 - j_0(Q\sigma) + 2j_2(Q\sigma)]}, \tag{1}$$

where D_E stands for a hard-sphere diffusion coefficient as given by the Enskog prescription, σ characterizes the size of the fluid particles and j_x are spherical bessel functions. Data given in Ref. [4] for rare gases and molten rubidium show a reasonable agreement between experiment and Eq. (1), as also does more recent data on more complex liquids such as Ga or molecular D_2 [4]. As a result, one could understand the quasielastic part of $S_c(Q,\omega)$ as a self-diffusion-like process of the liquid particles that enables a density fluctuation to relax.

Our interest to revisit such topic was motivated by recent measurements on the full spectrum for density oscillations of molten potassium [5] that has shown the inadequacy of the usual 'viscoelastic' ansatz [6] to account for the observed lineshape of the full $S_c(Q,\omega)$ spectra, and in fact, a further level in the memory function representation of the response function was needed to account for the quasielastic region of $S_c(Q,\omega)$. Here we report on a recent measurement of *both* $S_c(Q,\omega)$ and $S_S(Q,\omega)$ performed within a single experiment by means of polarized neutron scattering. Our aim is to compare the characteristic times involved in both single-particle and collective-diffusion processes as well as the relationship between the wavevector dependence of their corresponding linewidths $\Delta\omega_c$ and $\Delta\omega_S$. This would serve to attest in much detail the dominant character of the quasielastic peak $S_c(Q,\omega)$ as well as to explore the limits of validity of Eq. (1), which is supposed to hold close to Q_p. This comes as a consequence of the assumptions taken for its derivation that amount to neglect density fluctuations with wavelengths significantly above $2\pi/Q_p$.

2. Methods

The experiment was carried out using the IN14 triple axis spectrometer of the Institut Laue Langevin (Grenoble, France), using the polarization analysis option. The instrument was setup using a fixed incident wavevector $k_i = 1.97$ Å^{-1} which provided a resolution in energy transfers of 0.113 meV. A full polarized beam was employed with a measured value for the flipping ratio of 26.9. The instrument measures the spin-flip (sf) and non-spin-flip (nsf) double-differential cross-sections that are related to the coherent and incoherent cross-sections through [8]

$$\begin{aligned} \left.\frac{d^{\acute{e}}\sigma}{d\Omega\, dE}\right|_{sf} &= \frac{2}{3}\left.\frac{d^{\acute{e}}\sigma}{d\Omega\, dE}\right|_{inc}, \\ \left.\frac{d^{\acute{e}}\sigma}{d\Omega\, dE}\right|_{nsf} &= \frac{1}{3}\left.\frac{d^{\acute{e}}\sigma}{d\Omega\, dE}\right|_{inc} + \frac{1}{3}\left.\frac{d^{\acute{e}}\sigma}{d\Omega\, dE}\right|_{coh}, \end{aligned} \tag{2}$$

where the subscripts stand for the incoherent and coherent scattering contributions, respectively. The isolation of each one of the two components is then achieved through [8]

$$\begin{aligned} \left.\frac{d^{\acute{e}}\sigma}{d\Omega\, dE}\right|_{coh} &= \frac{1}{4K}\left[\frac{3(N^+ - N^-)}{P_0} + (N^+ + N^-)\right], \\ \left.\frac{d^{\acute{e}}\sigma}{d\Omega\, dE}\right|_{inc} &= \frac{3}{4K}\left[(N^+ + N^-) - \frac{(N^+ - N^-)}{P_0}\right], \end{aligned} \tag{3}$$

where K stands for a common scaling constant and N stands for counts with spin up (+) and spin down (−) states given by

$$\frac{2N^{\pm}}{K} = (1 \pm P_0)\left.\frac{d^{\acute{e}}\sigma}{d\Omega\, dE}\right|_{nsf} + (1 \mp P_0)\left.\frac{d^{\acute{e}}\sigma}{d\Omega\, dE}\right|_{sf} \tag{4}$$

with $P_0 = PP_A(1 - D)$ being the effective polarization. Here P_A stands for the efficiency of the Heusler analyzer, D is the beam depolarization and P is the polarization of the incident beam. Values for P, P_A are close to unity and the beam depolarization is usually small. A sample of high-purity metallic potassium was contained within a Nb cylinder of 10 mm diameter and 10 cm height and molten at 375 K. Constant Q scans were then performed for wavevectors ranging from 0.4 Å^{-1} up to 2.0 Å^{-1}. Every data point was measured with the neutron spin flipper located before the sample with flipper-on and flipper-off positions. Finally, the collective and single-particle dynamic structure factors are directly proportional to the respective coherent and incoherent cross-sections.

Computer molecular dynamics simulations were performed for an ensemble of 500 atoms close to melting $T_m = 336.7$ K at $T = 380$ K. We have employed a semi-empirical potential [7] that did reproduce adequately the structure and thermodynamics of both the hot solid and the liquid. An initial f.c.c. crystal configuration was melt at high temperature and equilibrated under NVT conditions with a number density $\rho = 0.01269$ Å^{-3} that comes close to the experimental estimate. Production runs of 50 ps were carried out in order to compute the properties of interest.

3. Results

3.1. Experiment

A set of $I_c(Q,\omega)$ and $I_S(Q,\omega)$ spectra is displayed in Fig. 1 for representative wavevectors below, on top, and past $Q_p \approx 1.6$. These quantities are given by

$$I_{c,s}(Q,\omega) \propto S_{c,s}(Q,\omega) \otimes R(Q,\omega) + \text{bgr}, \tag{5}$$

where $R(Q,\omega)$ is the instrument resolution and bgr a background term.

All the spectral intensities were approximated in terms of single Lorentzian functions.

Data shown in Fig. 2 refers to the incoherent spectra. The best joint fit for both the linewidth and amplitude yields a subquadratic Q-dependence $\Delta\omega_S(Q) = D_{\mathrm{eff}}Q^2$