

# Diffusion of low-density impurities in semiquantum liquids

L. L. Buishvili and A. I. Tugushi

Tbilisi State University

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Spatial diffusion of low-density impurities in semiquantum liquids is considered. The interaction between the impurities is disregarded in view of their low density. The diffusion coefficient is calculated for two limiting cases, for a delocalization time of the impurity particles shorter than the delocalization time of the solvent particles, and for the opposite limiting case.

It was shown by Andreev and Kosevich<sup>1-3</sup> that liquids in the temperature range  $\hbar/\tau < T < \Theta$  (where  $\tau$  is the liquid-particle delocalization time due to their tunneling and  $\Theta$  is the Debye temperature) have universal properties due to the presence of tunneling elementary excitations. These elementary excitations can be described in the two-level system (TLS) representation, with detachment energies in the wide range from  $\varepsilon_{\min} \approx 0$  to  $\varepsilon_{\max} \approx U$  (where  $U$  is the characteristic liquid-molecule interaction energy). If one introduces the probability  $P(\varepsilon)d\varepsilon$  of finding a TLS with energy in the interval  $(\varepsilon, \varepsilon + d\varepsilon)$ , the main premise of the theory is that the probability density is assumed constant:  $P(\varepsilon) = P = \text{const}$ . Liquids in the indicated temperature range are referred to as semiquantum liquids (SL). Note that the temperature  $\hbar/\tau$  is in fact the degeneracy temperature.

The heat capacity, viscosity, thermal conductivity, and nuclear spin-lattice relaxation time were determined in Refs. 1-5, where ultrasound absorption in LS was also investigated. The theoretical results are in good agreement with the experimental ones, so that the SL model proposed in Refs. 1-3, on which the notion of tunneling elementary excitations is based, should be regarded as adequate. The aim of the present paper is a theoretical study of the diffusion of low-density impurity particles in an SL.

We assume the impurity density to be low enough to neglect the interaction between the impurity particles.

Two cases must be distinguished in investigations of impurity-particle diffusion. The first is that of "fast" impurities, i.e., cases when the solvent particle-delocalization time  $\tau$  exceeds the impurity-particle delocalization time  $\tau_0$  (i.e.,  $\tau_0 < \tau$ ). The second case is that of "slow" impurities with the inverse inequality  $\tau_0 > \tau$ .

Obviously, either case can be realized, depending on the species of impurity particles and solvent atoms. The diffusion for these limiting cases must be considered separately.

We consider initially the first case, that of "fast" impurities. In view of the "slowness" of the solvent particles, their motion cannot adjust itself to the fast motion of the impurity particles, so that the latter motion can be regarded as a perturbation that causes transitions between the states of the TLS of the solvent particles.

We calculate the impurity-particle diffusion coefficient by a method similar to that used in Refs. 3 and 4 to calculate the kinetic coefficients, i.e., the method of reaction of the system to "thermal" perturbations.

Consider the formal problem of the energy dissipated when the system is acted upon by a periodic perturbation of the type  $V = -fg$ , where  $g$  is the impurity-particle-flux operator and  $f$  is a generalized force that varies harmonically with time at a frequency  $\omega$ . The meaning of the generalized force ("thermal" perturbation) can be established by comparing, on the one hand, the thermodynamic equation for energy dissipation  $Q = q\Delta\mu$  in the presence of a particle flux between subsystems whose chemical potentials differ by  $\Delta\mu$ , and on the other with the general formula for the energy dissipation  $Q = qf$  due to a perturbation of the type considered. The comparison yields an expression for the generalized-force amplitude:

$$f_0 = \frac{1}{i\omega} \frac{\partial \mu}{\partial c} \Delta c = \frac{1}{i\omega} \frac{\partial \mu}{\partial c} (\nabla c \mathbf{a}).$$

Here  $c$  is the mass density of the impurity particles,  $\omega$  is the perturbation frequency,  $\mathbf{a}$  is a spatial vector joining two neighboring positions of the impurity particles, and  $\nabla c$  is the gradient of the impurity density.

According to the assumption made above, the motion of the impurity particles causes transitions between states of TLS of solvent particles. The interaction Hamiltonian  $G = -qf(t)$  can therefore be written, in a representation in which an effective spin  $S = \frac{1}{2}$  is introduced for the TLS description, in the form

$$V = \frac{B}{2\hbar i\omega} (S^+ + S^-) \frac{\partial \mu}{\partial c} (\nabla c \mathbf{a}) \exp(-i\omega t) + \text{H.c.}, \quad (1)$$

where  $B$  is the coupling constant of the impurities and the TLS. These perturbations lead to an energy dissipation that can be calculated in standard manner<sup>6</sup>:

$$\frac{dE}{dt} = \varepsilon W_{+-} n_0, \quad (2)$$

where  $\varepsilon$  is the TLS-splitting energy,  $W_{+-}$  is the probability of transitions between TLS states and is governed by the operator  $V$  of Eq. (1), and  $n_0$  is the equilibrium difference of the TLS populations:

$$n_0 = \frac{1}{2} \text{th}(\varepsilon/2T). \quad (3)$$

Assuming that  $\hbar\omega \ll T$  and averaging over the TLS states via the probability  $Pd\varepsilon$ , we obtain for the energy absorbed per unit time and per unit volume of the liquid

$$\frac{dE}{dt} = c \frac{\rho}{m_0} \frac{P \langle B^2 a^2 \rangle \left( \frac{\partial \mu}{\partial c} \right)^2 (\nabla c)^2}{16 \hbar T}, \quad (4)$$

where  $m_0$  is the mass of the impurity particles and  $\rho$  is the density of the liquid.

On the other hand, in accordance with the definition of the diffusion coefficient, the same dissipation can be written in the form

$$\frac{dE}{dt} = \frac{\rho D}{m_0} \frac{\partial \mu}{\partial c} (\nabla c)^2. \quad (5)$$

Comparing (4) and (5) and taking into account the general expression<sup>6</sup> for the chemical potential of impurity particles in a weak solution:

$$\mu = T \ln \left( \frac{m}{m_0} c \right) + \psi,$$

we obtain for the diffusion coefficient

$$D = P \langle B^2 a^2 \rangle / 16 \hbar. \quad (6)$$

The following is noteworthy: the relation between the response of the system (the quantity  $q$ ) and the "external force"  $f$  acting on the system ( $f = \frac{1}{2} [f_0 \exp(-i\omega t) + \text{H.c.}]$ ) can be used to derive an expression for the generalized susceptibility. Using next the diffusion equation and the fluctuation-dissipation theorem, it is easy to obtain for the diffusion coefficient an expression identical with that given by the known Kubo formula.<sup>7</sup>

It is of interest to compare the obtained diffusion coefficient with experiment. In Ref. 8 was measured the diffusion coefficient of He<sup>3</sup> atoms dissolved in He<sup>4</sup> at temperatures  $T > T_\lambda$  (He<sup>4</sup> should exhibit semiquantum-liquid properties in this temperature range), and it was shown that at these temperatures the diffusion coefficient  $D$  is practically independent of temperature. This result agrees fully with that of Eq. (6).

Consider now a second limiting case, that of "slow" impurities. In this situation the solvent particles manage to "adjust" themselves to each position of the impurity particle, so that the solvent particles simply form a spectrum of the states between which the impurity-particle transitions will occur.

Admitting possible tunneling of impurity particles, one can readily see the analogy between the case considered above and the known problem, considered by Mott,<sup>9</sup> of carrier mobility in noncrystalline substances. The diffusion coefficient can be calculated by using this analogy in the following manner. The impurity particle can be formally ascribed an electric charge  $e$  and it can be assumed that it is acted upon by an alternating electric field of frequency and amplitude  $F$ . This is followed by calculation of the "conductivity" of the system at the frequency  $\omega$ , due to the motion of the charged impurity, and by the use of the known Einstein relation between the mobility and the diffusion coefficient. This will yield also the diffusion coefficient at the frequency  $\omega$ . The actually measured quantity is the diffusion coefficient  $D(0)$  at zero frequency, which can be obtained from  $D(\omega)$  by going to the limit  $\omega \rightarrow \infty$ . It will be shown below

that at frequencies  $\hbar\omega < T$  the diffusion coefficient is independent of frequency.

Let the charged impurity be acted upon by an alternating electric field  $F \cos \omega t$  (we emphasize once more that ascribing a charge to the impurity is only a formal device that facilitates the calculations, and the charge itself drops out of the final equations).

The Hamiltonian of the interaction of the impurity particle with the applied field is

$$W = e F x \cos \omega t. \quad (7)$$

Let  $\psi_E(\mathbf{r})$  be the wave function describing the state of an impurity particle of energy  $E$  (the wave function is assumed normalized to the volume  $V$ ).

Regarding (7) as a perturbation, we easily calculate the energy dissipated per unit time and unit volume of the liquid. The result is

$$Q = -\frac{\pi e^2 F^2 \hbar^3 V}{m_0^2 \hbar \omega} \int [w(E) - w(E + \hbar\omega)] \quad (8)$$

$$\times \nu(E) \nu(E + \hbar\omega) |J|_{E+\hbar\omega, E}^2 dE.$$

here  $\nu(E) dE$  is the density of the number of states of the impurity particle in the energy interval  $E, D + dE$ ,  $w(E)$  is the statistical probability of occupying a level of energy  $E$ , and  $J_{E+\hbar\omega, E}$  is a quantity defined by the equation

$$x_{E+\hbar\omega, E} = \frac{\hbar}{m\omega} \int \psi_{E+\hbar\omega} \frac{\partial}{\partial x} \psi_E d\mathbf{r} = \frac{\hbar}{m\omega} J_{E+\hbar\omega, E}, \quad (9)$$

$x_{E+\hbar\omega, E}$  is a matrix element of the operator  $x$ , taken between the states  $\psi_{E+\hbar\omega}$  and  $\psi_E$ .

Assuming that  $\hbar\omega \ll T$  and taking into account the formula that relates the conductivity with the dissipated energy

$$Q = \frac{1}{2} \sigma(\omega) F^2, \quad (10)$$

and also using the Einstein relation

$$\sigma = ne^2 D / T, \quad (11)$$

we ultimately obtain for the diffusion coefficient

$$D(\omega) = \frac{\hbar^3 V}{m_0^2 \hbar} \int |J|_{E+\hbar\omega, E}^2 \nu(E) \nu(E + \hbar\omega) dE. \quad (12)$$

In the limit  $\omega \rightarrow 0$ , we obtain from (12)

$$D(0) = \frac{\hbar^3 V}{m_0^2 \hbar} \int |J|_{E, E}^2 \nu^2(E) dE. \quad (13)$$

We see thus that in this case (that of "slow" impurities) the diffusion coefficient is likewise independent of temperature; this agrees with the experimental results of Ref. 10.

We emphasize in conclusion that we have assumed throughout tunneling of the impurity particles. When this is impossible, above-barrier transitions of the impurity particles still remains. The diffusion coefficient for this case will obviously have a temperature dependence  $D \sim \exp(-U_0/T)$ , where  $U_0$  is the activation energy.

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