

The Effect of the Anharmonicity in the Atomic Diffusion in Liquids: A Simple Model

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A simple analytical expression has been derived for the velocity autocorrelation function and diffusion coefficient that incorporates the effect of the anharmonicity. It is shown that the diffusion coefficient increases with the increase in the anharmonicity.

§1. Introduction

The ion diffusion in liquids has been studied for many years. It is well known that the atomic transport in materials are expressed in terms of time correlation functions. Zwanzig has proposed a simple model for the velocity autocorrelation function (VACF), and hence for the self diffusion coefficient.¹⁾ More recently, by using similar arguments to those used by Zwanzig, Tankeshwar and Tosi have proposed the following model for the calculation of VACF.²⁾

1. The particle in a liquid performs approximate harmonic oscillations with a frequency ω around the local potential minima formed by other particles. The particle remains there for a certain time, until it finds a saddle point or bottleneck in the potential surface and jumps to other potential minima.
2. The volume of the entire system consists of a number of equivalent subvolumes V^* . One effect of the atomic jump is to rearrange the equilibrium positions of the particles in a particular subvolume while the equilibrium positions of the remaining particles are unchanged. Another effect is to interrupt the harmonic oscillations of the normal modes associated with the region V^* . The motions in V^* after the jump are uncorrelated with the motions in V^* before the jump.
3. The waiting time distribution for the jump affecting the content of any V^* is written as $\text{sech}(t/\tau)$, where τ is the life time.
4. Harmonic oscillations in the region V^* are adequately described by a Debye approximation, characterized by longitudinal and transverse sound velocities.

§2. Theory

Consider a system consisting of N particles with mass m . The self diffusion coefficient D is given by the Green-Kubo formula

$$D = \frac{k_B T}{m} \int_0^\infty dt C(t), \quad (2.1)$$

where $C(t)$ is the VACF, k_B and T are the Boltzmann constant and temperature, respectively.

According to the model of Tankeshwar, the normalized VACF is given as

$$\begin{aligned} C(t) &= \frac{1}{N} \sum_{i=1}^N \langle v_i(t)v_i(0) \rangle / \langle v_i^2(0) \rangle \\ &= \sum_{\omega} \cos(\omega t) \operatorname{sech}(t/\tau), \end{aligned} \quad (2.2)$$

where $v_i(t)$ is the velocity of the i -th particle at time t .

In Eq. (2.2), the sum over particles becomes the sum over normal modes. For the case that a particular mode is dominant we have

$$C(t) = \cos(\omega t) \operatorname{sech}(t/\tau). \quad (2.3)$$

This model has been found to yield good results for the self diffusion coefficients of one component fluids like the Lennard-Jones fluids³⁾ and liquid alkali metals.⁴⁾ This model has been also extended to study the diffusion in multi-component fluids.^{2),5),6)}

The model presented in this paper differs from the above model in respect to the assumption 1. In our model, the particle performs anharmonic oscillations during the waiting process. Therefore, there is a frequency fluctuation around the equilibrium value, and the fluctuation becomes larger with the anharmonicity. The anharmonic effect is described as⁷⁾⁻⁹⁾

$$U(x) = cx^2 - fx^4, \quad (2.4)$$

where $c > 0$ and $f > 0$ are constants. The 4th order term indicates that the frequency becomes soft when the amplitude is large. This also corresponds to the decrease in the interaction force when the anharmonicity is increased.

The particle velocity in the potential given by Eq. (2.4) can be calculated easily from the Hamiltonian $H = p^2/2m + cx^2 - fx^4$ to be

$$v(t) = a_0 \cos(\gamma_0 + \gamma_1 E)t, \quad (2.5)$$

where a_0 is a constant and E is the particle energy. γ_0 and γ_1 are defined as

$$\gamma_0 = \left(\frac{2c}{m} \right)^{1/2}, \quad (2.6)$$

$$\gamma_1 = -3 \left(\frac{m}{2c} \right)^{1/2} \frac{f}{m^2}.$$

In Eq. (2.5) γ_0 expresses the harmonic vibration term and γ_1 expresses the anharmonic term. By substituting $v(t)$ into the definition of VACF, we obtain

$$C(t) = \frac{\beta^2 \cos(\gamma_0 t) - \gamma_1 \beta t \sin(\gamma_0 t)}{\gamma_1^2 t^2 + \beta^2}, \quad (2.7)$$

where $\beta = 1/k_B T$.

On the other hand, we are assuming that the particle which is executing anharmonic vibration can jump from one site to another site in a short time. This jump process is incorporated into the model as

$$C(t) = \frac{\beta^2 \cos(\gamma_0 t) - \gamma_1 \beta t \sin(\gamma_0 t)}{\gamma_1^2 t^2 + \beta^2} \operatorname{sech}(t/\tau). \quad (2.8)$$

If $\gamma_1 t \ll \beta$, Eq. (2.8) is equivalent to Eq. (2.3). Figure 1 shows the behavior of $C(t)$ calculated from Eq. (2.8). We can see the effect of the anharmonic term f on the behavior of $C(t)$.

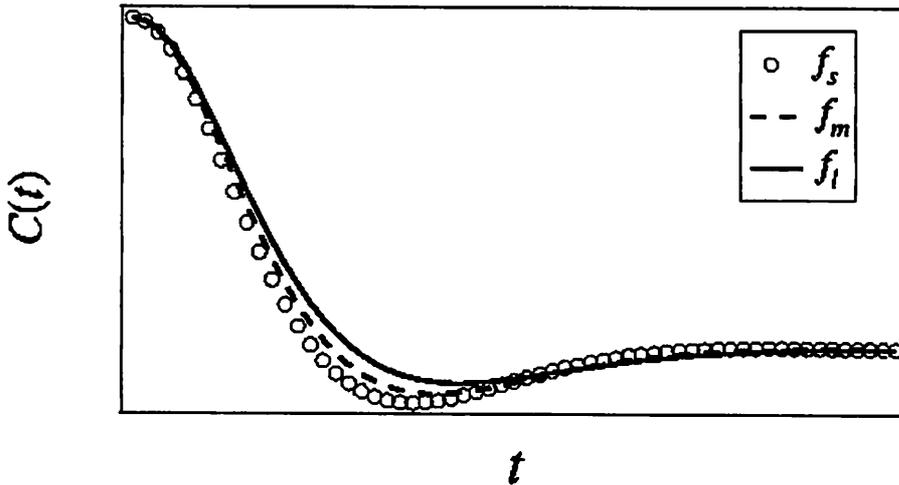


Fig. 1. The effect of the anharmonicity parameter f on the behavior of VACF $C(t)$. Here, $f_1 > f_m > f_s > 0$. The scales of the abscissa and ordinates are in arbitrary units.

§3. Diffusion Coefficient

The diffusion coefficient D is calculated not only by the integration of VACF, but also by using the expansion of VACF. The normalized VACF can be expanded as

$$C(t) = 1 - C_2 t^2 / 2! + C_4 t^4 / 4! \dots, \quad (3.1)$$

where C_2 and C_4 are constants. Comparing the expansion of Eq. (2.8) with Eq. (3.1), we obtain

$$C_2 = \gamma_0^2 + \tau^{-2} + 2\gamma_0 \gamma_1 \beta^{-1}, \quad (3.2)$$

$$C_4 = \gamma_0^4 + 5\tau^{-4} + 4\gamma_0^3 \gamma_1 \beta^{-1} + 6\gamma_0^2 \tau^{-2} + 12\gamma_0 \gamma_1 \beta^{-1} \tau^{-2}.$$

Tankeshwar and Tosi have obtained the expression for the self diffusion coefficient as²⁾

$$D = \frac{2 k_B T}{\pi m} \frac{(C_4 - (C_2)^2)^{1/2}}{(C_2)^{3/2}}. \quad (3.3)$$

By substituting Eq. (3.2) into Eq. (3.3), we obtain

$$D = A \frac{2}{\tau(\gamma_0^2 + \tau^{-2} + 2\gamma_0\gamma_1\beta^{-1})}, \quad (3.4)$$

where $A = 2k_B T / \pi m$. Figure 2 shows the behavior of the self diffusion coefficient when $\gamma_1\beta^{-1}$ is changed. We can see that D increases with the increase in the anharmonicity f , ($f \propto -\gamma_1\beta^{-1}$). The life time τ dependence of the self diffusion coefficient has been calculated from Eq. (3.4). The result is shown in Fig. 3. It is interesting to note that D exhibits a peaked behavior at a certain value of τ . The physical interpretation of this behavior is not clear at present.

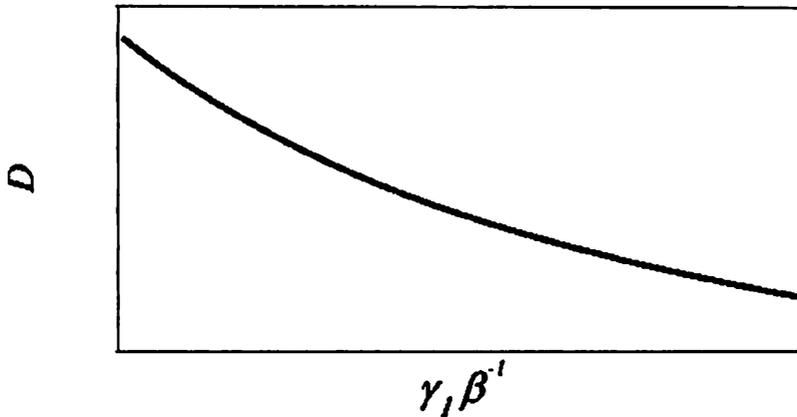


Fig. 2. Typical behavior of the self diffusion coefficient D as a function of $\gamma_1\beta^{-1}$. The scales of the abscissa and ordinates are in arbitrary units.

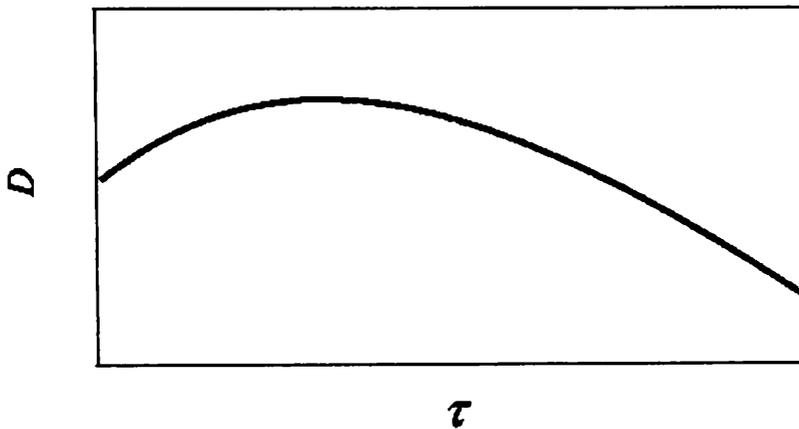


Fig. 3. Typical behavior of the self diffusion coefficient D as a function of the life time τ . The scales of the abscissa and ordinates are in arbitrary units.

§4. Conclusion

An analytical model has been proposed for the VACF and diffusion that incorporates the anharmonicity of the atomic vibration. It is shown that the diffusion coefficient increases when the anharmonic parameter increases.

Acknowledgements

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