Hindawi Publishing Corporation
Physics Research International
Volume 2011, Article ID 645264, 3 pages
doi:10.1155/2011/645264

Research Article

The Effect of the Anharmonicity in a Perturbation Estimate of the Self-Diffusion Coefficient

Takaki Indoh and Masaru Aniya

Department of Physics, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

Correspondence should be addressed to Takaki Indoh, inuwara2006@hotmail.co.jp

Received 30 September 2010; Accepted 24 January 2011

Academic Editor: Nathan Ida

A perturbative expression for the self diffusion coefficient is derived by considering that the particles are executing anharmonic vibrations around the sites with local potential minima and jump to neighbor sites after a certain waiting time. The derived expression is a natural extension of the expression obtained by Zwanzig that assumes harmonic oscillations. The relation between the low frequency oscillation and the deviation from the harmonic behavior is also shown.

1. Introduction

The dynamics of atoms in solids and liquids have been studied for many years. It is well known that the atomic transport properties in materials are described in terms of the velocity autocorrelation function (VACF). The VACF carries the information on the many body interactions of the system. Therefore, its calculation is not straightforward. Usually, the VACF is evaluated numerically with the help of computers. However, for the understanding of the physical essence of atomic transport properties, it is very useful if we have at hand an analytical expression for the VACF or related quantity such as the self diffusion coefficient. In the past, some works have been performed along this spirit [1–3]. Among these, the model proposed by Zwanzig is well known [1]. It has been widely used in the literature [4–6] and extended [7]. To describe the dynamics of ions within the materials, the anharmonic effect is also an important factor. For instance, the mobile ion in superionic conductors execute its motion in an anharmonic potential [8]. Therefore, the understanding of the effect of anharmonicity on the atomic transport is directly connected with the understanding of superionic behavior. Visco and Sen discussed the relation between the anharmonic oscillation effect and the normalized VACF [9]. The effect of anharmonicity on the diffusion in glass forming binary Lennard-Jones systems was discussed by Bordat et al. using molecular dynamics simulations [10]. In this study, we modified the assumption used by Zwanzig by incorporating the effect of the anharmonicity and derive a new perturbative expression for the self diffusion coefficient.

2. Theory

To describe the effect of anharmonicity, a modified version of the Zwanzig model for the self diffusion coefficient is used. The model is based on the following assumptions.

(1) The particles that form the liquid are executing anharmonic vibrations around the positions where the potential is minima. A fixed frequency ω characterizes adequately the anharmonic oscillations.

(2) When the particle diffuses, it jumps in a very short time to a new position which is almost equivalent to the old position. The waiting time distribution for the diffusion is given by $\exp(-t/\tau)$, where τ is the lifetime that reflects the interruption of the normal mode [1].

(3) After the jump, the particle loses its memory.

In our calculation, the effect of the anharmonicity is incorporated through the magnitude of the anharmonicity f. It causes the deviation from the harmonic oscillation and gives a new expression for the lifetime τ.

To discuss the transport property, it is necessary at first to derive the VACF of a particle in an anharmonic potential.

The Hamiltonian for a particle with mass m that executes anharmonic oscillations is given by

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 - \frac{1}{4}mfx^4. \tag{1}$$

Here, p is the particle momentum, ω_0 is the harmonic oscillator frequency as in the Zwanzig model, f is a positive constant that gives the magnitude of the anharmonicity, and x is the displacement of the particle. The equation of motion obtained from the Hamiltonian is

$$\frac{d^2x}{dt^2} + \omega_0^2 x - fx^3 = 0. \tag{2}$$

By solving the equation, we obtain the following expression [9, 11, 12]

$$x(t) = a\sum_{n=0}^{\infty} b_n \sin(2n+1)\omega t, \tag{3}$$

$$\omega = \omega_0 - \frac{3fa^2}{8\omega_0} + O(f^2a^4), \tag{4}$$

where a and b_n are constants. The outline of the derivation is given in the appendix. At this point, it is interesting to note that the expression given by (4) may have connection with the low energy excitation and the high anharmonic behavior that some materials exhibit [13–15]. By using (3) and (4), the VACF of a particle in an anharmonic potential is written as

$$\begin{aligned}\frac{\langle p_i(t)\cdot p_i(0)\rangle}{\langle p_i^2(0)\rangle} = {} & \left(\sum_{n=0}^{\infty} b_n^2(2n+1)^2\right)^{-1} \\ & \times \sum_{n=0}^{\infty} b_n^2(2n+1)^2 \cos[(2n+1) \\ & \times(\omega_0 - 3fa^2/8\omega_0) + O(f^2a^4)\cdot t].\end{aligned} \tag{5}$$

Consider a system that consists of N atoms with mass m. Under the assumptions that the oscillatory component of the VACF is described by (5) and that the waiting time distribution for the particle jump is accounted for by introducing the factor $\exp(-t/\tau)$, the following expression for the VACF of a diffusing particle is obtained. This expression is a new expression, which reduces to the expression derived by Zwanzig in the case where $f = 0$.

$$\begin{aligned}C(t) &= \frac{1}{N}\sum_{i=1}^{N}\frac{\langle p_i(t)\cdot p_i(0)\rangle}{\langle p_i^2(0)\rangle} \\ &= \cos\left[\left(\omega_0 - \frac{3fa^2}{8\omega_0}\right)t\right]\exp\left(-\frac{t}{\tau}\right).\end{aligned} \tag{6}$$

In the derivation, only the leading term of the expansion in (3) was retained. The accuracy of the expression can be improved by considering the higher terms.

By using (6), we obtain the following expression for the self diffusion coefficient D through the Green-Kubo formula

$$D = \frac{k_BT}{m}\int_0^{\infty} C(t)dt = \frac{kT}{m}\frac{\tau}{1 + \left(\omega_0 - (3fa^2)/(8\omega_0)\right)^2\tau^2}. \tag{7}$$

In particular, if $f \ll 1$, we have

$$D = \frac{k_BT}{m}\frac{\tau}{1+\omega_0^2\tau^2}\left(1 + \frac{3}{4}\frac{a^2\tau^2 f}{1+\omega_0^2\tau^2}\right). \tag{8}$$

The first term of (8) is the usual expression used in many works [1, 4, 5] and arises from the harmonic contributions. The second term of (8) is the correction that arises from the contribution of the anharmonicity.

From the Hamiltonian of (1), the maximum value of the potential is $m\omega_0^4/4f$. This potential maxima corresponds to the activation energy. On the other hand, τ^{-1} gives the jumping frequency of a hopping particle. The height of potential and τ^{-1} is usually related as

$$\frac{1}{\tau} = A\exp\left(-\frac{m\omega_0^4}{4fk_BT}\right), \tag{9}$$

where A is a constant. By inserting this expression into (8), we obtain

$$\begin{aligned}D = {} & \frac{k_BT}{m} \\ & \times\left\{\begin{array}{c} A^{-1}\exp\left(\dfrac{m\omega_0^4}{4fk_BT}\right)\cdot\left(1+\omega_0^2A^{-2}\exp\left(\dfrac{m\omega_0^4}{2fk_BT}\right)\right)^{-1} \\ +\dfrac{3}{4}a^2fA^{-3}\exp\left(\dfrac{3m\omega_0^4}{4fk_BT}\right) \\ \cdot\left(1+\omega_0^2A^{-2}\exp\left(\dfrac{m\omega_0^4}{2fk_BT}\right)\right)^{-2}\end{array}\right\}.\end{aligned} \tag{10}$$

At low temperature, (10) becomes

$$D = \frac{k_BT}{m}A\exp\left(-\frac{m\omega_0^4}{4fk_BT}\right)\left(\frac{1}{\omega_0^2} + \frac{3a^2f}{4\omega_0^4}\right). \tag{11}$$

We can note that this expression generalizes the harmonic expression derived by Zwanzig. The anharmonic contribution is expressed by the second term that contains the magnitude of the anharmonicity f.

3. Conclusion

A perturbative expression for the self diffusion coefficient that incorporates the anharmonicity of the atomic vibration has been derived. It is shown that the self diffusion coefficient increases with the magnitude of the anharminicity. In other words, the increase of the anharmonicity results in the decrease of the activation energy. This finding could have implications in diverse topics related to atomic transport,

such as in cases where the interatomic potential is soft or in the cases where the material is disordered. In particular, it should be noted that our model catches the essence of ion transport in superionic conductors. For instance, the derived expression shows clearly that the low frequency oscillation is related to the deviations from the harmonic behavior. The low frequency oscillation is one of the phenomena observed in many superionic conductors.

Appendix

To obtain the frequency ω of a particle in an anharmonic potential we must solve the following equation:

$$\frac{d^2x}{dt^2} + \omega_0^2 x - fx^3 = 0. \tag{A.1}$$

The formal solution of this equation is given by [11, 12]

$$x = a \cdot sn(\Omega(t - t_0), k), \tag{A.2}$$

where a and t_0 are constants, $sn(\dots, \dots)$ is an elliptic function, and

$$\Omega^2 = \omega_0^2 - \frac{1}{2} f a^2, \qquad k^2 = \frac{f a^2}{2\omega_0^2 - f a^2}. \tag{A.3}$$

The elliptic function given in (A.2) is a periodic function of $\Omega(t - t_0)$ and has a 1/4 period given by

$$K(k) = \int_0^{\pi/2} \left[1 - k^2 \sin^2\theta\right]^{-1/2} d\theta. \tag{A.4}$$

By expanding (A.4) in terms of k we obtain

$$K(k) = \frac{\pi}{2}\left[1 + \left(\frac{1}{2}\right)^2 k^2 + \left(\frac{3}{8}\right)^2 k^4 + \cdots\right]. \tag{A.5}$$

Therefore, the adimensional period of (A.2) becomes $\Omega(t_p - t_0) = 4K(k)$, where t_p is a constant that can be chosen in such a way that $t_p - t_0$ is the period. Thus, the characteristic frequency is given as

$$\begin{aligned}\omega &= \frac{2\pi}{t_p - t_0} = \frac{2\pi\Omega}{4K(k)} = \Omega\left(1 - \left(\frac{1}{2}\right)^2 k^2 + O(k^4)\right) \\ &= \omega_0\left(1 - \frac{f a^2}{4\omega_0^2} + O(f^2 a^4)\right)\left(1 - \frac{f a^2}{8 q \omega_0^2} + O(f^2 a^4)\right) \\ &= \omega_0 - \frac{3 f a^2}{8\omega_0} + O(f^2 a^4).\end{aligned} \tag{A.6}$$

References

[1] R. Zwanzig, "On the relation between self-diffusion and viscosity of liquids," *The Journal of Chemical Physics*, vol. 79, no. 9, pp. 4507–4508, 1983.

[2] F. Vauchot, F. Henn, and J. C. Giuntini, "Analytical calculation of the velocity auto-correlation function in ionic solids from a simple model," *Journal of Non-Crystalline Solids*, vol. 307–310, pp. 1060–1063, 2002.

[3] D. C. Wallace, "Liquid dynamics theory of the velocity autocorrelation function and self-diffusion," *Physical Review E*, vol. 58, no. 1, pp. 538–545, 1998.

[4] J. D. Gezelter, E. Rabani, and B. J. Berne, "Can imaginary instantaneous normal mode frequencies predict barriers to self-diffusion?" *Journal of Chemical Physics*, vol. 107, no. 12, pp. 4618–4627, 1997.

[5] E. Rabani, J. D. Gezelter, and B. J. Berne, "Calculating the hopping rate for self-diffusion on rough potential energy surfaces: cage correlations," *Journal of Chemical Physics*, vol. 107, no. 17, pp. 6867–6876, 1997.

[6] D. Bertolini, F. Demmel, and A. Tani, "Temperature dependence of de Gennes narrowing and transport properties of liquid rubidium: experimental and simulation results," *Physical Review B*, vol. 76, no. 9, Article ID 094204, 2007.

[7] H. X. Zhou and R. Zwanzig, "Barrier crossing coupled to a small set of oscillators," *Journal of Physical Chemistry A*, vol. 106, no. 33, pp. 7562–7564, 2002.

[8] J. X. M. Zheng-Johansson and R. L. McGreevy, "A molecular dynamics study of ionic conduction in CuI–II. Local ionic motion and conduction mechanisms," *Solid State Ionics*, vol. 83, no. 1-2, pp. 35–48, 1996.

[9] D. P. Visco Jr. and S. Sen, "Dynamics of an anharmonic oscillator that is harmonically coupled to a many-body system and the notion of an appropriate heat bath," *Physical Review E*, vol. 57, no. 1, pp. 224–229, 1998.

[10] P. Bordat, F. Affouard, and M. Descamps, "Effect of anharmonicity on the diffusion in glassforming binary Lennard-Jones systems," *Journal of Non-Crystalline Solids*, vol. 353, no. 41–43, pp. 3924–3927, 2007.

[11] E. A. Jackson, *Perspectives of Nonlinear Dynamics*, Cambridge University Press, Cambridge, UK, 1991.

[12] H. T. Davis, *Introduction to Nonlinear Differential and Integral Equations*, Dover, New York, NY, USA, 1962.

[13] A. P. Sokolov, "Light scattering by low-energy excitations in glasses," *Physica B*, vol. 219-220, no. 1–4, pp. 251–254, 1996.

[14] M. Aniya, T. Tomoyose, and M. Kobayashi, "Pressure and temperature dependences of the low energy excitation in superionic conductors based on the ionic plasma model," *Physica Status Solidi B*, vol. 196, no. 2, pp. K17–K19, 1996.

[15] T. Sakuma, M. Mutou, K. Ohki, M. Arai, H. Takahashi, and Y. Ishii, "Low-energy excitation in $CsPbX_3$(X=CI,Br)," *Solid State Ionics*, vol. 154-155, pp. 237–242, 2002.