A Note on the Asymptotic Long Time Behavior of the Velocity Autocorrelation Function

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The asymptotic long time behavior of the velocity autocorrelation function (VAF) in the hydrodynamic description is considered. It is shown that the model predicts a peaked behavior in the magnitude of the VAF at a certain value of the diffusion coefficient.

§1. Introduction

Many studies have been conducted during the last few decades in order to understand the dynamics of atoms and ions in solids and liquids. A widely used quantity to describe the dynamics of the particles is the velocity autocorrelation function (VAF).[1),2)] The VAF contains information on the memory, or delay effects of the system. That is, the VAF is associated with the response of the medium when it is perturbed by the motion of a particle. Since the physical processes occurring behind such delay phenomena are in essence of many-body nature, the description and understanding of the VAF is not straightforward. Reflecting this situation, the VAF has been the subject of study for many years.[1)–10)]

It has been recognized that the asymptotic long time behavior of the VAF in a three dimensional system is proportional to $t^{-3/2}$, where t is the time.[4)] Many theories have described such time dependence.[3),5)] The theory proposed by Ernst et al.[5)] is interesting because the VAF is expressed in terms of measurable quantities such as the shear viscosity and diffusion coefficient. In the present report, the implication of this theory will be shown by connecting the theory with a semi-empirical relation between the transport properties.

§2. Asymptotic long time behavior of VAF

The normalized VAF is defined as[1),2)]

$$C(t) = \frac{\langle v_x(t)v_x(0)\rangle}{\langle v_x^2(0)\rangle}, \tag{2.1}$$

where $\boldsymbol{v}(t)$ is the velocity of the particle at time t, and $\langle\cdots\rangle$ denotes the average taken in an equilibrium ensemble. Using hydrodynamic equations, Ernst et al.[5)] have shown that the VAF for a three dimensional system can be written as

$$C(t) \simeq \frac{2}{3n}[4\pi(D+\frac{\eta}{nm})t]^{-3/2}, \tag{2.2}$$

where n is the number density, m is the particle mass, D is the self-diffusion coefficient and η is the shear viscosity. The expression (2.2) is interesting, because it indicates what kind of physical quantities determine the long time behavior of the VAF.

Note that the VAF is proportional to $t^{-3/2}$. This time dependence has been interpreted to result from the pushing effect of the particle movement in a fluid. That is, the diffusing particle would push the other particles ahead when it moves.[4]

It is well known that there is an intimate connection between the self-diffusion coefficient and the shear viscosity of the liquids. Zwanzig has found the following relation[11]

$$\frac{D\eta}{k_B T n^{1/3}} = C', \tag{2.3}$$

where k_B is the Boltzmann constant, T is the temperature and C' is a constant in the range between 0.132 and 0.181. The expression (2.3) is in accord with data on organic liquids.[11] The same equation has been used also to develop a theory of liquids.[12),13]

Inserting Eq. (2.3) into Eq. (2.2), we obtain

$$C(t) \simeq \frac{2}{3n}(4\pi t)^{-3/2} f(D), \tag{2.4}$$

where

$$f(D) = \left(D + \frac{C' k_B T}{m n^{2/3} D}\right)^{-3/2}. \tag{2.5}$$

It is in Eq. (2.5) that we want to pay attention. Among the quantities appearing in Eq. (2.5), it is the self-diffusion coefficient that exhibits the largest material dependence. Therefore, as a first approximation, at a constant temperature, the quantity $mn^{2/3}$ could be considered as a constant. In such a case, $f(D)$ would behave as shown in Fig. 1. That is, the magnitude of VAF at long times would exhibit a peaked behavior at a certain value of the diffusion coefficient.

As far as the authors are informed, a comparative study on the magnitudes of VAF for different materials has not been performed. The result shown in this paper would have important implications in the study of certain materials. One example is a superionic conductor. According to a model for these kind of materials, the large ionic conductivity is related with the correlated ion movement mediated by the electronic cloud deformation.[14)–16] The model predicts that an intermediate bond strength is necessary to generate the correlated ionic motion even in the liquid state.[16)–18] It is probable that the behavior shown in Fig. 1 is related to these facts. However, since the result that we have found resides on the hydrodynamic model of VAF, the validity of the relationship Eq. (2.3) and the constancy of $mn^{2/3}$ at a given temperature, we must be careful in the interpretation of the result. The main objective of the present report is to point out the implications of the hydrodynamic expression of VAF, when coupled with the relationship proposed by Zwanzig.[11]

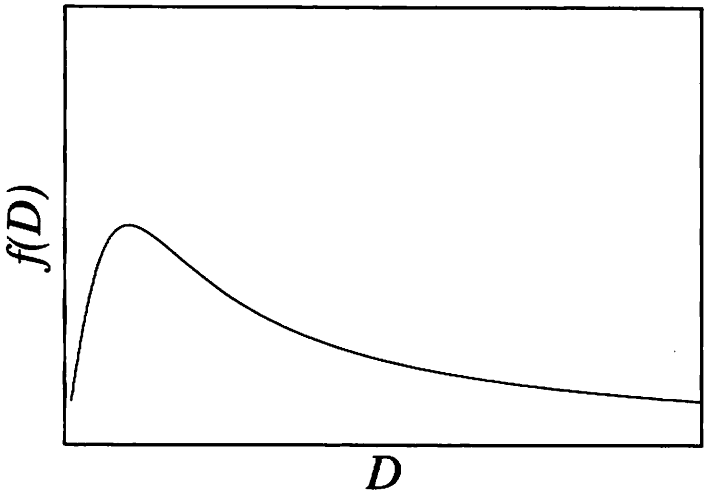

Fig. 1. Schematic behavior of the function $f(D)$.

§3. Conclusion

The VAF plays a fundamental role in the description of atomic dynamics in solids and liquids. In the present report, the long time behavior of VAF[5] in the hydrodynamic description has been considered. By connecting the expression of the VAF with a relationship[11] between the self-diffusion coefficient and shear viscosity, it is shown that the model predicts a peaked behavior in the magnitude of VAF at a certain value of the self-diffusion coefficient.

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