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Shear viscosities of liquid sodium and potassium using Green-Kubo and “first principles” pseudopotential formalisms

N. Harchaoui[a], S. Hellal[a], B. Grosdidier[b], J.G. Gasser[b,*]

[a] *Université Mouloud Mammeri: Laboratoire de Physique et Chimie Quantique (LPCQ), Département de Physique, Faculté des Sciences, 15010 Tizi-Ouzou, Algeria*
[b] *Université de Lorraine: Laboratoire de Chimie et Physique-Approches Multiéchelles des Milieux Complexes (LCP-A2MC), Institut de Chimie, Physique et Matériaux, 1 Bd Arago, 57070 Metz, France*

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ABSTRACT

This article presents an original work on velocity and stress autocorrelation functions, memory functions, spectral densities and atomic transport properties of two liquid alkali metals (sodium and potassium). For this, we carried out molecular dynamics (MD) simulations using Green-Kubo relation under the condition of very long-time duration to obtain reliable and accurate results.

An originality of the present work is that the interatomic forces are described by pair potentials built within the “first principles” pseudopotential formalism using the non-local and energy dependent model potential of Shaw. It is completely free of adjustable parameters since the energy dependent parameters are determined self-consistently at the Fermi energy on an absolute energy scale. The Green-Kubo relationship is the main theoretical tool that allows us determining the atomic transport coefficients from appropriate time-autocorrelation functions. An important new result concerns the memory function. We demonstrate, for the first time to our knowledge, that it can be depicted as a sum of wavelets. The wavelets with their amazing features emphasize the nature of dynamic processes at the microscopic level. We also compared, for the first time to our knowledge, the spectral density associated to the velocity autocorrelation function (VACF), to experimental values obtained by incoherent inelastic neutron scattering. Finally, the temperature dependence of the self-diffusion coefficient (our previous study) and that of shear viscosity (present work) are both in excellent agreement with experiment.

1. Introduction

Atomic transport phenomena certainly have a great importance both from a theoretical point of view as well as for the various technological applications. It is still a relevant research area [1–5]. Indeed, the knowledge of atomic transport coefficients is crucial, as they are input parameters in some hydrodynamic equations [6, 7]. In the past, Green [8] and Kubo [9] gave a famous relationship by which one can evaluate the atomic transport coefficients. This equation, related to the fluctuation-dissipation theorem [10, 11], involves integrals of relevant time autocorrelation functions. Subsequently, many investigators brought important refinements to the theory [12–21]. Progress was particularly stimulated by the development of molecular dynamics simulations [22, 23] as well as by the inelastic neutron scattering experiments [24] or by spin-echo techniques [25]. Such experimental results on dynamical properties are unfortunately very scarce. This is the main reason why we also need conventional methods [26, 27] to determine experimentally the atomic transport coefficients. However, the experimental data are relatively scattered. This is due to the inaccuracy of such experiments [2, 4].

Most physical properties such as those considered in this paper, are very sensitive to interacting forces between particles. It follows that accurate prediction of the atomic transport coefficients by using the Green-Kubo relationship requires precise molecular dynamics (MD) computations of relevant autocorrelation functions [1–4, 22, 23]. Due to the complexity of the atomic dynamics of ions, the interacting forces are described in terms of an “effective” pair potential $V_{eff}(r)$ [1, 28, 29]. In principle, the pair approximation [19] is only valid for simple liquids like alkali metals. For metals that are more complex the concept of “effective” potential corresponds to a pair potential having the same effect that all the interactions (including triplet and higher-order interactions). Within the framework of the theory, it has been shown that there is a relationship between the pair correlation function $g(r)$ and the effective potential $V_{eff}(r)$ [19, 30]. This potential can be derived from electronic structure calculations following the axiomatic principles of the well-documented pseudopotential method [1, 31, 32]. In our work

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[*] Corresponding author.
E-mail address: jean-georges.gasser@univ-lorraine.fr (J.G. Gasser).

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we used the “first principles” Optimized Model Potential (OMP) given by Shaw [31] and its successive improvements. The calculation of the OMP parameters has always been a central problem. Unlike Shaw's original paper that requires the knowledge of experimental values of the ionization and cohesive energies, for our effective potential calculations we obtained the pseudopotential parameters in a self-consistent manner [1, 33]. Importantly we suitably screened the bare model potential, a non-local and energy-dependent operator, following the “first principles” requirements [1, 31, 32]. We used the Ichimaru and Utsumi [34, 35] dielectric function, considered as one of the best. We checked the validity of the OMP model in our previous study on liquid alkali metals [1], in which we determinate their ionic structure and studied the self-diffusion. We already published [1] the important results for the individual transport properties (self-diffusion process). Unlike the viscosity, the diffusion of liquid alkali metals has been systematically studied in the literature [36–45]. We now complement our first work by collective transport properties (viscosity) in the current paper. We also calculate the memory function within the generalized Langevin equation [6, 45, 46] and using our new wavelet expansion [47].

This paper is written as follows. In section 2, we outline the main features of the relevant autocorrelation functions that we used to describe the atomic transport properties. We explicitly highlight the Green-Kubo equation to calculate the Stress Autocorrelation Functions (SACF) for viscosity and spectral density (subsection 2.1). All autocorrelation functions satisfy the generalized Langevin equation (subsection 2.2). Rewritten otherwise, the latter is the Volterra integral equation of the second kind for the so-called memory function. Moreover, we show that the Volterra integral equation admits a formal solution given by wavelet decomposition. In section 3, we detail the conditions under which we performed our molecular dynamics (MD) calculations. We comment upon our most relevant results in section 4. Finally, in section 5, we conclude and summarize the main results of this work.

2. Some theoretical aspects of atomic transport properties

The Green-Kubo relationship [8, 9] that involves integration of appropriate time-autocorrelation functions, leads to the evaluation of transport coefficients. The Green-Kubo integral is one of the many forms of the fluctuation-dissipation theorem [10, 11].

2.1. Time-autocorrelation function and the Green-Kubo formalism

We can express the velocity autocorrelation function (VACF) [7] as the statistical ensemble average:

$$\varphi(t) = \langle \vec{V}(t)\cdot\vec{V}(0)\rangle/3 \tag{1a}$$

where $\vec{V}(t)$ is the velocity of a tagged particle at time t. The corresponding spectral function $\varphi(\omega)$, also called the power spectral density, is defined as the Fourier transform:

$$\varphi(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\varphi(t)\exp(-i\,\omega\,t)\;dt \tag{1b}$$

Similarly, the stress autocorrelation function (SACF) is the result of the following ensemble average:

$$\zeta(t) = \frac{1}{k_B T\,\Omega}\langle\sigma^{\alpha\beta}(t)\sigma^{\alpha\beta}(0)\rangle \tag{2a}$$

where $\sigma^{\alpha\beta}$ are the off-diagonal components of the microscopic stress tensor which involves atomic positions and velocities as well as the pairwise interactions [6, 23]. The terms k_B, T and Ω are respectively the Boltzmann's constant, the absolute temperature and the volume of the system. So, the shear (or dynamical) viscosity is obtained as follows:

$$\eta = \int_0^\infty \zeta(t)dt \tag{2b}$$

The shear modulus $G_\infty(0)$ is given by [19]

$$G_\infty(0) = \zeta(t=0) \tag{2c}$$

The time characteristic known as the Maxwell relaxation time [19] is:

$$\tau_\eta = \eta/G_\infty(0) \tag{2d}$$

Broadly speaking, if $C(t)$ is an autocorrelation function (either $\varphi(t)$ or $\zeta(t)$), one can associate its spectral density $C(\omega)$ and its Laplace transform $\widetilde{C}(z)$. Therefore, we can also get the transport coefficient K (D or η) from the value of this spectral density: $C(\omega = 0) = K/\pi$.

2.2. The generalized Langevin equation and the associated memory function

Motions of atoms in liquids are a stochastic process. The generalized Langevin equation [6, 45, 46] that governs the time evolution of any autocorrelation function $C(t)$ is given by the following integro-differential equation:

$$\dot{C}(t) = -\int_0^t M(t-\tau)C(\tau)d\tau \tag{3a}$$

The commutativity of the convolution product allows writing:

$$\dot{C}(t) = -\int_0^t C(t-\tau)M(\tau)d\tau \tag{3b}$$

The differentiation of (3b) with respect to time leads to the linear Volterra integral equation of the second kind:

$$M(t) = -\ddot{C}_N(t) - \int_0^t \dot{C}_N(t-\tau)M(\tau)d\tau \tag{3c}$$

Now $M(t)$ is the unknown memory function and the kernel of Eq. (3c) is given by $\dot{C}_N(t)$, the first derivative with respect to time of the given normalized autocorrelation function $C_N(t) = C(t)/C(t = 0)$. We can write:

$$M(t=0) = -\frac{\ddot{C}(t=0)}{C(t=0)} \equiv \Omega_0^2 \tag{3d}$$

In the context of diffusion process, Ω_0 is the Einstein frequency. The latter can otherwise be calculated from the radial distribution function $g(r)$ and from the pair potential $V_{eff}(r)$ [6, 19]. Both functions $M(t)$ and $C_N(t)$ (or else $C(t)$) provide the same information, as we will show below.

Indeed, when Eq. (3a) is solved by Laplace transform. We get:

$$\widetilde{C}_N(z) = [-iz + \widetilde{M}(z)]^{-1} \tag{4a}$$

otherwise rewritten:

$$\widetilde{M}(\omega) = i\omega + C(t=0)/\widetilde{C}(\omega) \tag{4b}$$

The “friction like coefficient”, ξ, is defined as:

$$\xi = \int_0^\infty M(t)dt = \frac{C(t=0)}{\widetilde{C}(\omega=0)} \equiv \frac{C(t=0)}{K} \tag{4c}$$

The Volterra integral Eq. (3c) has the formal solution:

$$M(t) = -\ddot{C}_N(t) - \int_0^t R_{es}(t-\tau)\,\ddot{C}_N(\tau)d\tau \tag{5}$$

The resolvent $R_{es}(t)$ in (5) can be expanded in infinite series to yield:

$$M(t) = \sum_{S=0}^{\infty} m_S(t) \tag{6a}$$

We define the memory function calculated at the S-th order by: