The calculation of the viscosity from the autocorrelation function using molecular and atomic stress tensors

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The stress–stress correlation function and the viscosity of a united-atom model of liquid decane are studied by equilibrium molecular dynamics simulation using two different formalisms for the stress tensor: the atomic and the molecular formalisms. The atomic and molecular correlation functions show dramatic difference in short-time behaviour. The integrals of the two correlation functions, however, become identical after a short transient period which is significantly shorter than the rotational relaxation time of the molecule. Both reach the same plateau value in a time period corresponding to this relaxation time. These results provide a convenient guide for the choice of the upper integral time limit in calculating the viscosity by the Green–Kubo formula.

1. Introduction

The viscosity of a simple monatomic fluid system can be calculated in a molecular simulation by integrating the stress–stress correlation function. Where a molecular fluid is concerned, the stress can be calculated based on two different formalisms. One is the atomic formalism, in which the stress tensor is calculated based on the motion of individual ‘atoms’ comprising the molecules in the system:

\[
P^{(a)} V = \sum_{i,a} m_{ia} v_{ia} v_{ia} + \sum_{i,a} r_{ia} f_{ia},
\]

where \(m_{ia}, r_{ia}, v_{ia}\), and \(f_{ia}\) are the mass, position, velocity, and force on atom \(a\) of molecule \(i\). Note that the “atoms” may actually be real atoms (such as H and O in models for water) or be functional groups (such as \(\text{CH}_2\) or \(\text{CH}_3\) in united-atom models of complex molecular fluids). The other is the molecular formalism, in which the stress tensor is calculated based on the motion of the molecules in the system:

\[
P^{(m)} V = \sum_i m_i v_i v_i + \sum_i r_i F_i,
\]

where \(m_i, r_i, v_i\), and \(F_i\) are the mass, centre of mass position, centre of mass velocity, and the total force on molecules \(i\).

The equivalence of the two formalisms in predicting the macroscopic transport properties and pressure has been discussed by a number of authors [1–3]. In particular, Marechal and Ryckaert [2] showed that the difference between the transport coefficients calculated from the atomic and molecular tensor formalisms differ by a term proportional to the inverse square root of the upper integration time limit. However, since the Schwarz inequality was used in the derivation, this term is only an upper limit
on the difference. Their numerical example, carried out for a system of butane using constraint dynamics for fixed bond length, was less unequivocal and was based on a relatively short run by today’s standards (6750 time steps, corresponding to 51·3 ps). Allen [3] showed that the difference between the atomic stress tensor and molecular stress tensor is a tensor $\dot{\theta}$. The atomic stress–stress correlation function, can be expressed as a sum of three terms:

$$\langle p_{ab}^{(a)}(t)p_{ab}^{(a)}(0) \rangle = \langle p_{ab}^{(m)}(t)p_{ab}^{(m)}(0) \rangle + \langle \theta_{ab}(t)\theta_{ab}(0) \rangle + \frac{1}{4} \langle \theta_{ab}(t)\theta_{ab}(0) \rangle,$$

where $p_{ab}^{(a)}$, $p_{ab}^{(m)}$ are the atomic stress tensor and the symmetrized molecular stress tensor, respectively, and the subscript denotes the tensor element. The brackets denote an ensemble average, and $\theta_{ab}$ is the second derivative of the symmetric tensor defined as

$$\theta = \sum_{i,a} m_{ia} \delta r_{ia} \delta r_{ia},$$

where $m_{ia}$ and $\delta r_{ia}$ are the mass and position vector of atom $a$ in molecule $i$ from the centre of mass of the molecule. As pointed out by Allen [3], for a rigid molecule this quantity is equivalent to the mass-weighted orientational order parameter used in standard texts on molecular hydrodynamics and light scattering. The viscosity is obtained by integrating the stress–stress correlation functions (atomic or molecular).

$$\eta = \frac{V}{k_B T} \lim_{T \to \infty} \int_0^T \langle p_{xy}(t') p_{xy}(0) \rangle \, dt'.$$

It is clear that the integration of the second and third terms in equation (3) over time should vanish after long times for the two formalisms to be equivalent. Allen suggested that the second term is fast-decaying and the last term in equation (3), $\langle \theta_{ab}(t)\theta_{ab}(0) \rangle / 4$, may be slow decaying. There are, however, very few detailed numerical studies, and a clear understanding of the time scales involved for the above formula is lacking. This is particularly important for complex molecular systems such as relatively high molecular weight alkanes, for which the integration in equation (5) must be carried out until much more extended times than for simple atomic liquids. A rough estimate of this upper integration limit is the longest relaxation time of the system, which for short chain molecules without entanglement is the rotational relaxation time. Since the accuracy of the calculated transport coefficient depends crucially on the time scale at which the last two terms decay to zero, it is thus necessary to establish the time scale and the applicability of either or both of the two different formalisms in a molecular simulation.

The majority of previous simulations involving molecules were performed using the constraint method by fixing some internal degrees of freedom such as the bond length and bond angle. In such cases, the molecular pressure formalism seems to be a natural and convenient choice. The reversible multiple time algorithm recently developed by Berne and co-workers [4] has gained wide interest as an efficient method for simulating complex molecular systems based on the convenient atomistic approach using a realistic intramolecular potential. It is thus worthwhile to explore the two formalisms in detail to determine the more efficient method to use in calculating the transport and mechanical properties.

In this paper, we present a molecular dynamics calculation of various stress correlation functions and viscosity using the atomic and molecular stress tensor
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Figure 1. Top: Atomic stress–stress correlation function in reduced units. Middle: Correlation function $\langle \theta_{xy}(t) \theta_{xy}(0) \rangle / 4$ of equation (3) in reduced units. Bottom: Molecular stress–stress correlation function (MSCF) and the cross correlation function (CCF) in equation (3) in reduced units.
Figure 2. For legend see facing page.
formalisms. We find that, because of fast vibration of the bond length in a decane molecule, the atomic stress–stress correlation function shows strong oscillatory behaviour. We demonstrate that the second and the third terms in equation (3) decay to zero in a time period much shorter than the rotational relaxation of the system. Our results show that despite an order of magnitude difference between the atomic and molecular stress tensor correlation function at time zero, the integral of the two stress–stress correlations function is identical beyond a small decay time, thus giving clear numerical confirmation of the equivalence of two formalisms in the calculation of the viscosity. However, in practice, the sampling using the molecular stress tensor formalism is less expensive computationally.

2. Model and simulation method

The decane system is modelled by a united atom model, the same as that used in [5]. This model is essentially the same as that used by Siepmann et al. [6] in calculating the phase envelope of alkanes, with the modification that the fixed bond length is replaced by a stiff harmonic bond stretching potential. The intermolecular interaction and the interaction between atoms separated by three or more atoms in the same molecule is described by a Lennard-Jones potential. In addition, the intramolecular interactions consist of bond stretching, bond angle bending, and torsional potentials. The bond stretching and bond angle bending are harmonic potentials, and the torsional potential is that of Jorgenson et al. [7]. The potential form and parameters are given in detail in [5] and [6].

The equations of motion were integrated using a multiple time step technique with Nosé constant temperature dynamics. Details can be found in [4] and [8]. The simulation was carried out at a temperature of 480 K and density of 0.6136 g cm$^{-3}$. A time step of 1.18 fs was used. This rather short time step was used to permit a small time interval in sampling the stress tensor. This was necessary to capture accurately the oscillatory behaviour of the atomic stress–stress correlation function, as will become clear in the next section. A configuration from a previous production simulation was used as the initial configuration for this study [8]. All results presented in this work are from a production run of 2115 ps except as otherwise explicitly stated.

3. Results and discussion

Figure 1 presents the atomic stress–stress correlation function, the corresponding molecular correlation function, the cross term and the last term in equation (3). The dramatic contrast between the atomic and the molecular stress–stress correlation function is that the atomic correlation function shows strong oscillatory behaviour and its value at time zero is about an order of magnitude larger than that of the molecular correlation function; while the molecular stress–stress correlation function is a smoothly decaying function except for a small minimum at $t = 0.19$ ps. The

Figure 2. Top: Viscosity from integrating the atomic (dashed curve) and molecular (solid curve) stress–stress correlation functions as a function of the upper integration limit. The inset shows the short-time behaviour of the integrals. Middle: Integral of the cross correlation function (CCF). It has been appropriately scaled by the factor $V/k_B T$ to give the corresponding contribution to viscosity for comparison with top figure. Bottom: Integral of the third term on the RHS of equation (3) (including the factor 1/4). The same multiplication factor $V/k_B T$ has been applied for comparison.
oscillatory behaviour of the atomic stress–stress correlation function is due largely to the third term in equation (3), as can be seen by a comparison of parts (a) and (b) of figure 1. Besides the dominant frequency, it can be seen that several slower frequencies exist in a correlation function of the atomic stress tensor, which result in the modulated behaviour of the correlation function. A more detailed analysis of these frequencies is given below. Figure 1 (c) shows the correlation function of the molecular stress tensor and the cross term in equation (3). It is seen that the cross term starts with a negative value at $t = 0$ and reaches a maximum at about $t = 0.18$ ps and decays to zero at about 0.5 ps. The molecular stress correlation function, on the other hand, shows a persistent positive tail which, although small, remains recognizable. In fact, it decays to zero only after a long time, about 10 ps, corresponding to the rotational relaxation time of the system.

Figure 2 (a) shows the viscosity calculated by integrating the atomic and molecular correlation function as a function of the upper integral time limit $T$ in equation (5). The figure shows that after a short initial transient time of about 3 ps the atomic and the molecular viscosity become essentially identical. The integration reaches a plateau in about 10 ps. Both the atomic and the molecular tensor formalisms give a value of $\sim 190 \times 10^{-6}$ Pa s, which agrees with previously published equilibrium [5,8] and non-equilibrium [8] results. The corresponding contribution from the cross term and the last term of equation (3) are plotted in figure 2(b) and (c). It can be seen that the integrals quickly converge to zero. The contribution from the cross term converges to zero in about 0.5 ps, while the contribution from the last term converges to zero in about 3 ps. These times are much shorter than the orientational relaxation time of the system, 10.2 ps, which was obtained from the slope of figure 3, the relaxation function of the end-to-end orientation vector of the decane molecule versus time $t$ in a semi-log plot (the result shown in this figure was obtained from an independent run of 176 ps). This value agrees also with independent calculation by other authors [9].

To understand further the origin of the oscillatory behaviour in the atomic stress–stress correlation function, we determined the frequency spectrum of the atomic

Figure 3. Correlation of the end-to-end orientation vector as defined by the unit vector from atom 1 to atom 10 of the decane molecule. The semi-log plot shows the exponential relaxation of the orientation of the molecule.
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Figure 4. Spectrum of the atomic stress–stress correlation function. The strong peak corresponds to the dominant oscillatory frequency in the correlation function. The inset is a magnified version to show the weaker peaks.

stress–stress correlation function by Fourier transformation of the function into the frequency domain. Figure 4 shows the result of this transformation. The strong spike at 43.7 ps\(^{-1}\), which corresponds to a vibrational period of 0.023 ps, can be identified with the strong oscillatory frequency of figure 1 (a) by inspection. We attribute this strong peak to the bond vibrational frequency between two neighbouring united atoms of the model alkane molecule. In the harmonic oscillator approximation, using the bond vibration force constant \( k/k_B = 452900 \text{ K Å}^{-2} \), where \( k_B \) is the Boltzman constant, and the mass of \( m = 14 \text{ amu} \) for a CH\(_2\) group, the bond vibrational frequency is estimated to be \( (\sqrt{k/k_B})/2\pi = 36.9 \text{ ps}^{-1} \), where \( \mu \) is the reduced mass of the two CH\(_2\) groups forming a bond. This gives a vibrational period about 0.027 ps, slightly larger than the observed period in the atomic stress–stress correlation function, probably due to the effect of other atoms on the alkane chain and the surrounding chains. The inset in figure 4 shows the details of other smaller peaks of the spectrum on an enlarged scale. An exact identification of the peaks in the figure, however, is beyond the scope of this paper.

In summary, we have presented in this short article numerical results confirming that the molecular and atomic stress tensor formalisms are equivalent in the calculation of the viscosity by the Green–Kubo formula. In particular, the difference between the viscosity calculated from the molecular tensor and that from the atomic tensor converges to zero faster than the longest relaxation time, the rotational relaxation time for the relatively short alkane chains studied in this work. The short-time behaviour of the atomic stress–stress correlation function is dominated by the strong oscillatory behaviour due to the bond stretching vibration. We conclude that, for practical purposes, the molecular tensor formalism should be more efficient since it allows the use of a relatively larger time interval.

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