Comment on "Computation of the viscosity of a liquid from time averages of stress fluctuations"

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In a recent paper, Hess and Evans [Phys. Rev. E **64**, 011207 (2001)] propose a method different from the conventional Green-Kubo and Einstein methods to calculate viscosity in equilibrium molecular dynamics simulations. For a comparison, we calculate the shear viscosity of SPC/E water at 303 K using these three different methods. We find that the Hess-Evans method is not as good as the other two in practical application, especially for the fluids with high viscosity and complicated relaxation.

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Recently, based upon equilibrium molecular dynamics (EMD) simulations, Hess and Evans [1] have proposed a method to calculate shear and bulk viscosities from ensemble averages of the mean square of time averages of the stress fluctuations. The authors declare the method to be intermediate between the conventional Green-Kubo method and Einstein method. They also demonstrate the validity of their method by the agreement of viscosity results obtained by their method with those from nonequilibrium molecular dynamics (NEMD) simulations [2]. However, Hess and Evans [1] do not compare their method directly with the Green-Kubo and Einstein methods that are the standard methods to obtain viscosity and other transport properties in EMD simulations. In this paper, we compare in detail these three different EMD methods, and find some limitations of the Hess-Evans method in practical application.

We first compare the formulas of the Einstein method and the Hess-Evans method. Usually, according to Refs. [3–5], the Einstein method obtains shear viscosity by

$$\eta_E=\frac{V}{2k_BT}\frac{d}{dt}\langle[\Delta G(t)]^2\rangle \quad (t\to\infty), \tag{1}$$

where V is the volume, T the temperature, and k_B the Boltzmann's constant. $\langle[\Delta G(t)]^2\rangle$ is the so-called mean square displacement (MSD) of $G(t)$, similar to MSD for diffusion coefficient, and

$$\Delta G(t)=\int_0^t dt'\,\sigma(t'), \tag{2}$$

where σ is the off-diagonal elements of the stress tensor. The Hess-Evans method [1] obtains shear viscosity using a formula

$$\eta_{HE}=t\frac{V}{2k_BT}\langle\overline{\sigma}(t)^2\rangle \quad (t\to\infty), \tag{3}$$

where $\overline{\sigma}(t)$ is the time-segment (i.e., t, an interval between t' and $t'+t$) average of stress fluctuations and is defined as

$$\overline{\sigma}(t)=\frac{1}{t}\int_0^t dt'\,\sigma(t'). \tag{4}$$

In addition, for arbitrary t, $\eta_{HE}(t)$ is defined as an effective viscosity according to Ref. [6], and the effective viscosity reduces to dynamical viscosity in the limit of $t\gg\tau$ with τ means relaxation time. Comparing Eqs. (2) and (4), one will get

$$\overline{\sigma}(t)=\frac{1}{t}\Delta G(t), \tag{5}$$

and so Eq. (3) changes to

$$\eta_{HE}=\frac{V}{2k_BT}\frac{1}{t}\langle[\Delta G(t)]^2\rangle \quad (t\to\infty). \tag{6}$$

Both Eq. (6) and Eq. (1) are formal expressions of Einstein relation [3–5,7–9] and they lead to the same result in the limit of $t\to\infty$. However, Eq. (6) and Eq. (1) display different asymptotic behaviors in practical application because $\langle[\Delta G(t)]^2\rangle$ increases nonlinearly at initial time (see Fig. 1 and the Fig. 1 in Ref. [4]). The nonlinear increment of the MSD of $G(t)$ for viscosity resembles the initial nonlinear increment of MSD for diffusion coefficient, which is caused by cage effects. Because the initial part of the curve bends downward (Fig. 1), one can easily deduce that $\eta_{HE}(t)$ is always smaller than $\eta_E(t)$ according to Eqs. (1) and (6) and approaches to $\eta_E(t)$ in the limit of $t\to\infty$.

In our previous paper [10], which calculates both shear and bulk viscosities of water by using the Green-Kubo method, we totally carry out 20 independent runs with each lasting 200 ps in order to improve the precision of viscosity results. The large quantities of stress data recorded can thus be used to calculate viscosities by applying the three different methods mentioned above for a comparison. Take the shear viscosity as an example, we find that the initial part of $\langle[\Delta G(t)]^2\rangle$ is indeed nonlinear (Fig. 1), which agrees with the results of Ref. [4]. Then, we calculate the differentiation of the curve in Fig. 1 to obtain $\eta_E(t)$ and the ratio of $\langle[\Delta G(t)]^2\rangle$ to time to obtain $\eta_{HE}(t)$. We plot $\eta_E(t)$ and $\eta_{HE}(t)$ in Fig. 2 together with $\eta_{GK}(t)$ calculated using the Green-Kubo method [10]. Obviously, $\eta_E(t)$ and $\eta_{GK}(t)$ are equivalent, and they give a consistent shear viscosity value of $6.5\pm0.4\times10^{-4}$ Pa s at the beginning of plateau located at

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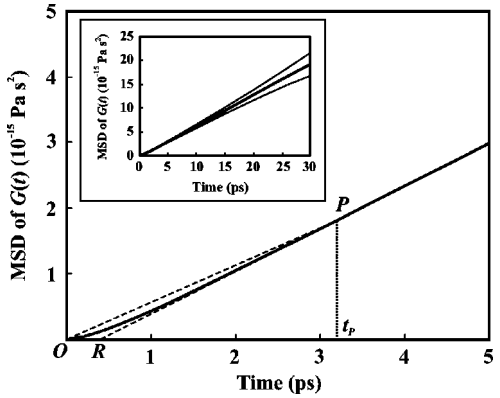

FIG. 1. MSD of $G(t)$ (thick solid line) for SPC/E water at 303 K. Given an arbitrary point P on the curve $\eta_{HE}(t_P)$ the slope of line PO, is always smaller than $\eta_E(t_P)$, the slope of tangential line PR. The inset shows the MSD of $G(t)$ up to 30 ps and the thin solid lines in it are the MSD of $G(t)$ plus and minus its error 2σ, respectively. Note the MSD of $G(t)$ in the figure has been multiplied by a factor of $V/2k_BT$.

3.2 ps. However, $\eta_{HE}(t)$ is very different from $\eta_E(t)$ and $\eta_{GK}(t)$. It increases with time and approaches toward the plateau value of 6.5×10^{-4} Pa s at much longer time ranges. In other words, the rate of $\eta_{HE}(t)$ approaching to the plateau value is much slower than that of $\eta_{GK}(t)$ and $\eta_E(t)$.

From a theoretical point of view, in the limit of $t\rightarrow\infty$, the Hess-Evans method can report a correct value of viscosity. However, for practical application, the Hess-Evans method shows some disadvantages. In Fig. 2, the statistic uncertainties of $\eta(t)$ shown by the error curves increase steadily with time because less and less stress data are available for the calculation of $\eta(t)$ at longer time due to the always limited lengths of EMD simulations. As for the Green-Kubo and Einstein methods, one can obtain high precision and high accuracy viscosity results at short time interval because of the appearance of a plateau. However, the Hess-Evans

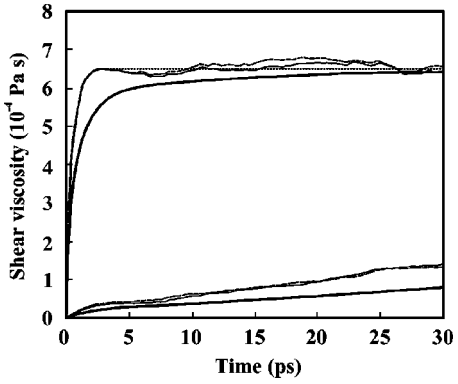

FIG. 2. Shear viscosity calculated by different methods. $\eta_{HE}(t)$ is thick solid line, $\eta_E(t)$ is thin solid line, and $\eta_{GK}(t)$ is thin dashed line. Their errors 2σ are also shown as functions of time on the underside of the figure. The dotted line is the common plateau of $\eta_E(t)$ and $\eta_{GK}(t)$, which begins from 3.2 ps [10].

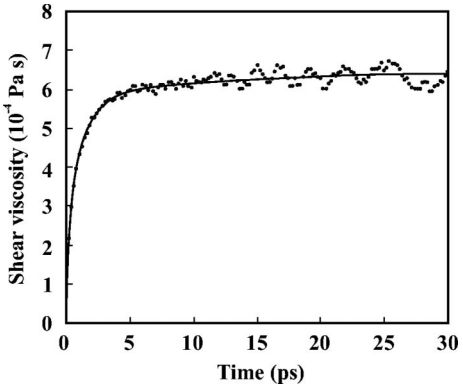

FIG. 3. Fluctuations of $\eta_{HE}(t)$ calculated by different statistical procedures. The dots are calculated according to the authors' procedure. The solid line, which is the same as the thick solid line in Fig. 2, is calculated according to our procedure (also see text).

method is not the case. If we take the values of $\eta_{HE}(t)$ at 6 ps ($\gg\tau=0.065$ ps according to Ref. [11]) and at 30 ps, we will get shear viscosity of $6.0\pm0.3\times10^{-4}$ Pa s and $6.4\pm0.8\times10^{-4}$ Pa s, respectively (Fig. 2). Compared with the results of the Green-Kubo and Einstein methods, the former value shows high precision but low accuracy while the later shows high accuracy but low precision. If one wants to improve the precision of viscosity value without losing its accuracy so that the Hess-Evans method can report a value as good as the other two methods, more extra EMD simulations have to be done.

Additionally, we notice that the statistics of the viscosity calculations of Ref. [1] is poor. Hess and Evans [1] carry out only one simulation with $240\,000\delta t$, while we carry out 20 independent runs with each run lasting $2\,000\,000\delta t$. The authors calculate and average shear viscosity from three stress components, while we collect five independent stress components [10]. Moreover, the number of blocks which they evaluate to obtain ensemble average of $\langle\overline{\sigma(t)}^2\rangle$ is too small. For instance, when the authors calculate $\langle\overline{\sigma(t)}^2\rangle$ at $t/t_{ref}=20.0$ based on 1920 stress data with time intervals of $0.5t_{ref}$, they evaluate only 48 [$=1920/(20/0.5)$] blocks with different initial time t_0. In fact, to improve statistics, we believe that 1880 ($=1920-20/0.5$) blocks with different t_0 should have been evaluated. We check these two different statistical procedures using the same stress data of ours. The results (Fig. 3) show clearly that our $\eta_{HE}(t)$ increases with time smoothly, while the authors' $\eta_{HE}(t)$ increases with time accompanying larger and larger fluctuations.

Now, it is necessary to compare the simulation systems studied by the authors and by us. The authors study a fluid (well above critical point) with low viscosity and simple relaxation, while we study a fluid (well below critical point) with high viscosity and complicated relaxation. In detail, the stress autocorrelation function of the authors' system is simply an exponential function [6], while that of our system is described by two complicated nonexponential functions [11]. Because of the difference in relaxations between these two simulated systems, to calculate viscosity using Hess-Evans method may be good enough in the authors' system despite

the poor statistics of $\langle \overline{\sigma}(t)^2 \rangle$ but it is not good enough in our system when compared with the results obtained by using Green-Kubo and Einstein methods.

In conclusion, the Hess-Evans method is correct to calculate viscosity theoretically but it shows some disadvantages in practical applications. Because the rate of $\eta_{HE}(t)$ approaching to the asymptotic value of viscosity is slower than that of $\eta_{GK}(t)$ and $\eta_E(t)$, while the errors of these $\eta(t)$ increase with time, the viscosity reported by Hess-Evans method is less precise than those by Green-Kubo and Einstein methods, especially for the fluids with high viscosity and complicated relaxation.

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