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### Communications

#### Molecular Dynamics Simulations on Thermodynamic and Structural Properties of Benzene Derivatives 1 – The Shear Viscosity of Benzene and Toluene

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We reported the experimentally measured viscosity of benzene and its derivatives under the pressure of 1 through 1,000 bar at 20 °C and 60 °C, respectively.<sup>1</sup> Viscosity was considered as the shear free energy and plotted against the pressure. Benzene has the different slope of the viscosity curve in contrast to substituted benzenes, chlorobenzene and toluene. The slope was interpreted as the free volume under the experimental conditions, assuming the thermodynamic relation,  $V = \left(\frac{\partial G}{\partial P}\right)_T$ .<sup>2</sup>

The shear viscosity is the transport coefficient of the momentum flux along the velocity gradient, which characterizes the macroscopic flow of molecular systems. One should be able to understand the molecular nature of the momentum flux in terms of molecular interactions and the dynamical structure of the molecular liquid. Furthermore, molecular dynamics simulations enable us to examine molecular systems at experimentally inaccessible physical states, e.g., at extremely low and high temperature and pressure. In our simulation of benzene at a supercritical state, we observed molecular ordering at extremely high pressure. Before we undertake the systematic simulations computing the shear viscosity of benzene derivatives at the supercritical state, we must address two questions. One is the validity of molecular mechanical parameters and the other is the formulation of the shear viscosity. Given a set of published parameters for benzene and toluene, we have devised a computational scheme with using the available molecular dynamics code. Three different formulations are implemented and examined. In our preliminary calculation, a modified Einstein formula yields experimental data.

216 benzene or toluene molecules were generated in a cubic periodic boundary under the experimental conditions, i.e., 1 bar and 20 °C and 60 °C, respectively. The molecular mechanical parameters of benzene and toluene were obtained from the standard CHARMM (Chemistry at HARvard Macromolecular Mechanics) 22 all hydrogen parameter set.<sup>3-4</sup> The system was heated from 100 K to 1500 K by 10 K in every 0.1ps and equilibrated at 1500 K in the 25ps dynamics simulation. It was then cooled to and equilibrated at 293.15 K employing the same dynamics protocol as the heating dynamics. This procedure generated equilibrated coordinates of the 216 molecules at 293.15 K and 1 bar. The constant temperature and pressure molecular dynamics simulation was carried out for 100ps and coordinate and velocity trajectories were saved in every 0.1ps. For 60 °C simulations, the 293.15 K equilibrated coordinates were used to initiate the constant temperature and pressure dynamics at 333.15 K.

Atomic coordinates and velocities were converted to COM coordinates and velocities of each molecules. CHARMM interaction energy routines were used to evaluate the force exerted on each molecule by all other molecules in the system. A user subroutine interface to the CHARMM program system was written to generate  $x, y, z, v_x, v_y, v_z, f_x, f_y,$  and  $f_z$  trajectories.

There are two equivalent formulae for the shear viscosity calculation using molecular dynamics trajectories. The Green-Kubo formula relates the shear viscosity  $\eta$  to the time correlation function of the off-diagonal elements of the stress tensor.<sup>5</sup>

$$\eta = \frac{1}{Vk_B T} \int_0^\infty \langle \eta_{\alpha\beta}(t) \eta_{\alpha\beta}(0) \rangle dt \quad (1)$$

$k_B$  is the Boltzmann constant,  $V$  is the volume and  $T$  is the absolute temperature of the system. The angular bracket in Eq. (1) denotes an average over time origins.  $\eta_{\alpha\beta}$  is the stress tensor element ( $\alpha, \beta = x, y, z$ ).

$$\eta_{\alpha\beta}(t) = \sum_i^N m_i v_{i\alpha}(t) v_{i\beta}(t) + \sum_{i \neq j}^N [\beta_j(t) - \beta_i(t)] F_{ij\alpha}(t) \quad (2)$$

where  $F_{ij\alpha}(t)$  is the force component on molecule  $i$  by molecule  $j$  and the summation is over all  $N$  molecules. However the autocorrelation function may contain the long time tails, which make the evaluation complicated.

The Einstein formula is an attractive alternative as it does not require the force on each molecule.<sup>5</sup>

$$\eta = \lim_{t \rightarrow \infty} \frac{1}{2Vk_B T} \frac{d}{dt} \langle [G_{\alpha\beta}(t) - G_{\alpha\beta}(0)]^2 \rangle \quad (3)$$

where

$$G_{\alpha\beta}(t) = \sum_i^N m_i v_{i\alpha}(t) \beta_i(t) \quad (4)$$

Because  $G(t)$  is not continuous under periodic conditions, we must utilize its derivative.<sup>5,6</sup>

$$\Delta G_{\alpha\beta}(t) = G_{\alpha\beta}(t) - G_{\alpha\beta}(0) = \int_0^t G'_{\alpha\beta}(\tau) d\tau \quad (5)$$

where the time derivative of  $G(t)$  is given by

$$G'_{\alpha\beta}(t) = \sum_i^N m_i v_{i\alpha}(t) v_{i\beta}(t) + \sum_i^N \alpha_i(t) f_{i\beta}(t) \quad (6)$$

Note that  $f_i$  is the total force on molecule  $i$ .

We evaluate the derivatives from the molecular dynamics trajectories and integrate over time to generate the stress tensor elements. Six shear viscosity components obtained using  $xy$ ,  $xz$ ,  $yx$ ,  $yz$ ,  $zx$ , and  $zy$  stress tensor elements in Eq. (3) respectively are averaged to yield the resultant shear viscosity. We used the last 20ps coordinate, velocity and force data of 100ps simulation trajectories.

**Table 1.** Shear Viscosity and Diffusion Constant of Benzene and Toluene<sup>a</sup>

	Unit	Benzene		Toluene	
$T$	K	293.15	333.15	293.15	333.15
$\eta$	cP	0.6869 (0.6300)	0.4567 (0.4110)	0.4451 (0.5980)	0.2775 (0.3884)
$D$	$\text{\AA}^2/\text{ps}$	0.3269	0.6223	0.2085	0.4463
$D\eta/T$	$10^{15}$ N/K	7.6598	8.5308	3.1657	3.7175

<sup>a</sup>The experimental shear viscosity from Ref. 1 is given in the parentheses. The pressure is 1 bar.

The shear viscosity is listed in Table 1 with the diffusion constant. The diffusion constants are evaluated from the mean square displacement using the Einstein formula.<sup>5</sup> The mean square displacements of the center of mass coordinate of 216 molecules are averaged to yield the diffusion constant.

$$D = \lim_{t \rightarrow \infty} \frac{1}{6} \frac{d}{dt} \langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle \quad (7)$$

Although the sampling is performed with the relatively short trajectories, the experimentally measured shear viscosity is well reproduced. As the 216 molecular system may not warrant a stationary, homogeneous and uniform fluid, the statistical precision is improved by averaging over all six off-diagonal stress tensor components. While the shear viscosity of benzene is slightly overestimated than the experimental result, that of toluene is underestimated from the trajectory used in this work. The shear viscosity of benzene is calculated within 10% of the experimental values. Following the Stokes-Einstein law, the molecular dynamics simulation yields near constant  $D\eta/T$ .<sup>2</sup>

The shear stress calculation necessarily involves the entire system. Therefore we must improve the statistical precision of the shear viscosity by sampling over long-time simulations, e.g. over 1ns. The 100ps trajectories of this work may not be long enough to warrant an equilibrium state. Although extended simulations are in progress, the current results indicate that the modified Einstein formula of Eqs. (3), (5) and (6) is robust in estimating the shear viscosity of molecular fluids.

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