Probe Molecule Diffusion in Small Normal and Isomeric Alkanes: An Equilibrium Molecular Dynamics Simulation Study

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Understanding diffusion and measuring diffusion constants of molecules in liquids are fundamental problems in statistical mechanics and the physics of the liquid state. They are important for basic and applied problems in physical chemistry and biology since many processes are diffusion limited. It is well known that the diffusion constant D of a large and massive particle (probe) of radius σ immersed in a solvent of much smaller and lighter molecule is related to the solvent viscosity by the Stokes-Einstein (SE) equation

$$D = \frac{k_{\mathrm{B}}T}{f\pi\eta\sigma} .$$ (1)

where k_{B} is the Boltzmann constant, T the absolute temperature, and $f = 6$ and 4 for the stick and slip limits, respectively. This relation has been verified experimentally in greate detail[1] and is theoretically well understood through Brownian particle dynamics.[2] If, however, the solute size and mass are comparable to those of the solvent molecules, then Eq. (1) is not expected to be valid, and a microscopic approach becomes necessary. Such investigation have been made possible only with computer simulations and theoretical studies in which solute size and mass can be varied independently.

In the simple Langevin theory of Brownian dynamics the diffusion constant D of a Brownian particle is related to the friction constant ξ exerted by the solvent molecules on the Brownian particle by the Einstein relation[3]

$$D = \frac{k_{\mathrm{B}}T}{\xi} .$$ (2)

and a microscopic expression for the friction constant has been obtained through a Green-Kubo formula by Kirkwood[4] in the form

$$\xi = \frac{1}{\tau_r} = \frac{1}{3k_{\mathrm{B}}T} \int_0^{\tau_o} \langle \mathbf{f}_i(t) \cdot \mathbf{f}_i(0) \rangle dt .$$ (3)

where $\mathbf{f}_i(t) = \mathbf{F}_i(t) - \langle \mathbf{F}_i(t) \rangle$. $\mathbf{F}_i(t)$ is the total force exerted on molecule i, and τ_r is the macroscopic relaxation time of the integrand. The expression in the integral is the auto-correlation function of the force exerted on the Brownian particle by the solvent molecule. This expression for ξ vanishes if the upper bound in the integral is set to infinity.[3] The introduction of a cutoff time τ_o was the solution to this problem given by Kirkwood, who assumed that the integral of the force auto-correlation fuention versus the upper bound presented a plateau region where it was almost independent

of the precise value of τ_o. The friction constant could then be evaluated from this plateau region. Lagr'kov and Sergeev[5] have proposed to choose as τ_o the first zero of the force auto-correlation function.

In a recent note,[6] we reported equilibrium molecular dynamics (MD) simulations for the systems of small normal and isomeric alkanes - normal butane and isobutane, normal pentane and isopentane, and normal hexane and isohexane. The primary study goal was to analyze the diffusion and viscosity dynamics of small normal and isomeric alkanes at different temperatures.

Molecular Models and MD Simulation Methods

In the present note, we have carried out equilibrium MD simulations for the systems which consist of a Lennard-Jones (LJ) particle and 100 small normal or isomeric alkanes to calculate the diffusion constants of LJ particle with molecular weight of 225 g/mole in the alkane matrices. The LJ particle modeled for the methyl yellow (MY) interacts with all the interaction sites of the alkane molecules with the LJ potential parameters of $\sigma = 6.0$ Å and $\varepsilon = 0.6$ kJ/mol. Each simulation was carried out in the NVT ensemble; the lengths of cubic simulation boxes were obtained from the experimental densities[7] for given temperatures of 248, 273 and 298 K. The usual periodic boundary condition in the x-, y-, and z-directions and the minimum image convention for pair potential were applied. Gaussian isokinetics was used to keep the temperature of the system constant.[8] We used a united atom (UA) model for alkanes, that is, methyl and methylene groups are considered as spherical interaction sites centered at each carbon atom. The bond bending interaction was also described by a harmonic potential with an equilibrium angle of 114° and a force constant of 0.079187 kJ/mol/degree^2. The torsional interaction was described by the potential developed by Jorgensen *et al.*[9] The bond-stretching was governed by a constraint force which keeps intramolecular nearest neighbors at a fixed distance. The advantage for this is to increase the time step as 5 femto-seconds with the use of RATTLE algorithm.[10] This model was used in the previous simulation studies.[11-15] For the time integration of the equations of motion, we adopted Gear's fifth-order predictor-corrector algorithm.[16] After a total of 1,000,000 time steps (5 nano-seconds) for equilibration, the equilibrium properties were then averaged over 10 blocks of 200,000 time steps (1 nano-seconds). The configurations of

all the molecules for further analyses were stored every 10 time steps (0.05 pico second) which is small enough for the tick of any time auto-correlation functions.

Diffusion constant (D) can be obtained through two routes: the Green-Kubo formula from velocity auto-correlation functions (VAC):

$$D = \frac{1}{3} \int_0^\infty \langle v_i(t) \cdot v_i(0) \rangle dt \qquad (5)$$

and the Einstein formula from mean square displacements (MSD):

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d\langle |r(t) - r(0)| \rangle^2}{dt}. \qquad (6)$$

Shear viscosity is calculated by a modified Green-Kubo formula for a better statistical accuracy[17,18]:

$$\eta = \frac{V}{kT} \int_0^\infty dt \sum_i \langle P_{i\alpha\beta}(0) P_{i\alpha\beta}(t) \rangle , \qquad (7)$$

where $P_{i\alpha\beta}$ is the $\alpha\beta$ component of the molecular stress tensor. P_i, of particle i by translational motion:

$$P_{i\alpha\beta}(t) = \frac{1}{V} \left[m v_{i\alpha}(t) v_{i\beta}(t) + \sum_{j \neq i} r_{ij\alpha}(t) f_{ij\beta}(t) \right], \qquad (8)$$

where $\alpha\beta$ = xy, xz, yx, yz, zx, or zy.

Results and Discussion

Self-diffusion constants and viscosities of normal and isomeric alkanes are obtained from Eqs. (6) and (7). We compare the results of self-diffusion constants (D) and viscosities (η) of normal and isomeric alkanes before and after the insertion of the probe molecule into the alkane matrices. We plot in Figure 1 the log-log plot of self-diffusion constant (D) versus molecular mass (M) and that of viscosity (η) versus M at 273 K. The insertion of the probe molecule with mass of 225 g/mol and diameter of 6.0 Å causes the increment of viscosity of normal alkanes (C4-C6) by 7.5% and isomeric alkanes by 8.2%, and the decrement of self-diffusion constant of normal alkanes by 8.2% and
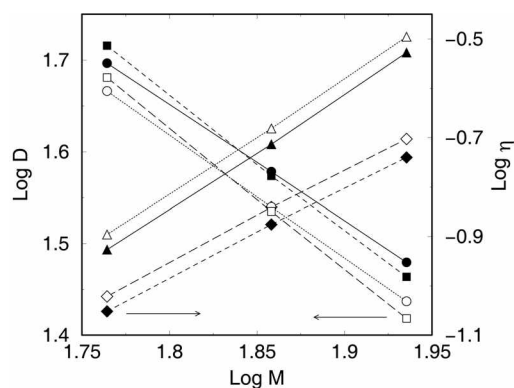

Figure 1. Log-log plot of D (10^{-6} cm²/sec) *vs.* M (g/mol) and that of η (cp) *vs.* M at 273 K. ●: D of normal alkanes, ■: D of isomeric alkanes, ▲: η of normal alkanes, and ◆: η of isomeric alkanes before (black) and after (white) the insertion of the probe molecule.

Table 1. Comparison of the probe diffusion constant (D_{MY}) in normal and isomeric alkanes. C4n and C4i indicate normal butane and isomeric butane, respectively, and etc.

D_{MY} obtained from Eq. (6) :						
T	C4n	C5n	C6n	C4i	C5i	C6i
248.15	4.084	3.612	3.483	4.604	4.005	3.612
273.15	5.188	4.580	4.019	5.691	5.024	4.894
298.15	6.220	5.690	5.283	7.013	6.239	5.869

D_{MY} obtained from Eq. (2) :						
T	C4n	C5n	C6n	C4i	C5i	C6i
248.15	4.254	3.980	3.735	4.759	4.403	4.112
273.15	5.284	4.823	4.483	5.962	5.346	4.976
298.15	6.512	5.894	5.302	7.554	6.668	6.050

D_{MY} obtained from Eq.(1) with f = 6:						
T	C4n	C5n	C6n	C4i	C5i	C6i
248.15	1.582	0.928	0.751	2.311	1.435	0.955
273.15	2.622	1.599	1.043	3.500	2.308	1.679
298.15	4.080	2.461	1.620	5.043	3.406	2.407

isomeric alkanes (C4-C6) by 8.7% since the system volumes of MD simulation remain constant before and after the insertion of the probe molecule into the alkane matrices. The trend of self-diffusion constant and viscosity of normal and isomeric alkanes along the molecular weight is not changed but only absolute value of each property is increased or decreased. As shown in Figure 1. the exponents in the plots of $D \sim M^{-\alpha}$ and $\eta \sim M^{-\beta}$ are also almost equal before and after the insertion of the probe molecule.

The probe diffusion constant (D_{MY}) in normal and isomeric alkanes is evaluated from the mean square displacement (MSD) through the Einstein formula, Eq. (6). Since only one molecule of the probe is considered in the MD simulations. the statistical treatment for D_{MY} is much poorer than that for D of the alkane matrices. The results are gathered in the first set of Table 1. As expected from the comparison of viscosities of normal and isomeric alkanes at 273 K in Figure 1. D_{MY} in isomeric alkanes is greater than that in normal alkanes at three different temperatures.

We also calculated the friction constants of the probe molecule through the Green-Kubo formula by Kirkwood. Eq. (3).[4] The force auto-correlation (FAC) function of the probe molecule obtained from our MD simulations shows a well-behaved smoothly decaying curve (not shown). The initial decay is very rapid. occurring in a time ~0.3 ps. while a subsequent long tail decays only after several ps. It is notorious that the calculation of friction constant from the force auto-correlation function is very hard due to the non-decaying long-time tails. As Kubo pointed out in his "fluctuation-dissipation theorem".[19] the correlation function of random force **R** will decay in a time interval of τ_c (microscopic time or collision duration time). whereas that of the total force **F** has two parts. the short time part or the fast part similar to that of the random force and the slow part which should just cancel the fast part in the time integration.[20] This means that the time integral of Eq. (3) up to $\tau_o = \infty$ is equal

to zero. The time integral in Eq. (3) attains a plateau value for τ_o satisfying $\tau_c \ll \tau_o \ll \tau_r$. if the upper limit of the time integral, Eq. (3), is chosen that $\tau_c \ll \tau_o \ll \tau_r$ because the slow tail of the correlation function is cut off. However, we were unable to get the plateau value in the running time integral of the force auto-correlation function. Kubo suggested that the friction constants should be obtained from the random FAC function not from the total FAC and that there exists a difficulty to separate the random force part from the total force.[19] We could obtain the friction constants by the time integral of the total FAC choosing the upper limit of τ_o as the time which the FAC has the first negative value by assuming that the fast random force correlation ends at that time as proposed by Lagr'kov and Sergeev.[5]

We give in the second set of Table 1 the probe diffusion constant evaluated from the friction constant through Einstein relation, Eq. (2), using the Lagr'kov and Sergeev criterion for the friction constant.[5] One can see the relative discrepancies between the probe diffusion constants obtained from the mean square displacement (MSD) and the friction constant from the results listed in Table 1. It is found that the Lagr'kov and Sergeev criterion leads to an overestimation of the probe diffusion constant by about 6%, which is in quite a good agreement.

The third set of the probe diffusion constant obtained through the Stokes Einstein (SE) equation, Eq. (1), with f = 6 (stick limit) is also listed in Table 1. The probe diffusion constant evaluated from the alkane viscosity (η) underestimates the result obtained from the mean square displacement (MSD) severer in normal alkanes than in isomeric alkanes. The best agreement, about 72%, is obtained in isomeric butane at 298 K. The disagreement is getting worse as the length of chain increases and the temperature decreases. These discrepancies, which can reach 42% averagely, are understood by equating Eqs. (1) and (2):

$$\xi = f\pi\eta\sigma . \qquad (9)$$

This relation is the well-known Stokes law for the hydrodynamic friction based on continuum mechanics[21]: the friction constant is directly proportional to the solvent viscosity. In Figure 2 we plot the friction constant of the probe molecule
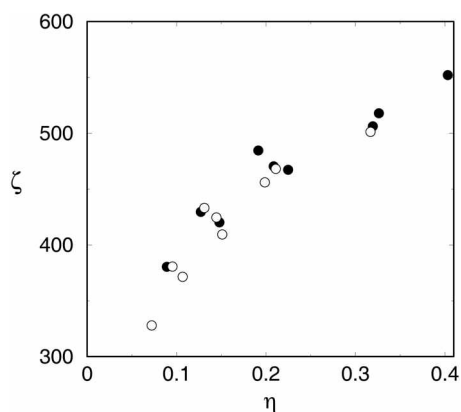

Figure 2. Friction constant (ξ, g/psmol) of the probe molecule *vs.* viscosity (η, cp) of normal ($\bullet$) and isomeric alkanes ($\circ$).

versus viscosity of normal and isomeric alkanes. Clearly it shows a severe deviation from the direct proportionality.

In summary, the insertion of a probe molecule with mass of 225 g/mol and diameter of 6.0 Å causes the increment of viscosity and the decrement of self-diffusion constant of small normal and isomeric alkanes. The probe diffusion constant evaluated from the friction constant through Einstein relation using the Lagr'kov and Sergeev criterion overestimates the probe diffusion constant obtained from the mean square displacement (MSD) by about 6%, which is in quite a good agreement. This indicates that the Einstein relation in the simple Langevin theory of Brownian dynamics and the Green-Kubo formula by Kirkwood are valid for the LJ particle probe diffusion in small normal and isomeric alkanes. However, there exists a severe discrepancy between the probe diffusion constants obtained from the mean square displacement (MSD) and from the Stokes-Einstein equation due to the break down of the Stokes law for the probe diffusion in small normal and isomeric alkanes.

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