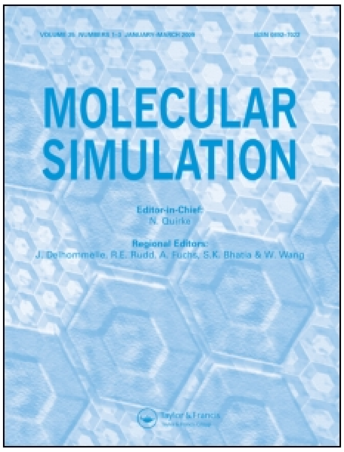

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Molecular dynamics simulation study of probe diffusion in liquid *n*-alkanes

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We performed molecular dynamics simulations for the probe diffusion and friction dynamics of Lennard-Jones (LJ) particles modelled for methyl yellow (MY) in liquid *n*-alkanes of $C_{12}-C_{200}$ at temperatures of 318, 418, 518 and 618 K. Two LJ particles are chosen: MY1 with a mass of 114 g/mol, LJ parameters of $\sigma = 4.0$ Å and $\varepsilon = 0.4$ kJ/mol, and MY2 with a mass of 225 g/mol, $\sigma = 6.0$ Å and $\varepsilon = 0.6$ kJ/mol. We observed a clear transition in the power law dependence of MY2 diffusion on the molecular weight of *n*-alkanes at lower temperatures of 318 and 418 K. The sharp transitions occur near *n*-dotriacontane (C_{32}). However, no such transition is found for MY1 at all the temperatures and for MY2 at higher temperatures of 518 and 618 K. We also calculated the friction constants of both MY probe molecules in liquid *n*-alkanes. For the larger probe molecule (MY2), at lower temperatures, a large deviation of slope from the linear dependence of the friction of MY2 on the chain length of *n*-alkane is observed, which indicates a large reduction of friction in longer chains when compared with the shorter chains, enhancing the diffusion of the probe molecules (MY2).

Keywords: diffusion; friction; probe molecules; *n*-alkanes; MD simulation

1. Introduction

The solvent–oligomer transition has been observed for the first time in a recent study [1] in which the diffusion of methyl yellow (MY) in the oligomeric host of *n*-alkanes and *n*-alcohols was studied by forced Rayleigh scattering as a function of molecular weight and viscosity of the medium. It was observed that the diffusion constant of the probe molecule follows a power law dependence on the molecular weight of the oligomers, $D_{\mathrm{MY}} \sim M^{-\gamma}$ well. As the molecular weight of the oligomers increases, the exponent γ shows a sharp transition from 1.88 to 0.91 near docosane (C_{22}) in *n*-alkanes and from 1.31 to 0.60 near 1-hexadecanol ($C_{16}OH$) in *n*-alcohols at 45°C. A similar transition is also found in a molecular dynamics (MD) simulation for the diffusion of a Lennard-Jones (LJ) particle with a size similar to that of MY in *n*-alkanes [1]. This transition seems to reflect a change in the dynamics of oligomeric chain molecules that the motion of the segments, not the entire molecules, becomes responsible for the transport of the probe molecule as the molecular weight of the oligomer increases.

In a previous study, an MD simulation study on the tracer diffusion of methane in *n*-alkane from *n*-butane to polyethylene with a degree of polymerisation of 2000 was reported [2]. They showed no solvent–oligomer transition, but another transition at which the chain length dependence of the methane diffusivity, α, changed from 1.1 to nearly 0. The exponent of 1.1 is close to the α value found in the oligomer region of the recent study [1], 0.91. This seems to result from the small size of methane relative to MY. Since the size of methane is similar to that of the monomer unit ($—CH_2—$) of the matrix *n*-alkanes, it is expected that methane is already in the oligomer regime even in a small *n*-alkane such as *n*-butane. The molecular size of MY is comparable to that of *n*-hexadecane and the small *n*-alkanes belong to the solvent regime for MY.

A similar situation was found by von Meerwall and Ferguson [3] in the diffusion study of hexafluorobenzene (C_6F_6) in *n*-alkanes from *n*-octane to *n*-hexatriacontane (C36). Although the *n*-alkanes used by them include *n*-docosane, which corresponds to the transition point found in the recent study [1], they found no transition and the dependence of the diffusion of C_6F_6 on the matrix molecular weight of the power law, $D \sim M^{-1.26}$ at 80°C. This value is closer to 0.91 obtained in the oligomer regime than to 1.88 obtained in the solvent regime. This might indicate that C_6F_6 is small enough even in *n*-octane to exhibit a diffusion behaviour in the solvent regime for MY.

The diffusion of the probe molecule reflects the local friction of the diffusing medium, and one of the experimental methods to obtain the monomeric friction constant ζ_0 is to measure the friction constant of probe molecules in polymeric media [4–7]. It is also well established experimentally that the diffusion constant of a probe molecule in polymer solutions is independent of the matrix polymer molecular weight at the Rouse regime [5–7]. In this study, we calculate the friction constant of the probe molecule and investigate the friction effect of liquid *n*-alkanes on the probe diffusion.

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We report new results of equilibrium molecular dynamics (MD) simulations for probe molecules in small liquid *n*-alkanes at several temperatures of 318, 418, 518 and 618 K. We have chosen 12 liquid *n*-alkanes of various chain lengths, $12 \leq n \leq 200$. The primary goal of this study is to analyse the diffusion and friction dynamics of probe molecules in *n*-alkanes at different temperatures. In general, the smaller the probe molecule is, the smaller the exponent, γ, is. For example, carbon dioxide shows an exponent of 0.44 in various organic solvents [8]. We try to investigate the exponent dependence on the molecular size of the probe relative to the molecular size of the diffusing media. In the primary MD simulation for diffusion of a probe molecule [1], the system considered was at a temperature of 318 K only. We also try to investigate the exponent dependence of the probe diffusion in liquid *n*-alkanes on the temperature.

2. Molecular models and molecular dynamics simulation

We have chosen 12 systems of liquid *n*-alkanes – $C_{12}H_{26}$, $C_{16}H_{34}$, $C_{20}H_{42}$, $C_{24}H_{50}$, $C_{28}H_{58}$, $C_{32}H_{66}$, $C_{36}H_{74}$, $C_{44}H_{90}$, $C_{80}H_{162}$, $C_{120}H_{242}$, $C_{160}H_{322}$ and $C_{200}H_{402}$ – for which a united atom (UA) model is employed, that is, methyl and methylene groups are considered as spherical interaction sites centered at each carbon atom [9–13]. The interaction between the sites on different *n*-alkane molecules and between the sites separated by more than three bonds in the same *n*-alkane molecule was described by a LJ potential. All the sites in a chain have the same LJ size parameter $\sigma_i \equiv \sigma_{ii} = 3.93$, and the well depth parameters were $\varepsilon_i \equiv \varepsilon_{ii} = 0.94784$ kJ/mol for interactions between the end sites and $\varepsilon_i = 0.39078$ kJ/mol for interactions between the internal sites. The Lorentz–Berthelot combining rules $[\varepsilon_{ij} \equiv (\varepsilon_i \varepsilon_j)^{1/2}, \sigma_{ji} \equiv (\sigma_i + \sigma_j)/2]$ were used for interactions between an end site and an internal site, and between the probe LJ particle and all the sites of *n*-alkanes. A cut-off distance of $2.5\sigma_i$ was used for all the LJ interactions.

The C–C bond length of 1.54 Å was fixed by a constraint force with the use of RATTLE algorithm [14]. 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. [15]:

$$U_{\text{torsion}}(\phi) = a_0 + a_1 \cos\phi + a_2 \cos^2\phi + a_3 \cos^3\phi, \quad (1)$$

where ϕ is the dihedral angle, $a_0 = 8.3973$ kJ/mol, $a_1 = 16.7862$ kJ/mol, $a_2 = 1.1339$ kJ/mol and $a_3 = -26.3174$ kJ/mol. For the time integration of the equations of motion, we adopted Gear's fifth-order predictor–corrector algorithm [16] with a time step of 5 fs for all the systems.

Two kinds of probe molecule are selected – MY1 with a molecular weight of 114 g/mol and MY2 with a molecular weight of 225 g/mol. MY2 is modelled for the real probe molecule, MY, interacting with all the interaction sites of *n*-alkanes with LJ potential parameters $\sigma = 6.0$ Å and $\varepsilon = 0.6$ kJ/mol, and MY1 interacting with the LJ potential parameters $\sigma = 4.0$ Å and $\varepsilon = 0.4$ kJ/mol in order to study the effect of the molecular size of the probe molecule. For small *n*-alkane systems ($n \leq 80$), only one probe molecule inserted at the centre of the simulation box and for large systems ($n \geq 120$), eight probe molecules are inserted at the centres of eight equally divided sub-boxes of the simulation box without any interaction between the probe molecules. Initially, the LJ parameters of the probe molecules are set as zero and are gradually increased up to the given values. We observed that the probe molecules come very close after a long time of MD simulation, after which we started over the MD simulation for the eight probe molecules at the centres of eight sub-boxes of the simulation box.

Each simulation was carried out in an NpT ensemble with probe molecule(s) to determine the volume of each system at the given temperatures, and after the equilibrium density and hence the length of cubic simulation box were obtained, a new NVT MD simulation was performed for each system to store the configurations of the probe molecule and *n*-alkanes for later analyses. 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 [17,18]. After a total of 1,000,000 time steps (5 ns) for equilibration, the equilibrium properties were then averaged over five blocks of 200,000 time steps (1 ns). The configurations of all the molecules for further analyses were stored every 10 time steps (0.05 ps), which is small enough for the tick of any time auto-correlation function.

The self-diffusion constant (D_{self}) of liquid *n*-alkane and the diffusion constant (D_{MY}) of the probe LJ particle can be obtained using the Green–Kubo formula from velocity auto-correlation (VAC) function:

$$D = \frac{1}{3}\int_0^\infty \mathrm{d}t \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle. \quad (2)$$

The shear viscosity (η) of liquid *n*-alkane is also calculated using the Green–Kubo formula from stress auto-correlation (SAC) function:

$$\eta = \frac{V}{kT}\int_0^\infty \mathrm{d}t \langle P_{\alpha\beta}(0) \cdot P_{\alpha\beta}(t) \rangle, \quad (3)$$

where $P_{\alpha\beta}$ is the $\alpha\beta$ component of the molecular stress tensor, $\mathbf{P}$:

$$P_{\alpha\beta}(t) = \frac{1}{V}\sum_i \Big[m v_{i\alpha}(t) v_{i\beta}(t) + \sum_{j \neq i} r_{ij\alpha}(t) f_{ij\beta}(t)\Big], \quad (4)$$

where $\alpha\beta = xy, xz, yx, yz, zx$ or zy. A microscopic expression for the friction constant has been obtained using the Green–Kubo formula by Kirkwood [19] from the time integral of the force auto-correlation (FAC) function [20,21] in the form:

$$\zeta = \frac{1}{3kT}\int_0^{\tau} dt\langle \mathbf{f}_i(0)\cdot\mathbf{f}_i(t)\rangle, \tag{5}$$

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.

3. Results and discussion

The self-diffusion constants (D_{self}) of liquid *n*-alkanes are easily obtained from VAC function using the Green–Kubo formula, Equation (2). However, there exists a severe difficulty in the calculation of viscosity (η) from SAC function using Equation (3). It is obvious that the calculation of viscosity using Equation (3) is very hard due to the non-decaying long-time tails of the SAC function. For example, a plateau value of the integral of the SAC function for C_{80} at 318.15 K was finally obtained over approximately 50 ns (10,000,000 time steps)! It is expected to require twice the number of time steps for C_{120} at low temperatures and for this reason we were unable to calculate the viscosities of *n*-alkanes beyond C_{80}. The expression in the integral of Equation (5) is the auto-correlation function of the force exerted at the centre of *n*-alkane or on the probe molecule(s) by the liquid *n*-alkane. This expression for ζ vanishes if the upper boundary of the integral is set to infinity [22]. The introduction of a cut-off time τ_0 was the solution given by Kirkwood [19] to this problem who assumed that the integral of the FAC function versus the upper boundary presented a plateau value of τ_0. The friction constant could then be evaluated from this plateau region. Lagr'kov and Sergeev [23] have proposed to choose τ_0 as the first zero auto-correlation function. We were unable to get the plateau value in the running time integral of the FAC function, but we were able to obtain the friction constants proposed by Lagr'kov and Sergeev [23].

The log–log plots of the self-diffusion constant (D_{self}) and the friction constant (ζ) of liquid *n*-alkanes versus the molecular weight (M) of liquid *n*-alkanes at four different temperatures are shown in Figure 1. The slopes are almost linear at the given temperatures except for *n*-alkanes with a higher number of C. For example, an enhancement in D_{self} from the assumed linear behaviour of the log–log plot of D_{self} versus M is observed at 318.15 K for C_{120}–C_{200}, at 418.15 K for C_{160}–C_{200}, and at 518.15 K and 618.15 K for C_{200}. The corresponding reduction in ζ from the assumed linear behaviour of the log–log plot of ζ versus M is also observed. The independence of the self-diffusion constant of liquid *n*-alkane on the molecular weight is expected with the increase in the molecular weight of *n*-alkane. In order to confirm the enhancement in D_{self} and the reduction in ζ, MD simulations for much longer *n*-alkane chains such as C_{240}–C_{400} are presently under study. The restricted linear behaviours at the given temperatures indicate that the behaviours of D_{self} and ζ versus M are well described by $D_{\mathrm{self}} \sim M^{-\alpha}$ and $\zeta \sim M^{\beta}$. The obtained exponents are between 2.28 (318 K) and 1.56 (618 K) for α and between 1.03 (318 K) and 1.07 (618 K) for β.

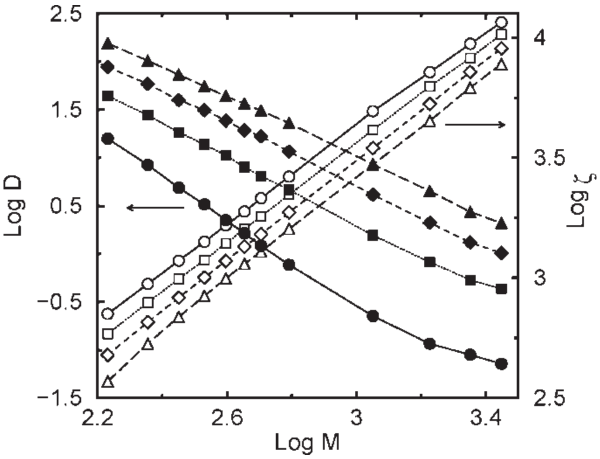

Figure 1. Log–log plots of D_{self} (10^{-6} cm²/s) and ζ (g/ps mol) of *n*-alkane versus M (g/mol). From top, $T = 618$(▲), 518(◆), 418(■) and 318 K(●) for D_{self}, respectively, and the corresponding plot of ζ versus M of *n*-alkane (white symbols).

As shown in Figure 2, the temperature dependence of the calculated self-diffusion constant of liquid *n*-alkanes at all the temperatures considered are suitably described

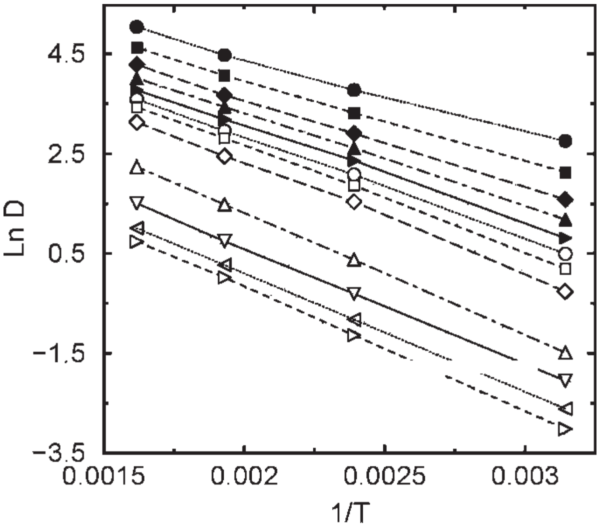

Figure 2. Arrhenius plot of D_{self} (10^{-6} cm²/s) versus 1/*T*. From top, C_{12}–C_{200}.

by Arrhenius plots, $D_{\text{self}} = D_0 \exp(-E_{\text{D,self}}/RT)$, where D_0 is the pre-exponential factor, RT has the usual meaning, and $E_{\text{D,self}}$ is the activation energy of the *n*-alkane self-diffusion. The self-diffusion activation energies obtained from the slope of the least square fit are between 2.95 (C_{12}) and 5.02 kcal/mol (C_{200}). $E_{\text{D,self}}$ is small for small *n*-alkanes. The values of $E_{\text{D,self}}$ is plotted in Figure 3 as a function of chain length, *n*. As the chain length *n* increases the increment of $E_{\text{D,self}}$ decreases, and it is expected to approach an asymptotic value as *n* increases further. It was reported that $E_{\text{D,self}}$ increases linearly with log *M* from 2.32 kcal/mol for *n*-heptane to 5.81 kcal/mol for *n*-hexacontane (C_{60}) [24,25]. Fleischer [26] also determined $E_{\text{D,self}}$ to be about 4.8 kcal/mol for several polyethylene molecules independent of molecular weight from 9 to 52.7 kg/mol, from which we can deduce that the $E_{\text{D,self}}$ of *n*-alkane reaches an asymptotic limit over C_{600}.

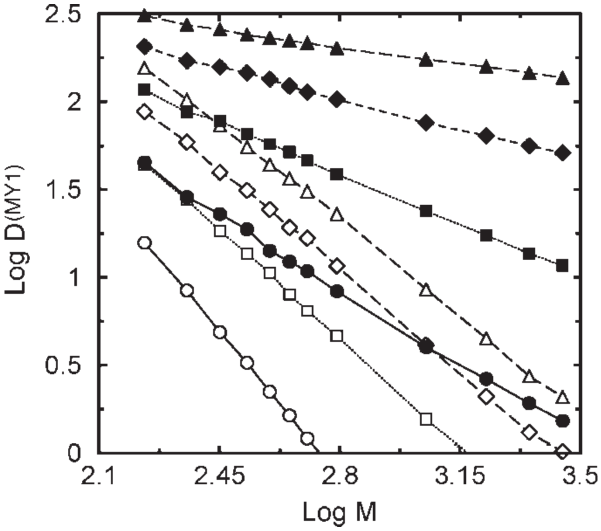

Figure 4. Log–log plots of D_{MY1} ($10^{-6}\,\text{cm}^2/\text{s}$) versus M (g/mol) of *n*-alkane. From top, $T = 618$ (▲), 518 (◆), 418 (■), and 318 K (●), respectively, and the corresponding plot of D_{self} versus *M* of *n*-alkane (white symbols).

In Figures 4 and 5 we show the dependence of D_{MY} on the molecular weight of liquid *n*-alkane at four different temperatures for the two probes, MY1 and MY2, respectively, with the corresponding plots of D_{self} of *n*-alkane for comparison. Clearly, the D_{MY} for both the probes decreases with the molecular weight of *n*-alkane according to the power law $D_{\text{MY}} \sim M^{-\gamma}$. Such a power law dependence has been observed earlier for the probe diffusion in small molecular liquids. For example, diffusion constants of Me_4Sn (molecular weight of 178.7 g/mol) show an exponent of 1.9 in *n*-alkanes (from *n*-hexane to *n*-hexadecane) at 298 K [27,28]. This value is in agreement with the exponent found with MY1 (molecular weight of 114 g/mol) in the C_{12}–C_{200} *n*-alkanes, 1.2 at 318 K. The values of the other exponents obtained for MY1 are $\gamma = 0.82$ (418 K), 0.50 (518 K) and 0.28 (618 K), which are much smaller than those obtained for D_{self} of the *n*-alkanes as compared in Figure 4.

A transition in the power law exponent is observed in the same plot for MY2 at the low temperatures of 318 and 418 K in Figure 5 unlike the linear behaviour in the log–log plot of D_{MY1} versus *M* of *n*-alkane at all the temperatures and for MY2 at the high temperatures of 618 and 518 K. The transitions at the low temperatures seem rather obvious and the transition points are near

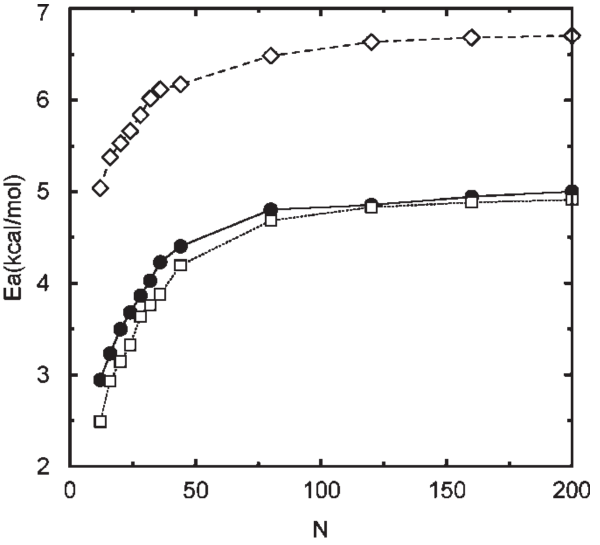

Figure 3. Activation energies (kcal/mol) of D_{self} of liquid *n*-alkanes (●), D_{MY1} (□), and D_{MY2} (△) in liquid *n*-alkanes (◆) versus carbon number *n*.

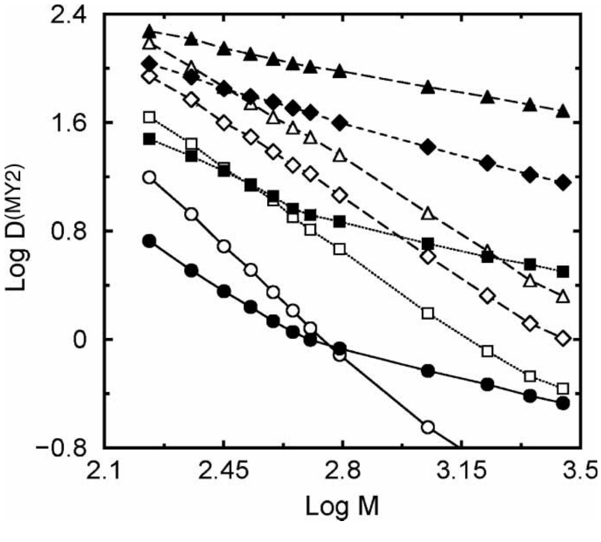

Figure 5. Log–log plots of D_{MY2} ($10^{-6}\,\text{cm}^2/\text{s}$) versus *M* (g/mol) of *n*-alkane. From top, $T = 618$ (▲), 518 (◆), 418 (■), and 318 K (●), respectively, and the corresponding plot of D_{self} versus *M* of *n*-alkane (white symbols).

n-dotriacontane (C_{32}). The calculated exponents are 1.21 and 0.58 in the low- and high-molecular weight regions, respectively, at 418 K, and 1.59 and 0.65 at 318 K. They were 1.58 and 0.52 with the transition point at C_{24} in a previous MD simulation study of $N = 27$ *n*-alkane molecules [1] at 318 K, and the experimentally measured values are 1.88 and 0.91 with the transition point at C_{22} at 318 K [5]. Assuming the log–log plots of D_{MY2} versus M of *n*-alkane at 618 and 518 K in Figure 5 as straight lines, the corresponding exponents are 0.48 and 0.72, respectively, and comparing these values with those for MY1 at the same temperatures, 0.28 and 0.50, we found that the smaller the probe is the smaller the exponent is. This is in good agreement with the existing experimental results for the probe diffusion in smaller molecular weight liquids [4,27,28]. For example, carbon dioxide shows an exponent of 0.44 in various organic solvents [4].

D_{MY1} are always larger than D_{self} at all the temperatures due to the relatively small molecular size of MY1. As the molecular weight of *n*-alkane increases, D_{MY1} decreases much slower than D_{self} and the two diffusion constants never cross each other. In the context of the Brownian motion that is behind any diffusion process, processes slower than or comparable to solvent fluctuations will be affected by the full spectrum of the solvent fluctuations and experience the full shear viscosity of the medium. On the other hand, processes much faster than the solvent fluctuations do not experience the Brownian fluctuating force and are not damped viscously. The case of MY1 belongs to the latter. Thus one expects a reduction in the microscopic friction for the probe molecules that diffuse at a rate faster than the solvent fluctuations [29]. Therefore, for small solute molecules that diffuse in a time scale shorter than the solvent fluctuations, longer chain *n*-alkanes offer a reduced friction relative to the shorter chain *n*-alkanes. D_{MY2} are also always larger than D_{self} at the high temperatures of 618 and 518 K, and D_{MY2} and D_{self} never cross each other as well as in D_{MY1} at all the temperatures.

D_{MY2} and D_{self} cross each other at the low temperatures of 418 and 318 K. At 418 K, D_{MY2} in C_{12} to C_{20} is smaller than the D_{self} of C_{12} to C_{20}, D_{MY2} in C_{24} is almost equal to the D_{self} of C_{24}, and D_{MY2} in C_{28} to C_{200} are larger than D_{self} of C_{28} to C_{200}. The slope in the log–log plot of D_{self} versus M is -1.76 up to C_{120}, but the corresponding slope of D_{MY2} is -1.21 up to C_{32} and -0.58 from C_{32} to C_{200}. At 318 K, the same kind of transition is observed in which D_{MY2} is smaller than D_{self} except for C_{44}–C_{200}. The slope in the log–log plot of D_{self} versus M is -2.28 up to C_{80}, but the corresponding slope of D_{MY2} is -1.59 up to C_{32} and -0.65 from C_{32} to C_{200}. Clearly, the transition is related to the size of the probe molecule and temperature. As discussed above, one expects the reduced friction in longer chains when compared with the shorter chains for small solute molecules that diffuse faster than the solvent fluctuations. On the other hand, solute molecules slower than or comparable to solvent fluctuations will be affected by the full spectrum of the solvent fluctuations and experience the full shear viscosity of the medium. One expects no such transition for a molecule large enough to experience the full friction of the medium in both short and long chains.

The temperature dependence of D_{MY} in *n*-alkanes is well described by the Arrhenius equation (not shown) as well as those of D_{self} of *n*-alkanes as shown in Figure 2. Both $E_{\mathrm{D,MY}}$ in liquid *n*-alkanes are acquired from the slope of the Arrhenius plot and Figure 3 shows the molecular weight dependence of $E_{\mathrm{D,MY}}$ in *n*-alkanes. The values of $E_{\mathrm{D,MY1}}$ in all the *n*-alkanes are always slightly less than $E_{\mathrm{D,self}}$ of *n*-alkanes, and the behaviour of $E_{\mathrm{D,MY1}}$ is very similar to that of $E_{\mathrm{D,self}}$ as a function of the molecular weight of *n*-alkane. This indicates that MY1 diffuses more easily than *n*-alkane molecules at all the temperatures and D_{MY1} is always larger than D_{self} as seen in Figure 4, and processes faster than the solvent fluctuations do not experience the Brownian fluctuating force as discussed above. The values of $E_{\mathrm{D,MY2}}$ in all the *n*-alkanes are always larger than those of $E_{\mathrm{D,self}}$. It is also expected that as the chain length of *n*-alkane increases, both $E_{\mathrm{D,MY}}$ reach asymptotic values, which are approximately estimated as 5.5 and 7.0 kcal/mol, respectively.

In Figure 6 we show the log–log plot of friction constant (ζ_{MY}) versus the molecular weight (M) of *n*-alkane. For the smaller probe molecule, MY1, the obtained slope in the form of $\log \zeta_{\mathrm{MY1}} \leq \delta \log M$ increases almost linearly up to C_{24} and the increment of the slope decreases from C_{28} to C_{200} at all the temperatures as the chain length of *n*-alkane increases. This indicates the

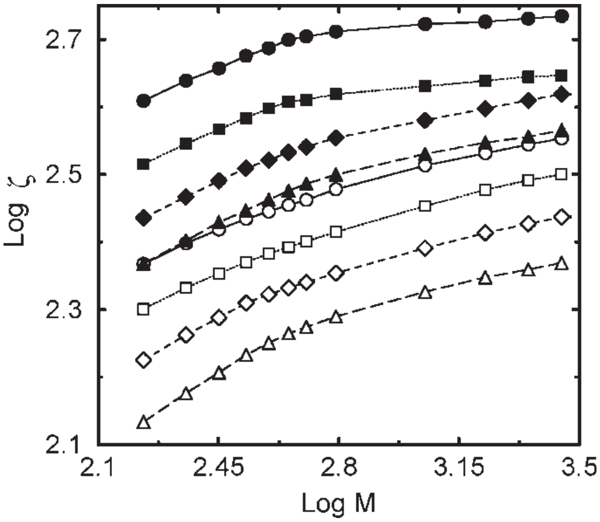

Figure 6. Log–log plots of ζ (g/ps mol) of MY1 and MY2 versus M (g/mol). From top, $T = 318$ K (●), 418 (■), 518 (◆), and 618 (▲) for MY2, respectively, and the corresponding plot of D_{MY1} versus M of *n*-alkane (white symbols).

reduced friction in longer chains when compared with the shorter chains for small solute molecules that diffuse faster than the solvent fluctuations. However, the reduction in the microscopic friction for the probe molecules is not large enough to cause a transition in the power law exponent in the log–log plot of D_{MY1} versus M of n-alkane as shown in Figure 6. For the larger probe molecule, MY2, the calculated friction constants are much larger than those of MY1 at all the temperatures. At high temperatures of 518 and 618 K, the behaviour of the slope in the log–log plot of ζ_{MY2} versus M is very similar to that of MY1 except that the clear change of slope from the assumed linear dependence of the friction of MY2 on the chain length of n-alkane starts at C_{36} instead of C_{28} in the case of MY1 and that the initial slopes in the log–log plot of ζ_{MY2} versus M at high temperatures are larger than those in the log–log plot of ζ_{MY1} versus M at all the temperatures. This is due to the relatively larger size of MY2.

At low temperatures of 318 and 418 K, Figure 6 shows a large deviation of slope from the linear dependence of the friction of MY2 on the chain length of n-alkane starting at C_{36}, but the initial slopes in the log–log plot of ζ_{MY2} versus M are almost equal at all the temperatures. This tells us that solute molecules slower than or comparable to solvent fluctuations will be affected by the full spectrum of the solvent fluctuations and experience the full shear viscosity of the medium. As the molecular weight of n-alkane increases, D_{self} of n-alkanes decreases much faster than D_{MY2} and at the higher molecular weights of n-alkane, MY2 diffuses faster than the solvent fluctuations. Therefore there is a large reduction of friction in longer chains when compared with the shorter chains, which enhances the diffusion of the probe molecules, MY2. We believe that this is the origin of the 'solvent–oligomer' transition as seen in Figure 5.

4. Conclusion

We have carried out equilibrium MD simulations to calculate probe diffusion and friction constants of MY in liquid n-alkanes of increasing chain length at temperatures of 318, 418, 518 and 618 K. Twelve liquid n-alkane systems from C_{12} to C_{200} are chosen and LJ particles with masses of 225 and 114 g/mol are modelled for MY. We observe that the diffusion constant of the probe molecule follows a power law dependence on the molecular weight of n-alkanes, $D_{\mathrm{MY}} \sim M^{-\gamma}$ well. As the molecular weight of n-alkanes increases, the exponent γ shows sharp transitions near n-dotriacontane (C_{32}) for the large probe molecule, MY2, at low temperatures of 318 and 418 K. For the small probe molecule, MY1, D_{MY1} in C_{12} to C_{200} at all the temperatures are always larger than D_{self} of n-alkanes and longer chain n-alkanes offer a reduced friction relative to the shorter chain n-alkanes, but this reduction in the microscopic friction for MY1 is not large enough to cause a transition in the power law exponent in the log–log plot of D_{MY1} versus M of n-alkane. For the large probe molecule, MY2, at high temperatures, the situation is very similar to that for MY1. At low temperatures and at low molecular weights of n-alkanes, D_{MY2} are smaller than D_{self} of n-alkanes due to the relatively large molecular size of MY2, and MY2 experiences the full shear viscosity of the medium. As the molecular weight of n-alkane increases, D_{self} of n-alkanes decreases much faster than D_{MY2} and at the higher molecular weights of n-alkane, MY2 diffuses faster than the solvent fluctuations. Therefore, there is a large reduction of friction in longer chains when compared with the shorter chains, which enhances the diffusion of MY2. The calculated friction constants of MY1 and MY2 in liquid n-alkanes support these observations.

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