

## Research Article

# Diffusion and Friction Dynamics of Probe Molecules in Liquid *n*-Alkane Systems: A Molecular Dynamics Simulation Study

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We present a molecular dynamics simulation study of the probe diffusion and friction dynamics of Lennard-Jones particles in a series of liquid *n*-alkane systems from  $C_{12}$  up to  $C_{400}$  at 318 K, 418 K, 518 K, and 618 K, to investigate the power law dependence of self-diffusion of polymer liquids on their molecular weights. Two LJ particles MY1 with a mass of 114 g/mol and MY2 with a mass of 225 g/mol are used as probes to model methyl yellow. We observed that a clear transition in the power law dependence of *n*-alkane self-diffusion on the molecular weight ( $M$ ) of *n*-alkane,  $D_{\text{self}} \sim M^{-\gamma}$ , occurs in the range  $C_{120} \sim C_{160}$  at temperatures of 318 K, 418 K, and 518 K, corresponding to a crossover from the “oligomer” to the “Rouse” regime. We also observed that a clear transition in the power law dependence of the diffusion coefficient  $D_{\text{MY}2}$  on the molecular weight ( $M$ ) of *n*-alkane,  $D_{\text{MY}2} \sim M^{-\gamma}$ , occurs at low temperatures. The exponent  $\gamma$  for  $D_{\text{MY}2}$  shows a sharp transition from 1.21 to 0.52 near  $C_{36}$  at 418 K and from 1.54 to 0.60 near  $C_{36}$  at 318 K. However, no such transition is found for the probe molecule MY2 at temperatures of 518 K and 618 K and for MY1 probe at temperatures of 418 K, 518 K, and 618 K, but the power law exponent  $\gamma$  for MY1 at 318 K shows instead a linear or a rather slow transition. The dependence of the probe diffusion ( $D_{\text{MY}2}$ ) on the matrix molecular weight ( $M$ ) reflects a significant change of the matrix dynamics associated with the probe diffusion: a crossover from the “solvent-like” to the “oligomer” regime. As the molecular weight of *n*-alkane increases, the ratio of  $D_{\text{self}}/D_{\text{MY}2}$  becomes less than 1 and the probe molecules encounter, in turn, two different microscopic frictions depending on  $M_{\text{MY}}/M_{\text{matrix}}$  and the temperature. It is believed that a reduction in the microscopic friction on the probe molecules that diffuse at a rate faster than the solvent fluctuations leads to large deviations of slope from the linear dependence of the friction of MY2 on the chain length of the *n*-alkane at 318 K and 418 K.

## 1. Introduction

The study for the power law dependence of self-diffusion of pure polymer liquids on the molecular weight of polymers has a long history: self-diffusion in polymer melts (and solution) can be described by the theory of Bueche [1] and by the reptation model of de Gennes [2, 3]. The latter depicts the diffusion process of a molecule of molecular weight  $M$  as wiggling through a tube confined by the neighboring molecules which for linear molecules predicts  $D_{\text{self}} \sim M^{-2}$  for  $M > M_C$ , where  $M_C$  is the entanglement coupling molecular weight [2, 3].

In 1959, self-diffusion investigations of polymer melts were made by McCall et al. [4] who measured diffusion of two fractions of polyethylene ( $M = 4100$  and  $5800$  g/mol) besides higher alkanes; they found the power law  $D_{\text{self}} \sim M^{-5/3}$ .

Detailed investigation by Klein [5] of the self-diffusion of melts of polyethylene fractions from  $M = 3600$  up to  $23000$  g/mol in matrices of comparable and higher molecular weight polyethylenes confirmed the reptation model down to the lowest molecular weight. Pulsed field gradient NMR experiments for  $D_{\text{self}}$  of melts of four monodisperse molecular weight polystyrenes and nine fractions of linear and branched polyethylene [6] revealed that the  $D_{\text{self}} \sim n^{-2}$ , where the number of monomeric units holds in the range of  $n$  from about 20 up to 1500, i.e., the diffusion occurs via reptation.

Below  $M_C$ , the polymer chain dynamics of untangled chains is commonly described by the Rouse model [7] when  $D_{\text{self}} \sim M^{-1}$  for  $M < M_C$ , which describes the conformational dynamics of an ideal chain. In this model, the single chain diffusion is represented by Brownian motion of beads connected by harmonic springs. There are no excluded

volume interactions between the beads, and each bead is subjected to a random thermal force and a drag force as in Langevin dynamics. This model was proposed by Prince E. Rouse in 1953. An important extension to include hydrodynamic interactions mediated by the solvent between different parts of the chain was worked out by Bruno Zimm in 1956. [8] While the Rouse model overestimates the decrease of the diffusion coefficient  $D$  with the number of beads  $N$  as  $N^{-1}$ , the Zimm model predicts  $D \sim N^{-\nu}$  (where  $\nu$  is the Flory exponent), which is consistent with the experimental data for dilute polymer solutions. In a polymer melt, the Rouse model correctly predicts long-time diffusion only for chains shorter than the entanglement length. For long chains with noticeable entanglement, the Rouse model holds only up to a crossover time  $\tau_e$ . For longer times, the chain can only move within a tube formed by the surrounding chains. This slow motion is usually approximated by the reptation model.

There are relatively few molecular dynamics (MD) studies in the molecular weight region from small molecules to the Rouse regime. MD studies of this molecular weight region will shed light on understanding the dynamics of a technologically important class of molecules, oligomers. At molecular weights below the Rouse regime,  $D_{\text{self}}$  of  $n$ -alkanes again show power law behavior. For example,  $D_{\text{self}}$  of  $n$ -alkanes from  $n$ -octane to polyethylene of the molecular weight of several thousands was reported to follow the relation  $D_{\text{self}} \sim M^{-\gamma}$ , in which the exponents  $\gamma$  are in the range of 2.72~1.75 depending on temperature. [6, 9, 10] Although the power law dependence has the same functional form as in the Rouse and reptation models, the origin is totally different. The molecular weight dependence of  $D_{\text{self}}$  in the Rouse and reptation models is attributed to the topological entanglement effect not the segmental friction, while the exponent  $\gamma$  found below the Rouse regime reflects the molecular weight dependence of the local friction and not the topological effect.

The solvent-oligomer transition has been observed for the first time in a recent study, [11] in which 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 the molecular weight and the viscosity of the medium. It was observed that the diffusion coefficient of the probe molecule  $D_{\text{MY}}$  follows a power law dependence on the molecular weight of the oligomers, with  $D_{\text{MY}} \sim M^{-\gamma}$ . As the molecular weight of the oligomers increases, the exponent  $\gamma$  shows a sharp transition from 1.88 to 0.91 near docosane ( $\text{C}_{22}$ ) in the  $n$ -alkanes and from 1.31 to 0.60 near 1-hexadecanol ( $\text{C}_{16}\text{OH}$ ) in the  $n$ -alcohols at 45°C. A similar transition is also found in a molecular dynamics (MD) simulation for the diffusion of a Lennard-Jones particle of a size similar to MY in  $n$ -alkane systems [11]. This transition reflects a change of the dynamics of oligomeric chain molecules in which 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 this article, we use molecular dynamics (MD) simulations to study the probe diffusion and friction dynamics

of Lennard-Jones particles in liquid  $n$ -alkane systems up to  $\text{C}_{400}$  at temperatures of 318 K, 418 K, 518 K, and 618 K and extend our previous work on the subject [12, 13]. We have chosen 14 liquid  $n$ -alkane systems of various chain lengths,  $12 \leq N \leq 400$ . Our aim is to analyze the effect of diffusion and friction dynamics on probe molecules by extending the length of  $n$ -alkanes. We 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 [11], the system considered was at the temperature of 318 K only. We also try to investigate the exponent dependence of the probe diffusion in liquid  $n$ -alkane systems on the temperature.

In short, compared with our previous studies for  $\text{C}_{12} \sim \text{C}_{80}$  [12] and  $\text{C}_{12} \sim \text{C}_{200}$  [13], extending the length of  $n$ -alkane up to  $\text{C}_{400}$ , the first transition (“solvent-like” to “oligomer”) in  $D_{\text{MY1}} \sim M^{-\gamma}$  is newly observed at 318 K near  $\text{C}_{80}$  with ambiguity, but no transition at 418 K, 518 K, and 618 K is reconfirmed in this work. That is,  $D_{\text{MY2}} \sim M^{-\gamma}$  is also reconfirmed at 318 K and 418 K near  $\text{C}_{36}$  but not near  $\text{C}_{32}$  [12]. The second transition (“oligomer” to “Rouse”) in  $D_{\text{self}} \sim M^{-\gamma}$  is newly observed at 318 K, 418 K, and 518 K near  $\text{C}_{120} \sim \text{C}_{160}$  and at 618 K near  $\text{C}_{160}$  with ambiguity, which is undetectable in the previous studies due to the short length of  $n$ -alkanes only for  $\text{C}_{12} \sim \text{C}_{80}$  [12] and  $\text{C}_{12} \sim \text{C}_{200}$  [13]. In addition, the first transition is explained in terms of “retardation” in reducing diffusion of the probe molecules, and the investigation for the second transition is under work for pure  $n$ -alkanes, up to  $\text{C}_{400}$ .

## 2. Molecular Models and Molecular Dynamics Simulation

We have chosen two kinds of probe molecules to study the effect of the molecular size of the probe molecule—MY1 with a molecular weight of 114 g/mol and MY2 with a molecular weight of 225 g/mol. MY2 is modeled for the real probe molecule, methyl yellow (MY), which interacts with the individual sites of  $n$ -alkanes with Lennard-Jones (LJ) potential parameters  $\sigma = 6.0$  Å and  $\epsilon = 0.6$  kJ/mol, while MY1 interacts with LJ potential parameters of  $\sigma = 4.0$  Å and  $\epsilon = 0.4$  kJ/mol. For small  $n$ -alkane systems ( $N \leq 80$ ), only one probe molecule was inserted at the center of the simulation box, and for large systems ( $N \geq 120$ ), 8 probe molecules are inserted at the centers of 8 equally divided sub-boxes of the simulation box without any interaction between the probe molecules. We observed that the probe molecules come very close to each other after long times in our MD simulation. At this time, we then started the MD simulation over again with 8 probe molecules at the centers of 8 sub-boxes of the simulation box.

14 systems of liquid  $n$ -alkane systems are selected— $\text{C}_{12}\text{H}_{26}$ ,  $\text{C}_{20}\text{H}_{42}$ ,  $\text{C}_{28}\text{H}_{58}$ ,  $\text{C}_{36}\text{H}_{74}$ ,  $\text{C}_{44}\text{H}_{90}$ ,  $\text{C}_{80}\text{H}_{162}$ ,  $\text{C}_{120}\text{H}_{242}$ ,  $\text{C}_{160}\text{H}_{322}$ ,  $\text{C}_{200}\text{H}_{402}$ ,  $\text{C}_{240}\text{H}_{482}$ ,  $\text{C}_{280}\text{H}_{562}$ ,  $\text{C}_{320}\text{H}_{642}$ ,  $\text{C}_{360}\text{H}_{722}$ , and  $\text{C}_{400}\text{H}_{802}$ —for which a united atom (UA) model was employed, in which the methyl and methylene groups are considered as spherical interaction sites centered at each carbon atom [14–18]. 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 Lennard-Jones (LJ) potential. All the sites in a chain have the same LJ size parameter  $\sigma_i \equiv \sigma_{ii} = 3.93$ . 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 ( $\varepsilon_{ij} \equiv (\varepsilon_i \varepsilon_j)^{1/2}$ ,  $\sigma_{ij} \equiv (\sigma_i + \sigma_j)/2$ ) 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 cutoff distance of  $2.5\sigma_i$  was used for all the LJ interactions.

The C-C bond length of  $1.54 \text{ \AA}$  was fixed by a constraint force in our simulations with the RATTLE algorithm. [19] The bond bending interaction was also described by a harmonic potential with an equilibrium angle of  $114^\circ$  and a force constant of  $0.079187$  kJ/mol-degree<sup>2</sup>. The torsional interaction was described by the potential developed by Jorgensen et al. [20]:

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

where  $\phi$  is the dihedral angle, and  $a_0 = 8.3973$  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 [21] with a time step of 5 femtoseconds for all the systems.

Each simulation was carried out in an NpT ensemble with probe molecule(s) in  $N = 100$  *n*-alkanes to determine the volume of each system at the given temperatures, and after a total of 2,000,000 time steps (10 nanoseconds) for each system, the equilibrium density and hence the length of cubic simulation box were obtained. New NVT MD simulations were then performed for each system to store the configurations of the probe molecule(s), and  $N = 100$  *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. [22, 23] After a total of 1,000,000 time steps (5 nanoseconds) for equilibration, the equilibrium properties were averaged over 5 blocks of 200,000 time steps (1 nanosecond). The configurations of all the molecules for further analyses were stored every 10 time steps (0.05 picoseconds) which is small enough to determine any of the time auto-correlation functions.

The self-diffusion coefficient ( $D_{\text{self}}$ ) of liquid *n*-alkane and diffusion coefficient ( $D_{\text{MY}}$ ) of the probe LJ particle can be obtained through the Green-Kubo formula from velocity autocorrelation (VAC) function:

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

A microscopic expression for the friction coefficient has been obtained through a Green-Kubo formula by Kirkwood [24] from the time integral of the force auto-correlation (FAC) function [25, 26] in the following form:

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

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*.

During our MD simulations for the short chains of *n*-alkanes, we observed the "evaporation" of the systems, which indicates that the volumes of the systems increase infinitely as the temperature increases. No other phase transition is observed.

### 3. Results and Discussion

**3.1. Log(*D*) vs Log(*M*).** The self-diffusion coefficients ( $D_{\text{self}}$ ) of liquid *n*-alkanes and diffusion coefficients of the probes MY1 ( $D_{\text{MY1}}$ ) and MY2 ( $D_{\text{MY2}}$ ) in liquid *n*-alkane systems are easily obtained from velocity auto-correlation (VAC) function through the Green-Kubo formula, equation (2). The logarithm of diffusion coefficients  $D$  ( $10^{-6}$  cm<sup>2</sup>/s) of *n*-alkanes, MY1, and MY2 in *n*-alkanes at  $T = 318, 418, 518$ , and  $618$  K are listed in S Table 1 of Supplementary Materials. The calculated  $D_{\text{self}}$  are almost equal for both the *n*-alkane systems with MY1 and MY2 probes embedded in the *n*-alkane systems. The log-log plots of the self-diffusion coefficients ( $D_{\text{self}}$ ) of liquid *n*-alkanes and those of the diffusion coefficients of MY1 ( $D_{\text{MY1}}$ ) in liquid *n*-alkane systems vs the molecular weight (*M*) of liquid *n*-alkanes at four different temperatures are shown in Figure 1.

The  $\log(D_{\text{MY1}}) - \log(M)$  plot shows a linear behavior from which the slopes give the exponent  $\gamma = 0.28$  at  $618$  K ( $\blacktriangle$ ),  $\gamma = 0.47$  at  $518$  K ( $\blacklozenge$ ), and  $\gamma = 0.80$  at  $418$  K ( $\blacksquare$ ) from  $D_{\text{MY1}} \sim M^{-\gamma}$ . It is generally accepted that  $D_{\text{MY}}$  in the low-molecular-weight matrix appears to follow the general behavior found in the probe diffusion in small molecular liquids.  $D_{\text{MY}}$  decreases with the molecular weight of the matrix according to the power law originates from the Einstein relation  $D = k_B T / \zeta$  for a Brownian particle with the friction coefficient  $\zeta$ , the Boltzmann constant  $k_B$ , and the Stokes law  $\zeta = C\pi\eta d$  from hydrodynamic arguments for a quasimacroscopic size where  $d$  is the radius of the probe,  $\eta$  the viscosity of the solvent molecules, and  $C$  the hydrodynamic boundary condition which 4 for slip and 6 for "stick." [27, 28] The time-correlation function formula [29] gives  $\eta \sim M^{1/2}$  and so  $D \sim M^{-1/2}$ , which gives the exponent  $\gamma = 0.5$ , and this value is close to  $\gamma = 0.47$  at  $518$  K. There should exist the temperature effect on the exponent  $\gamma$ . However, the linearity of the  $\log(D_{\text{MY1}}) - \log(M)$  plot is quite ambiguous at the temperature of  $318$  K: linear or transitional. The exponent obtained assuming linear behavior was  $\gamma = 1.14$ , or the assumed transition occurs for  $C_{80}$  from the exponent  $\gamma = 1.27$  to  $0.95$  at  $318$  K ( $\bullet$ ).

In Figure 2, for the probe MY2, the  $\log(D_{\text{MY2}}) - \log(M)$  plot also shows a linear behavior at high temperatures, and the exponent  $\gamma$  calculated from the slope is  $0.47$  at  $618$  K ( $\blacktriangle$ ) and  $0.68$  at  $518$  K ( $\blacklozenge$ ). However, the clear transition in the power law dependence of  $D_{\text{MY2}}$  on the molecular weight (*M*) of *n*-alkanes occurs near  $C_{36}$  from  $\gamma = 1.21$  to  $0.52$  at  $418$  K ( $\blacksquare$ ) and near  $C_{36}$  from  $\gamma = 1.54$  to  $0.60$  at  $318$  K ( $\bullet$ ). Note that  $\gamma = 0.47$  at  $618$  K is close to  $0.5$  predicted from the Einstein-Stokes (ES) equation. In addition, the transition of the probe diffusion ( $D_{\text{MY}}$ ) on the matrix molecular weight (*M*) reflects a significant change of the matrix dynamics associated with the probe diffusion. For example, the

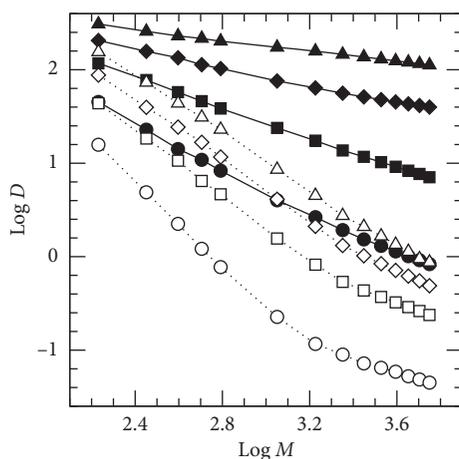


FIGURE 1: Log-log plots for  $D_{\text{self}}$  ( $10^{-6} \text{ cm}^2/\text{s}$ ) of  $n$ -alkanes vs  $M$  (g/mol) at  $T = 618 \text{ K}$  ( $\Delta$ ),  $518 \text{ K}$  ( $\diamond$ ),  $418 \text{ K}$  ( $\square$ ), and  $318 \text{ K}$  ( $\circ$ ), respectively, and those for  $D_{\text{MY1}}$  ( $10^{-6} \text{ cm}^2/\text{s}$ ) in  $n$ -alkane systems vs  $M$  (g/mol) at  $T = 618 \text{ K}$  ( $\blacktriangle$ ),  $518 \text{ K}$  ( $\blacklozenge$ ),  $418 \text{ K}$  ( $\blacksquare$ ), and  $318 \text{ K}$  ( $\bullet$ ).

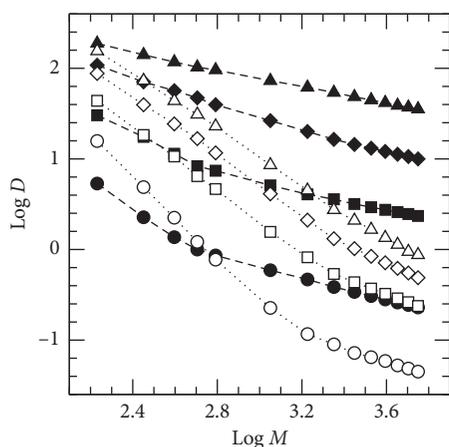


FIGURE 2: Log-log plots for  $D_{\text{self}}$  ( $10^{-6} \text{ cm}^2/\text{s}$ ) of  $n$ -alkanes vs  $M$  (g/mol) at  $T = 618 \text{ K}$  ( $\Delta$ ),  $518 \text{ K}$  ( $\diamond$ ),  $418 \text{ K}$  ( $\square$ ), and  $318 \text{ K}$  ( $\circ$ ), respectively, and those for  $D_{\text{MY2}}$  ( $10^{-6} \text{ cm}^2/\text{s}$ ) in  $n$ -alkane systems vs  $M$  (g/mol) at  $T = 618 \text{ K}$  ( $\blacktriangle$ ),  $518 \text{ K}$  ( $\blacklozenge$ ),  $418 \text{ K}$  ( $\blacksquare$ ), and  $318 \text{ K}$  ( $\bullet$ ).

diffusion behaviors of MY2 in the whole  $n$ -alkane matrix at  $618 \text{ K}$  and  $518 \text{ K}$  and those of MY2 up to  $C_{36}$   $n$ -alkane matrix at  $418 \text{ K}$  and  $318 \text{ K}$  originate from the ES equation but with the increasing exponent  $0.47$ ,  $0.68$ ,  $1.21$ , and  $1.54$ , which is interpreted as the  $n$ -alkane matrix being “solvent-like.” On the contrary, the diffusion behavior of MY2 in the  $C_{36}$   $n$ -alkane matrix at  $418 \text{ K}$  and  $318 \text{ K}$  shows that the exponent  $0.52$  increases to  $0.60$ , which corresponds to a reduction in the microscopic friction for the probe molecules that diffuse at a rate faster than the solvent fluctuations. [30] The friction of the  $n$ -alkane solvent for MY diffusion mainly comes from the segmental motion of the chain and not from the motion of the whole chain. We believe that this is the origin of the transition, and we henceforth call the matrix molecular weight regime at each side of the transition point as the “solvent” and “oligomer” regimes for convenience. Note that the transition is determined by the ratio of  $M_{\text{MY}}/M_{\text{matrix}}$  and the temperature.

At this point, it is interesting to compare  $D_{\text{MY1}}$  and  $D_{\text{MY2}}$  in  $n$ -alkane systems with  $D_{\text{self}}$  of  $n$ -alkane as plotted in Figures 1 and 2.  $D_{\text{MY1}}$  (the black symbols in Figure 1) in  $n$ -alkane systems are greater than  $D_{\text{MY2}}$  (the black symbols in Figure 2) at all temperatures since MY1 with a molecular weight of  $114 \text{ g/mol}$  in the  $n$ -alkane matrix diffuses more easily than MY2 with a molecular weight of  $225 \text{ g/mol}$  in the same matrix.  $D_{\text{MY1}}$  are also greater than  $D_{\text{self}}$  (the white symbols in Figures 1 and 2) at all the temperatures. However,  $D_{\text{MY2}}$  are greater than  $D_{\text{self}}$  at  $618 \text{ K}$  and  $518 \text{ K}$  and become greater than  $D_{\text{self}}$  near  $C_{28}$  at  $418 \text{ K}$  and near  $C_{44}$  at  $318 \text{ K}$ . However,  $D_{\text{MY2}}$  is slightly smaller than  $D_{\text{self}}$  for low-molecular-weight  $n$ -alkanes due to the relatively large molecular size of MY2. As the molecular weight of  $n$ -alkane increases,  $D_{\text{self}}$  decreases much faster than  $D_{\text{MY2}}$ , and the two diffusion coefficients become similar around  $C_{24}$  at  $418 \text{ K}$  and  $C_{40}$  at  $318 \text{ K}$ , which can be interpreted as occurring when the hydrodynamic radius of MY2 becomes comparable to that of  $n$ -alkane constituting the diffusing media. At higher molecular weights of  $n$ -alkanes,  $D_{\text{MY2}}$  does not decrease much as the molecular weight of the  $n$ -alkane matrix increases, while  $D_{\text{self}}$  decreases continuously and becomes smaller than  $D_{\text{MY2}}$  near  $C_{28}$  at  $418 \text{ K}$  and near  $C_{44}$  at  $318 \text{ K}$ . In the context of the Brownian motion that is behind any diffusive 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 contrary, processes much faster than the solvent fluctuation do not experience the Brownian fluctuating force and are not viscously damped. Thus, one expects a reduction in the microscopic friction for the probe molecules that diffuse at a rate faster than the solvent fluctuations. [30] Therefore, for small solute molecules which diffuse in a time scale shorter than the solvent fluctuations, longer chain  $n$ -alkane solvents offer a reduced friction relative to the shorter chain  $n$ -alkanes. We call this “retardation” in reducing diffusion due to the reduction in the microscopic friction on the probe molecules.

Again, in Figure 1 or Figure 2, plots of  $\log(D_{\text{self}}) - \log(M)$  at  $618 \text{ K}$  shows an ambiguous behavior ( $\Delta$ ): linear or transitional, in which the exponent,  $D_{\text{self}} \sim M^{-\gamma}$ , obtained assuming linear behavior was  $\gamma = 1.52$  or the assumed transition occurs for  $C_{160}$  from the exponent  $\gamma = 1.57$  to  $1.28$ . However, a clear transition in the power law dependence of  $D_{\text{self}}$  of  $n$ -alkane on the molecular weight ( $M$ ) of  $n$ -alkanes occurs at low temperatures. As the molecular weight of  $n$ -alkanes increases, the exponent  $\gamma$  shows a sharp transition near  $C_{160}$  from  $1.65$  to  $1.08$  at  $518 \text{ K}$  ( $\diamond$ ), near  $C_{160}$  from  $1.74$  to  $0.89$  at  $418 \text{ K}$  ( $\square$ ), and most dramatically near  $C_{120}$  from  $2.28$  to  $0.78$  at  $318 \text{ K}$  ( $\circ$ ).

Probably the clear transition in the power law dependence of  $D_{\text{self}}$  of  $n$ -alkane on the molecular weight ( $M$ ) of  $n$ -alkane systems at low temperatures may correspond to crossing over from the “oligomer” to the “Rouse” regimes as discussed in “Introduction”. The “oligomer” regime is characterized by the exponents  $\gamma$  in the range of  $2.72$ – $1.75$  for self-diffusion  $D_{\text{self}} \sim M^{-\gamma}$  depending on the temperature [6, 9, 10] and the “Rouse” regime [7] when  $\gamma\gamma = 1$  ( $D_{\text{self}} \sim M^{-1}$ ) for  $M < M_C$ . Our results for the exponents  $\gamma$  of

1.65, 1.74, and 2.28 at 518 K, 418 K, and 318 K in the oligomer region are larger than those of 1.08, 0.89, and 0.78 (roughly  $\gamma \approx 1$ ) at the same temperature ranges in the Rouse regime. Note that the transitions occur near  $C_{120} \sim C_{160}$ , the exponent  $\gamma$  in the oligomer region increases, and the one in the Rouse region decreases as the temperature decreases.

As the molecular weight of the matrix is increased further, we can expect a transition from the oligomer to the “polymer” (Rouse) regime where the molecular weight dependence of the probe diffusion disappears. It has been shown experimentally that the diffusion of small molecules in polymer solutions of sufficiently large molecular weight is nearly independent of the molecular weight or viscosity of the polymers [31]. Therefore,  $D_{MY}$  in the high-molecular-weight polymer must be larger than that extrapolated from the oligomer regime. The last point for  $n$ -alkanes in Figure 2 of [11] is the diffusion of MY in the polyethylene of  $M_w = 4,000$ , which clearly departs from the extrapolated line of the oligomer regime. Chu and Thomas measured the diffusion of pyrene and phthalic anhydride in poly(-dimethylsiloxane) of various molecular weights (from 237 to 423,000). [32] They observed a single transition at which the power law exponent,  $\gamma$ , changed from 0.4 to 0.04. Their transition molecular weight was 3,780 (average degree of polymerization; 48.8) and interpreted it as the change of the matrix property from “solvent-like” to “polymer-like.”

As the temperature decreases, no clear transition in the power law dependence of diffusion ( $D_{MY1}$ ) of probe molecule (MY1) on the molecular weight ( $M$ ) of  $n$ -alkanes ( $D_{MY1} \sim M^{-\gamma}$ ) is observed except the ambiguity in linear or transitional at 318 K, but two clear transitions in  $D_{MY2} \sim M^{-\gamma}$  are observed at 418 K and 318 K for the short chain of  $n$ -alkane. In the case of  $D_{self} \sim M^{-\gamma}$ , all the transitions are observed for the long chain of  $n$ -alkane except the ambiguity in linear or transitional at 618 K. From this point of view, the temperature seems to be an important effect to change the diffusion and friction dynamics of the probe molecules and  $n$ -alkane matrix to let occur the two kinds of transition in the power law dependence of diffusion ( $D$ ) of  $n$ -alkanes and probe molecules (MY1 and MY2) in  $n$ -alkanes on the molecular weight ( $M$ ) of  $n$ -alkanes.

**3.2.  $\text{Log}(\zeta)$  vs  $\text{Log}(M)$ .** Logarithm of friction coefficients  $\zeta$  (g/ps·mol) of  $n$ -alkanes, MY1, and MY2 in  $n$ -alkanes at  $T = 318, 418, 518,$  and  $618$  K are listed in S Table 2 of Supplementary Materials. The expression in the integral of equation (3) is the auto-correlation functions of the force exerted on the center of  $n$ -alkane or on the probe molecule(s) by the liquid  $n$ -alkane. This expression for  $\zeta$  vanishes if the upper bound in the integral is set to infinity [33]. The introduction of a cutoff time  $\tau_o$  was the solution to this problem given by Kirkwood [24], who assumed that the integral of the force auto-correlation (FAC) function vs the upper bound presented a plateau value of  $\tau_o$ . The friction coefficient could then be evaluated from this plateau region. Lagr'kov and Sergeev [34] proposed to choose  $\tau_o$  as the first zero in the auto-correlation function. We were unable to get the plateau value in the running time integral of the force auto-correlation function,

but we could obtain the friction coefficients from the method proposed by Lagr'kov and Sergeev [34].

In Figure 3, we show the log-log plot of friction coefficients ( $\zeta$ ) of  $n$ -alkanes vs the molecular weight ( $M$ ) of  $n$ -alkanes at all temperatures, and the slopes are almost linear at given temperatures except for a dent for  $n$ -alkanes over  $C_{200}$  at 318 K. This small reduction in  $\zeta$  from the assumed linear behavior of the log-log plot of  $\zeta$  vs  $M$  is quite ambiguous. In order to confirm the reduction in  $\zeta$ , MD simulations for much longer  $n$ -alkane chains such as  $C_{1000}$  at low temperatures are required. The restricted linear behaviors at given temperatures indicate that the behavior  $\zeta$  vs  $M$  are well described by  $\zeta \sim M^\beta$ . The obtained exponents  $\beta$  are 0.98, 1.01, 1.03, and 1.06 at 318 K, 418 K, 518 K, and 618 K. Roughly,  $\beta \approx 1$  which holds for the Rouse model of  $D_{self} \sim M^{-1}$  and  $\zeta \sim \eta \sim M^1$  for  $M < M_C$  [7] as discussed in “Introduction”. However, the ES equation predicts that  $\zeta \sim \eta \sim M^{1/2}$ .

We show the log-log plot of friction coefficient ( $\zeta_{MY}$ ) vs the molecular weight ( $M$ ) of  $n$ -alkane in Figure 4. For the smaller probe molecule, MY1, the slope from  $\zeta_{MY1} \sim M^{-\beta}$  increases almost linearly up to  $C_{44}$ , and the increment of the slope decreases from  $C_{80}$  to  $C_{400}$  at all the temperatures as the chain length of  $n$ -alkane increases. The values of  $\beta$  for  $\zeta_{MY1}$  are 0.28, 0.23, 0.21, and 0.20 at 618 K, 518 K, 418 K, and 318 K in the shorter  $n$ -alkane systems and are almost equal to 0.11 at the same temperature ranges for the longer  $n$ -alkane systems. These smaller values of  $\beta$  in the longer chains compared to the shorter chains for small solute molecules reflect a more reduced friction in the longer chains, which indicates that MY1 diffuses at a rate much faster than the solvent fluctuations in the longer chains as discussed above. However, the reduction in the microscopic friction for the probe molecules is not large enough to be abrupt, and the transitions are rather smooth. For the larger probe molecule, MY2, the friction coefficients are much larger than those of MY1 at all the temperatures. At high temperatures of 618 and 518 K, the behavior of the slope in the log-log plot of  $\zeta_{MY2}$  vs  $M$  is very similar to that of MY1 at all temperatures, with  $\beta = 0.25$  and  $0.22$  at 618 K and 518 K, respectively, in the shorter chains and  $\beta = 0.10$  and  $0.11$  at 618 K and 518 K, respectively, in the longer chains, except the smooth change of slope from the assumed linear dependence of the friction of MY2 on the chain length of  $n$ -alkane starts at  $C_{44}$  instead of  $C_{80}$  in the case of MY1.

At low temperatures of 418 and 318 K, Figure 4 shows a rapid change of slope from the linear dependence of the friction of MY2 on the chain length of  $n$ -alkane starting at  $C_{36}$ ,  $\beta = 0.044$  and  $0.033$  at 418 K and 318 K, respectively, but the initial slopes in the log-log plot of  $\zeta_{MY2}$  vs  $M$ , 0.21 and 0.20, are almost equal to those at high temperatures. This tells us that solute molecules are slower than or comparable to solvent fluctuations and will be affected by the full spectrum of the solvent fluctuations and experience the full shear viscosity (friction) of the medium. As discussed above,  $D_{self}$  of  $n$ -alkanes decreases much faster than  $D_{MY2}$  as the molecular weight of  $n$ -alkane increases, and at the higher molecular weights of  $n$ -alkane, MY2 diffuses faster than the solvent fluctuations. Therefore, there is a large reduction of

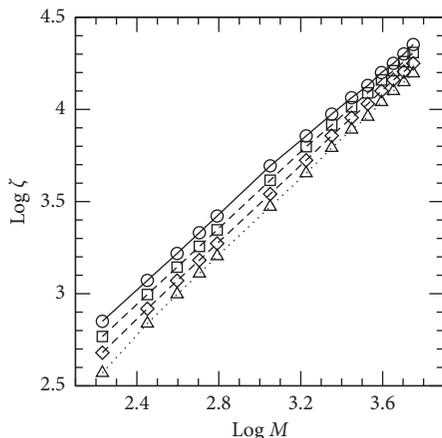


FIGURE 3: Log-log plots for  $\zeta$  (g/ps-mol) of  $n$ -alkanes vs  $M$  (g/mol). From top,  $T = 318$  K (○), 418 (□), 518 (◇), and 618 (△), respectively.

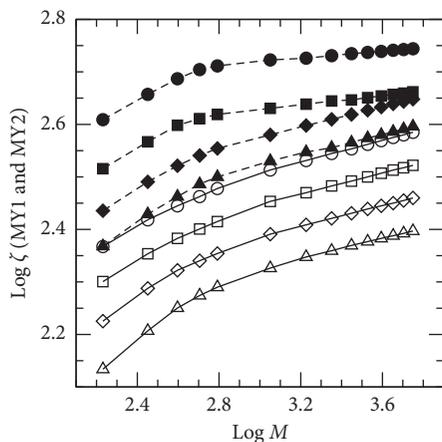


FIGURE 4: Log-log plots for  $\zeta$  (g/ps-mol) of MY1 and MY2 in  $n$ -alkane systems vs  $M$  (g/mol). From top,  $T = 318$  K (●), 418 (■), 518 (◆), and 618 (▲) for  $\zeta_{MY2}$  and the corresponding plot for  $\zeta_{MY1}$  (the white symbols).

friction in longer chains compared to 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 1. The “retardation” in reducing diffusion due to the reduction in the microscopic friction on the probe molecules is demonstrated.

#### 4. Conclusion

We have observed two kinds of transition in the power law dependence of diffusion ( $D$ ) of  $n$ -alkanes and probe molecules (MY1 and MY2) in  $n$ -alkanes on the molecular weight ( $M$ ) of  $n$ -alkanes. The first type of transition in the diffusion coefficient as a function of molecular weight  $D_{MY2} \sim M^{-\gamma}$  occurs at low temperatures of 418 K and 318 K where the exponent  $\gamma$  shows a sharp transition from 1.21 to 0.52 near  $C_{36}$  at 418 K and from 1.54 to 0.60 near  $C_{36}$  at 318 K. However, no such transition is found for the larger and heavier probe MY2 at temperatures of 518 K and 618 K and for the lighter probe MY1 at temperatures of 418 K, 518 K,

and 618 K with an ambiguous behavior at 318 K. Hence, the ratio  $M_{MY}/M_{matrix}$  and the temperature are important factors for this transition which reflect a significant change of the matrix dynamics associated with the probe diffusion: crossing over from the “solvent-like” to the “oligomer” regime. It is believed that a reduction in the microscopic friction on the probe molecules that diffuse at a rate faster than the solvent fluctuations results in the large deviation of slope from the linear dependence of the friction of MY2 on the  $n$ -alkane chain length at 318 K and 418 K. We call this as “retardation” in reducing diffusion due to the reduction in the microscopic friction on the probe molecules. The second kind of a clear transition in the exponent of  $D_{self} \sim M^{-\gamma}$  occurs near  $C_{120} \sim C_{160}$  at temperatures of 318 K, 418 K, and 518 K with an ambiguous linearity at 618 K. It is believed that this transition corresponds to crossing over from the “oligomer” to the “Rouse” regime. The exponents  $\gamma$  obtained from our simulations in the oligomer region are 1.57, 1.65, 1.74, and 2.28 at 618 K, 518 K, 418 K, and 318 K compared to the exponents  $\gamma$  in the range of 2.72–1.75 obtained experimentally, while those in the Rouse regime are 1.28, 1.08, 0.89, and 0.74 (roughly  $\gamma \approx 1$ ) at the same temperatures characterized by  $D_{self} \sim M^{-1}$  for  $M < M_C$ .

#### Data Availability

The data used to support the findings of this study are included within Supplementary Materials, which provide the self-diffusion coefficients ( $D_{self}$ ) and the friction coefficients ( $\zeta_{self}$ ) of liquid  $n$ -alkanes and those of MY1 ( $D_{MY1}$  and  $\zeta_{MY1}$ ) and MY2 ( $D_{MY2}$  and  $\zeta_{MY2}$ ) in liquid  $n$ -alkane systems at four different temperatures of 318 K, 418 K, 518 K, and 618 K.

#### Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

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#### Supplementary Materials

The data used to support the findings of this study are included, which provide the self-diffusion coefficients ( $D_{self}$ ) and the friction coefficients ( $\zeta_{self}$ ) of liquid  $n$ -alkanes and those of MY1 ( $D_{MY1}$  and  $\zeta_{MY1}$ ) and MY2 ( $D_{MY2}$  and  $\zeta_{MY2}$ ) in liquid  $n$ -alkane systems at four different temperatures of 318 K, 418 K, 518 K, and 618 K. (*Supplementary Materials*)

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