

Institute for Basic Sciences, Seoul National University for financial support of this research.

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Molecular Dynamics Study of the Self-Diffusion Coefficient and Velocity Autocorrelation Function of a Polymer Molecule in Solution

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A molecular dynamic computer experiment was performed on a system of 108 particles composed of a single polymer chain and solvent molecules. The state considered was in the immediate neighborhood of the triple point of the system. The polymer itself is an analog of a freely jointed chain. The Lennard-Jones potential was used to represent the interactions between all particles except for that between the chain elements forming a bond in the polymer chain, for which the interaction was expressed by a harmonic potential. The self-diffusion coefficient and velocity autocorrelation function (VACF) of a polymer were calculated at various chain lengths N_p and various interaction strengths between solvent molecules and a polymer chain element. For self-diffusion coefficients D , the Einstein relation holds good; as chain length N_p increases the D value decreases, and D also decreases as ϵ_{cs} (the interaction parameter between the chain element and solvent molecules) increases. The relaxation time of velocity autocorrelation decreases as ϵ_{cs} increases, and it is constant for various chain lengths. The diffusion coefficients in various conditions reveal that our systems are in a free draining limit as is well known from the behavior of low molecular weight polymers, this also agrees with the Kirkwood-Riesman theory.

Introduction

There have been extensive studies by a molecular dynamic method on diffusion phenomena and on the behavior of velocity autocorrelation functions of pure liquids¹⁻⁵ and of a system of a structure-less particle immersed in solvent.⁶⁻⁸ These computational results can be compared with theories developed well, for example, the Enskog-Chapman theory⁹ and theory of Brownian motion.¹⁰ In addition, these computer experiments revealed new phenomena, for example, a negative tail¹ and slowly decaying motion of velocity autocorrelation function,²⁻⁵ which were soon theoretically explained.¹¹

But in case of polymeric systems there has been less study

because the potential forms of various configurational states of a polymer are not exactly known, and the theories are quite complicated.

Recently several authors simulated a single polymer chain immersed in solvent by the Monte Carlo method¹²⁻¹⁴ and molecular dynamic method,¹⁵⁻¹⁶ assuming simple potentials between particles almost just as in the case of simple liquids and also assuming simple models for the polymer molecule. These studies revealed many interesting results which are reasonable in view of the behavior of real polymer solutions in spite of the simplicity of models adopted.

In contrast to the results on simple liquids, the results of the two methods for polymer systems do not always give rise to the same results. This is because in the Monte Carlo

method the motion of a particle is arbitrary, as a result the hydrodynamic interaction between polymer segments is not considered,¹²⁻¹⁴ whereas it is taken into account in the molecular dynamics method. But whether this is the cause for giving the different results for dynamical properties is not clear yet.

In this study, simulations were performed on a single polymer chain in solvent near its triple point, by varying the chain length and the interaction strength between solvent and the element of polymer chain.

A brief outline of this paper is as follows. In Section 2 we describe the model of the system which we have simulated. Section 3 includes the description of the molecular dynamic method. The results obtained for the diffusion coefficient and velocity autocorrelation functions are discussed in sections 4 and 5, respectively.

Model

So far we have simulated two systems. One is for the study of chain length effect, the total number of particle being maintained to 108 while the number of chain elements N_p being varied as 5, 10, 15 and 20. The other is for the study of the effect of interaction strength between solvent and chain elements (ϵ_{cs}), *i. e.*, ϵ_{cs} is changed as 0.5, 1 and 2 times of ϵ_{ss} . Here ϵ_{ss} and ϵ_{cs} denote, respectively, the Lennard-Jones interaction parameter between two solvent molecules and between a chain element and a solvent molecule; the ϵ_{cc} expresses the parameter between two chain elements separated more than one bond length. The condition $\epsilon_{ss} = \epsilon_{cc}$ was imposed.

A harmonic potential U_H represents the potential between two chain elements directly bonded in the polymer molecule, and the Lennard-Jones potential U_{LJ} operates between all particles except for the directly bonded chain elements. These are represented by the following equations:

$$U_H = \frac{1}{2} k_f (|\vec{r} - \vec{r}_{eq}|)^2 \quad (1)$$

and

$$U_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

In our system, the following parametric values are used: $\sigma = 3.817 \text{ \AA}$, $\epsilon_{ss} = 2.0 \times 10^{-14} \text{ erg}$, $kT/\epsilon_{ss} = 0.675$, $k_f = 2 \times 10^5 \text{ dyne/cm}$, $\Delta t = 10^{-14} \text{ sec.}$, $m = 2.415 \times 10^{-23} \text{ g}$ and $\rho = 0.75$. Here density ρ is in reduced units (*i. e.*, in σ^{-3}), m denotes the mass of each particle, the ρ , ϵ , and m values correspond to those of methane,¹⁷ and Δt is the time-step used in the computation. The results will be given in reduced units, lengths are measured in units of σ , and time in units $\sigma (m/\epsilon)^{1/2}$.

Periodic boundary conditions are imposed in the three dimensions of the system, and we use the minimum image convention¹⁸ for the calculation of potential between particles.

Molecular Dynamic Calculations

To integrate Newton's equation of motion we have used

Verlet's explicit time-centered-finite-difference algorithm¹⁸ which uses the following equations for calculating $\vec{r}_i(t)$:

$$m \frac{d\vec{r}_i}{dt} = \vec{F}_i = -\frac{\partial}{\partial \vec{r}_i} U(\vec{r}_1 \cdots \vec{r}_N) \quad (3)$$

$$\vec{r}_i(t + \Delta t) = -\vec{r}_i(t - \Delta t) + 2\vec{r}_i(t) + \frac{(\Delta t)^2}{m} \vec{F}_i(t) \quad (4)$$

and

$$\vec{V}_i(t) = [\vec{r}_i(t + \Delta t) - \vec{r}_i(t - \Delta t)] / 2\Delta t \quad (5)$$

where $\vec{V}_i(t)$ is the velocity of the i -th particle.

The velocity autocorrelation function (VACF) was calculated through the formula

$$\frac{\langle \vec{V}(0) \cdot \vec{V}(t) \rangle}{\langle \vec{V}(0) \cdot \vec{V}(0) \rangle} = \frac{\sum_{n=1}^{j-k} \vec{V}(n\Delta t) \cdot \vec{V}((n+k)\Delta t)}{\sum_{n=1}^{j-k} V^2(n\Delta t)} \quad (6)$$

where k is an integer, $t = k\Delta t$, and j is the total number of integration steps carried out from a given initial state.

Self-Diffusion Coefficient

One of easily observable dynamical properties of a polymer molecule in solution is the self-diffusion coefficient D . The quantity D can be determined by the following two equations: the Green-Kubo formula²⁰ gives D ,

$$D = \frac{1}{3} \int_0^\infty \langle \vec{V}(0) \cdot \vec{V}(t) \rangle dt \quad (7)$$

and the Einstein relation²¹

$$\langle R^2 \rangle = 6Dt \quad (8)$$

where $\langle R^2 \rangle$ is mean square distance moved by the center of mass during time t . Among these two methods, we, however, adopted the second method because in the first method the VACF tends to be dominated by a statistical noise due to the small number of particles employed here as will be discussed in section 5.

Figure 1. shows the molecular dynamics result on the relation of $\langle R^2 \rangle$ vs. time when the number of chain elements N_p is ten, and ϵ_{cs} , ϵ_{cc} and ϵ_{ss} are equal. The result shows almost a linear relationship between $\langle R^2(t) \rangle$ and time.

In Table I are shown the diffusion coefficients D for various chain lengths N_p 's, which were obtained from the slopes of the straight lines in Figure 2. From Table I, we see that as chain length N_p increases, the self-diffusion coefficients D decreases. This fact can be explained from two viewpoints, one is the molecular theory of transport phenomena of dilute gases,²² and the other is the phenomenological hydrodynamic theory of dilute polymer solutions, especially, the Kirkwood-Riesman theory²³ as illustrated below.

In molecular viewpoint, as the chain length increases the velocity of the polymer decreases at constant temperature, *i. e.*, D decreases with N_p . On the one side, as N_p increases the polymer size $\langle s^2 \rangle$ increases (see Table 1), accordingly the collision rate of solvent molecules with the polymer molecule increases, this effect also causes the decrease of D with N_p . By these two effects the diffusion coefficient of

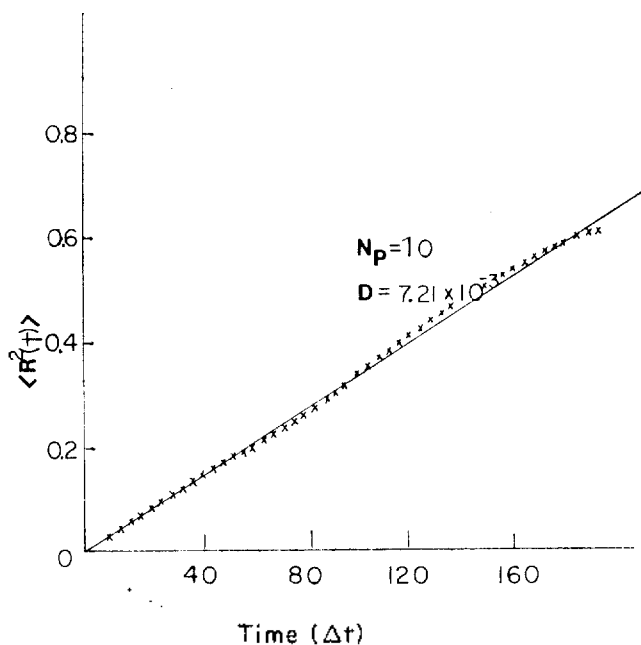


Figure 1. The $\langle R^2(t) \rangle$ vs. t curve when $N_p=10$ and $\epsilon_{cs}=\epsilon_{cc}=\epsilon_{ss}$. Molecular dynamics results are represented by crosses, the solid line represents the smoothed line.

TABLE 1. Chain Length Effect ($\epsilon_{cs}=\epsilon_{cc}=\epsilon_{ss}$)

| N_p | 5 | 10 | 15 | 20 |
|--------------------------|-------|-------|-------|------|
| Relax. ^a time | 18 | 19 | 21 | 21 |
| $D(10^3)^b$ | 13.50 | 7.21 | 4.90 | 2.82 |
| $\langle s^2 \rangle^c$ | 0.885 | 1.746 | 2.936 | 3.52 |

^a The relaxation time was obtained from the velocity autocorrelation function (VACF) [Eq.(6)]; ^b The self-diffusion coefficient D was calculated from the Einstein relation $\langle R^2(t) \rangle = 6Dt$ (in reduced units); ^c The mean square radius of gyration $\langle s^2 \rangle$ was calculated from the relation $\langle s^2 \rangle = \langle N_p^{-1} \sum_{i=1}^{N_p} [\bar{r}_i - \bar{r}_{C.M.}]^2 \rangle$, where $\bar{r}_{C.M.}$ denotes the position vector of the center of mass of a polymer molecule.

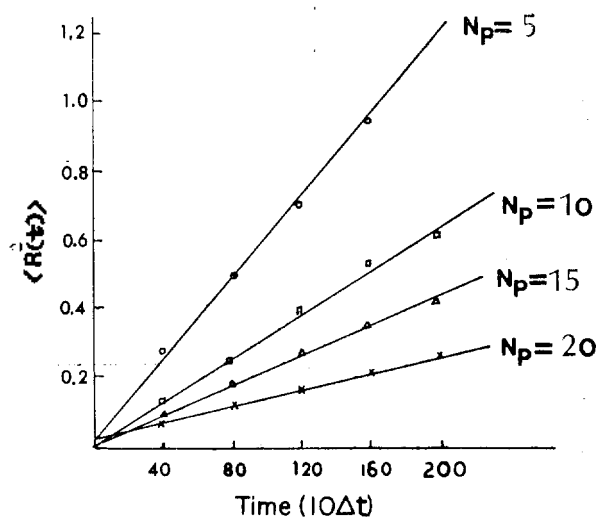


Figure 2. The $\langle R^2(t) \rangle$ vs. t curves for polymers with various chain lengths when $\epsilon_{cs}=\epsilon_{cc}=\epsilon_{ss}$ in all cases.

the polymer molecule decreases with N_p .

In hydrodynamic language, there have been developed several theories of dilute polymer solutions concerning the diffusion coefficient and intrinsic viscosity. We consider next the Kirkwood-Riesman theory since the latter well explains our molecular dynamics results more simply than other hydrodynamic theories.

The Kirkwood-Riesman theory²³ predicts that in a range of low molecular weights of polymers, as chain length increases the diffusion coefficient decreases inversely with N_p according to Eq. (9):

$$D = kT / (N_p \xi) \quad (9)$$

where ξ is the friction coefficient of each segment. The case where Eq. (9) applies is considered as the free-draining limit. In other words, each segment offers equal resistance to the flow of solvent as though it would offer if other segments do not perturb the flow in its neighbors. In our system, ξ is equal in all systems irrespective of N_p . Thus our D values in Table 1 well accord with this case.

Ceperly *et al.*¹⁴ simulated a polymer solution by the Monte Carlo method, and found that the diffusion coefficient is proportional to N_p^{-1} , in a good agreement with our results (Table 1). This is another evidence that in our system the hydrodynamic interaction between segments is almost negligible.

The diffusion coefficient for $N_p=10$ can be compared with the result of Bruns and Bansal¹⁵ for $N_p=9$ where their condition is not far from ours. When our $D=7.21 \times 10^{-3}$ is reduced according to their time scale Bruns and Bansal's value accords very well with ours. But our values are quite small when compared with the values of Bishop *et al.*¹⁶ because they simulated at a very high temperature and low density.

Figure 3 and Table 2 show the effect of interaction strength

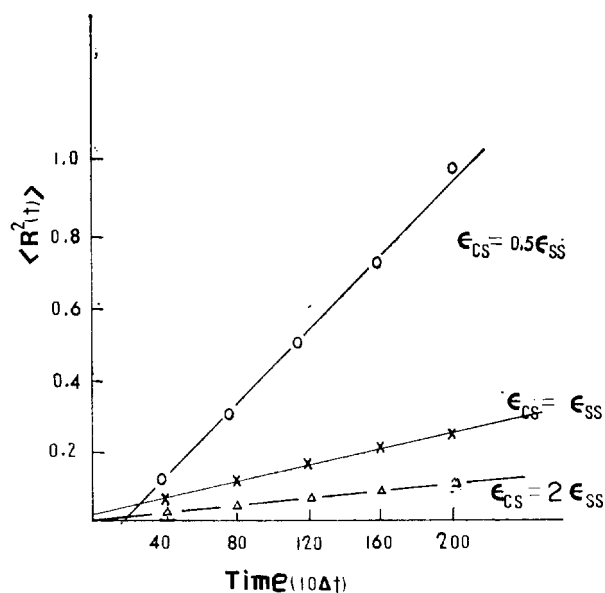


Figure 3. The $\langle R^2(t) \rangle$ vs. t curves for three values of ϵ_{cs} when $N_p=20$.

ϵ_{cs} for the polymer of $N_p=20$. As ϵ_{cs} increases the diffusion coefficient decreases. It can be explained as follows: as ϵ_{cs} increases, the collision rate of solvent molecules with the polymer molecule increases, and the number density of solvent molecules in the neighborhood of the polymer molecule increases as shown in a previous work,²⁴ thus the diffusion coefficient decreases.

In hydrodynamic language, ξ decreases as ϵ_{cs} decreases. So from Eq. (9), we can see that the diffusion coefficient increases as ϵ_{cs} decreases.

As can be seen from Figure 4, for a system with $\epsilon_{cs}=0.5 \epsilon_{ss}$, the curve of $\langle R^2(t) \rangle$ vs. time has a parabolic form for a relatively long time after the computation started, then it turns to be linear whereas the curve for $\epsilon_{cs}=2 \epsilon_{ss}$ becomes linear after a relatively short time. This fact reveals that in a poor solvent ($\epsilon_{cs}=0.5 \epsilon_{ss}$) a polymer molecule moves

$$\lim_{t \rightarrow 0} \langle R^2(t) \rangle = V_0^2 t^2 \quad (10)$$

where V_0 indicates the initial velocity of the molecule. Equation (10) tells us that in an early period of time, the plot of $y \equiv \langle R^2(t) \rangle$ vs t yields a parabola, this region corresponds to the parabolic region in Figure 4 due to the free motion. The free motion, however, disappears at an early

TABLE 2: Interaction Strength Effect. ($N_p=20$)

| ϵ_{cs} | 0.5 | 1 | 2 |
|---------------------------|-------|------|------|
| Relax. ^a time | 38 | 23 | 11 |
| $\langle s^2 \rangle^a$ | 1.93 | 3.35 | 3.96 |
| D (10^3) ^a | 10.50 | 2.82 | 1.01 |

^aThe method for calculating these quantities is the same as in Table 1.

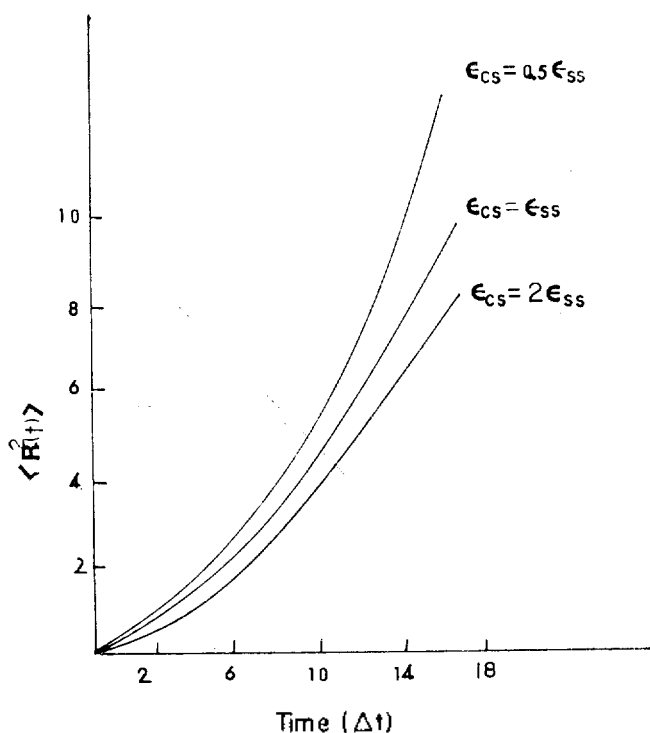


Figure 4. The $\langle R^2(t) \rangle$ vs. t curves in the early period of time. The conditions are the same as those in Figure 3.

freely for a relatively long time as found by Toukubo.²⁵ The above fact can be explained by the theory of Brownian motion at nearly zero time, *i.e.*,²⁶ period for larger ϵ_{cs} and random motion of the polymer molecule starts; thus Einstein's linear relationship of $\langle R^2(t) \rangle$ vs. t [Eq. (8)] holds as shown in Figures 3 and 4.

5. Velocity Autocorrelation Function

In our work, the normalized velocity autocorrelation function (VACF) Eq. (6), reveals roughly an exponential decay form during the relaxation-time period and the characteristic long time behavior as shown in Figures 5 and 6.

We see from Figure 5 and Table 1 that the relaxation time does not change considerably with N_p within statistical errors. This is caused by the two effects: (i) as the chain length increases the momentum of the polymer molecule increases, and as a result the relaxation time becomes larger, (ii) the radius of gyration $\langle s^2 \rangle$ of the polymer increases with N_p , so collision rate increases causing the relaxation time small. These two opposite effects offset each other, the relaxation time becomes about constant irrespective of N_p .

The long time behavior of the VACF as the chain length varies is not clear whether it is due to the "backscattering"⁸ or noise because in this region the VACF strongly depends on the particle number.

Let us now consider the ϵ_{cs} effect. As can be seen from Figure 6. and Table 2, the relaxation time decreases as ϵ_{cs} increases. This phenomenon is strongly related to the self-diffusion motion at the initial period of time as discussed in section 4. When ϵ_{cs} is small, polymer molecules persist the free motion for a relatively long time, causing the relaxation time larger.

It seems that there exists no hydrodynamic theory of the

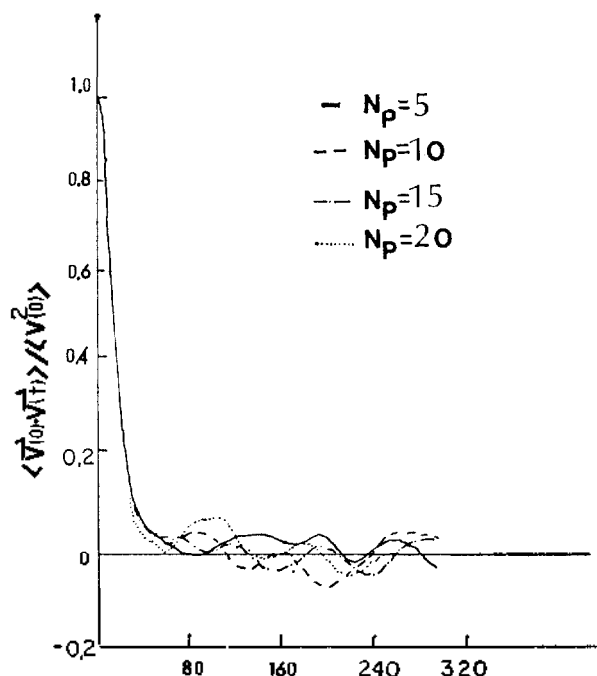


Figure 5. The normalized velocity autocorrelation functions for various chain lengths. The conditions are the same as those in Figure 2.

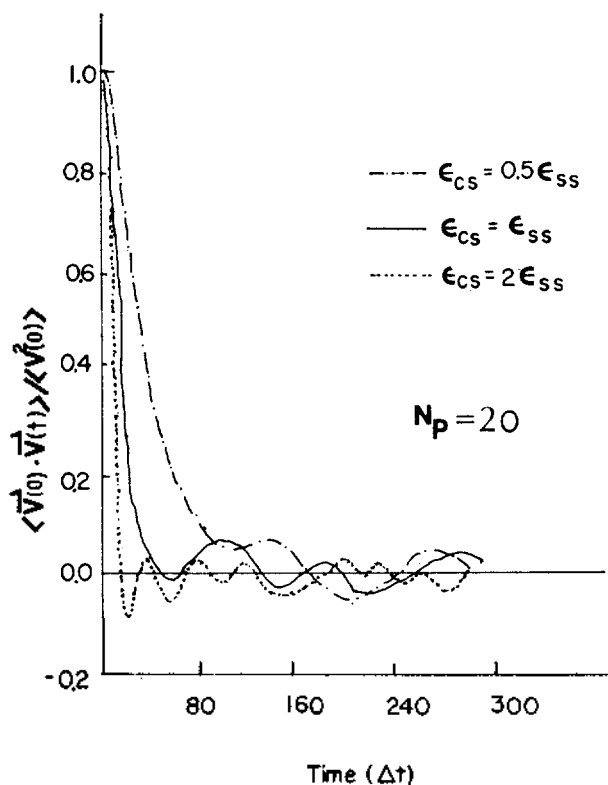


Figure 6. The normalized velocity autocorrelation functions for various ϵ_{CS} . The conditions are the same as those in Figure 3.

VACF of a polymer molecule in solution. Thus the discussion in terms of hydrodynamic language on our results will be postponed.

Another important phenomenon concerning the VACF is the part in which it decays proportionally to $t^{-3/2}$. But in our system, there does not exist this slowly decaying long time tail,^{2,11} which is caused by a collective movement of solute molecules.

Acknowledgement. We deeply acknowledge the Korea Research Center for Theoretical Physics and Chemistry for a partial support of this work.

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