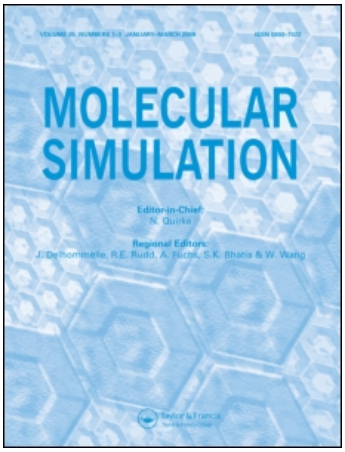

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Dynamical Properties of Condensed Charged Polymer Melts

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DYNAMICAL PROPERTIES OF CONDENSED CHARGED POLYMER MELTS

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Dynamical properties of condensed charged polymer melts are studied with a two-dimensional model and molecular dynamics simulation. Screened Coulombic interactions are assumed for the interactions between the monomer charges as well as the counterions which were introduced to neutralize the total monomer charges of polymer chains. Through molecular dynamics calculations, we have obtained the radial distribution function and velocity auto-correlation function, and their density dependences. As a structural characteristics in condensed charged polymer melts, we find that the monomers tend to form triangular structures locally. The radial distribution function for the center monomers implies that the polymer chains on our two-dimensional model are not entangled. The diffusion properties for both the counter-ions and innermost monomers are studied in detail. In this paper, we have also computed neutral polymer melts to study the effects of the presence of the long-range Coulombic interactions on the dynamical properties of polymer melts. We find that the Coulombic interactions significantly reduce the self diffusion. Snapshots analyses obtained from the molecular dynamics simulation suggest that the reptation model is not a proper model for two-dimensional polymer-chain melts, in which there are little entanglement effects in agreement with the result of the analyses for the radial distribution function.

1 INTRODUCTION

A system consisting of single or many charged polymer chains is an important material, and has been studied both from theoretical [1] and experimental [2, 3] points of view. In our previous papers [4, 5, 6] we have investigated the equilibrium properties of a single charged polymer chain using Monte Carlo simulation. This corresponds to an infinitely dilute salt-free polymer melt, in which the long-range Coulombic interactions were replaced by an effective screened Coulombic interactions. In such a limiting system, a central problem of interest is the equilibrium conformations of the chain as a function of the temperature of the system in relation to the counter-ion condensation at and below a certain temperature.

In this paper, we study an opposite case, a system of condensed polymer chain melts, in which many chains interact through Coulomb interactions as well as short range interactions which are essentially to take into consideration the excluded volume effects of charged particles. We study the dynamical properties of a dense solution of charged polymer chains plus the corresponding counter-ions, using molecular dynamics simulation. Such dense polymer solutions have attracted much

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attention, such as in relation to the problem of reptation dynamics [7, 8, 9, 10, 11, 12]. According to the theory of de Gennes and Edwards [7, 8, 9], a dense solution of polymers follows the Rouse-model for short time, $\langle R^2 \rangle \sim t^{1/2}$, where $\langle R^2 \rangle$ is mean square displacement of monomers, and the reptation model for a longer time, $\langle R^2 \rangle \sim t^{1/4}$. In the latter case, a polymer chain moves along the contour of the chain because of the topological constraint imposed by other polymer chains, thus the diffusion is much reduced. However, it has not yet been very well confirmed if such a reptation model is realistic at molecular levels.

In this work, we explore these problems with a molecular dynamics simulation for our two-dimensional model. The two-dimensional model is important both from the theoretical and experimental points of view. Theoretically, a two-dimensional model is interesting enough since there could be orders not observed in three dimension. It is not obvious if the three-dimensional picture of reptation should also apply to two-dimensional case. Experimentally, a two-dimensional model corresponds to polymers confined in a very thin layer. It should be possible to perform experiments related to our two-dimensional model.

Our model is described in Section 2. The results are presented in Section 3. Discussion and future problems are given in Section 4.

2 MODEL

Our system consists of 25 polymer chains, each having 20 monomers, and 500 counter-ions. All these ions move in a two-dimensional continuous space. The charges are uniformly distributed on each monomer. Each counter-ion has a charge of the same magnitude as that of monomers, but of an opposite sign. Since the number of monomers and that of counter-ions are equal, the neutrality of the whole system is ensured.

The ratio of the monomer diameter σ_a and the counter-ion diameter σ_b is set to be $\sigma_a/\sigma_b = 4$ in our model. The mass of a counter-ion and that of a monomer are assumed to be the same for simplicity. As the natural length of the spring we take $l_0 = 1.25\sigma_a$, so that a counter-ion can pass through adjacent monomer pairs, as seen in Figure 1(a), when the length of the spring between the monomers is equal to or larger than l_0. In the present two-dimensional model, the above condition leads to a significant effect on the counter-ion mobility, since in usual two-dimensional models, a polymer chain blocks for any counter ion to pass through the chain itself. But this is not the case in the present model.

In order to keep chains stable during the molecular dynamics simulation, every adjacent monomer pair is assumed to be connected by a very strong spring. In the present molecular-dynamics calculation, the following three kinds of potentials are used, which are plotted in Figure 1(b):

(1) the soft-core potential

$$U_1 = \varepsilon \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12}. \tag{1}$$

Here, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $(i, j) = (a, a)$, (b, b) or (a, b).

(2) the screened Coulombic interaction

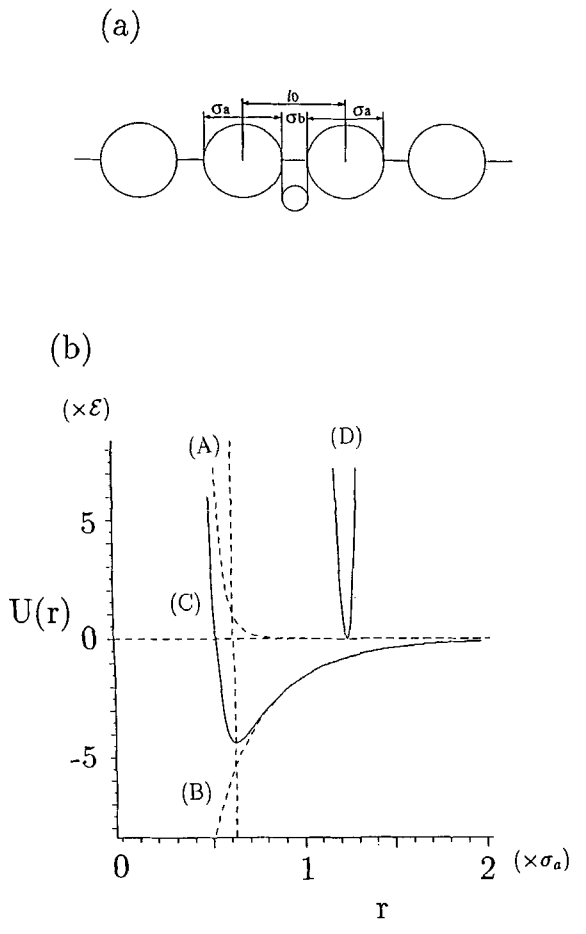

Figure 1 (a) Illustration of the geometrical sizes of monomers and counter-ions used in the present model. (b) The potential functions used in the simulation. (A): the soft-core potential between a monomer and a counter-ion, (B): the screened Coulombic attractive potential between a monomer and a counter-ion, (C): the sum of (A) and (B), and (D): the spring potential for an adjacent monomer pair on a polymer chain.

$$U_2 = C\frac{q_i q_j}{r_{ij}}\exp(-\kappa r_{ij}) \tag{2}$$

where $q_i = 1$ for a monomer and -1 for a counter-ion, respectively. The above two potentials act on any pair of two ions (monomers and counter-ions).
(3) the spring potential

$$U_3 = \frac{k}{2}(l_0 - r_{ij})^2 \tag{3}$$

where k is the strength of the spring and r_{ij} is the distance between adjacent monomer pairs. This potential acts only between adjacent monomer pairs on the polymer chains, and not between further distant monomer pairs.

For the unit of length and the unit of mass, we use the polymer diameter, σ_a, and the monomer mass m_a, respectively. For the unit of energy, we use the constant ε of the soft-core potential of Equation (1). Consequently, the unit of time $\tau = \sigma_a\sqrt{m_a/\varepsilon}$ is used throughout this paper. For κ in Equation (2), we set $\kappa\sigma_a = 2$. Since the screened Coulombic interaction rapidly decays to zero, we use a force-cut method in the present molecular dynamics computations, instead of using the well-known Ewald summation for the Coulombic interactions. For the force-cut range, we adopt the value of $4\sigma_a$. We have adjusted the constant C in Equation (2) in such a way that the total potential $U_1 + U_2$ between a monomer and a counter-ion has its minimum when the monomer and the counter-ion touch each other.

We have used Nosé's constant temperature techniques for molecular dynamics, and the temperature was set to $T = 5\varepsilon$ which is slightly larger than the absolute value of 4.3ε for the interaction energy between a contact pair of a monomer and a counter-ion. The temperature used in this work therefore allows the counter-ions to pass through a gap between an adjacent monomer pair, since condensation of a counter-ion on a monomer is not enough to be bound for a long time due to thermal fluctuations. The time mesh used in the present simulation was 0.001τ which is approximately 1/50 of the inverse of the vibrational frequency of the spring connecting adjacent monomer pairs.

We have investigated two cases of different densities, $\rho = 0.4$ and 0.65. Here, ρ is the ratio of the area occupied by the monomers and counter-ions to L^2, the total area of the system:

$$\rho = \frac{N_a\sigma_a^2\pi + N_b\sigma_b^2\pi}{4L^2}, \tag{4}$$

where N_a and N_b are the total numbers of monomers and counter-ions, respectively. L is the side length of the square simulation cell. Examples of typical configurations obtained from the molecular dynamics simulations for these densities are shown in Figure 2.

3 RESULTS

With the model and the method described in the previous section, we have performed the molecular dynamics simulation. Below, we show the results for the radial distribution function, velocity autocorrelation function and self diffusion.

3.1 *Radial distribution function*

In Figure 3, we show the density profile of the counter-ions and monomers around any adjacent monomer pairs along the chain. The distance between adjacent monomer pairs is not a constant in the present model; monomers are connected by each spring, and they can make oscillations. In the calculations of Figure 3, we have used a relative distance, onto which all adjacent monomer pairs are mapped. We can see from the figure that the counter-ions mostly populate a position around (0.5,0), in the mid-region between adjacent monomer pairs. On the other hand, the monomers mostly populate a position around (0.5,0.8), in the region which is

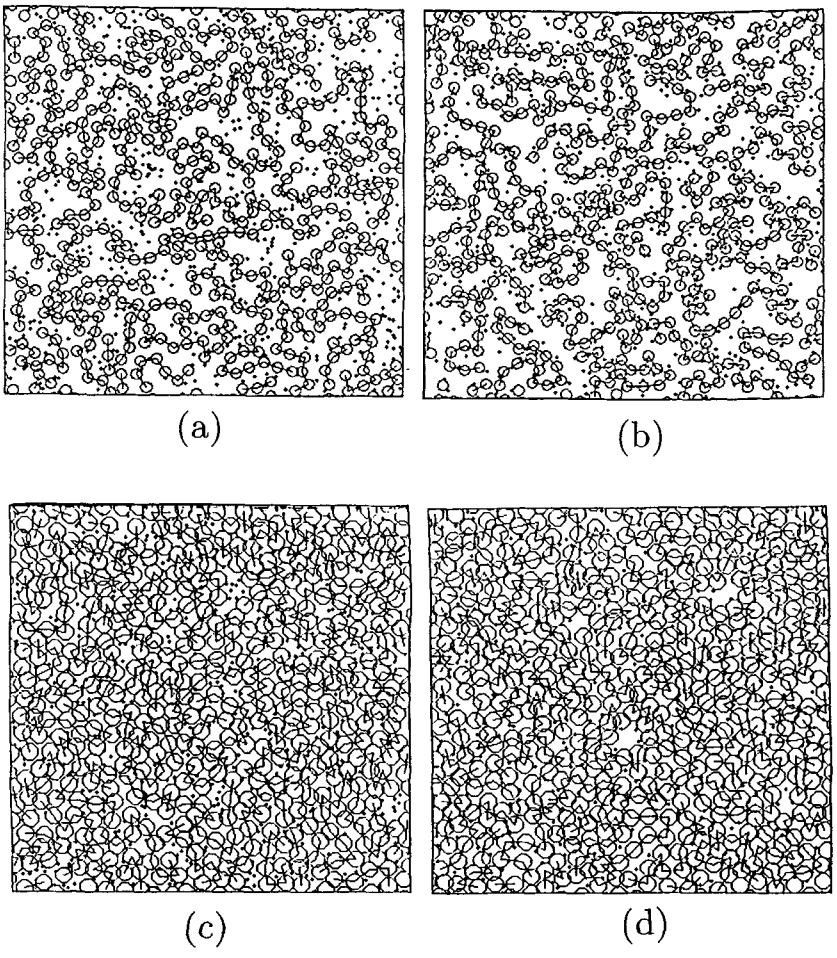

Figure 2 Snapshots of the system for (a) $\rho = 0.4$ without Coulombic interactions, (b) $\rho = 0.4$ with Coulombic interactions, (c) $\rho = 0.65$ without Coulombic interactions, and (d) $\rho = 0.65$ with Coulombic interactions. Small dots and circles denote the counter-ions and monomers, respectively. Monomers belonging to a same polymer chain are connected by the lines.

equidistant from the two monomers, (0,0) and (1.0,0), thereby forming a triangular structure.

To investigate the static properties of monomers and counter-ions, we have calculated the radial distribution function $g(r)$. In Figure 4, we show $g(r)$ for monomers. The peak at $r = 1.25\sigma_a$ corresponds to adjacent monomer pairs of polymer chains. For $\rho = 0.4$, there is a peak at $r = 2.5\sigma_a$, which is twice the position of the peak $r = 1.25\sigma_a$. This suggests a significantly larger probability than in the case of the higher density that three successive monomers form a straight structure locally. There is also a peak at around $r = \sigma_a$ for $\rho = 0.65$, which comes from non-bonded contact monomers on the same chain or monomers of different chains. This peak appears to be slightly weaker when the Coulombic interactions are taken

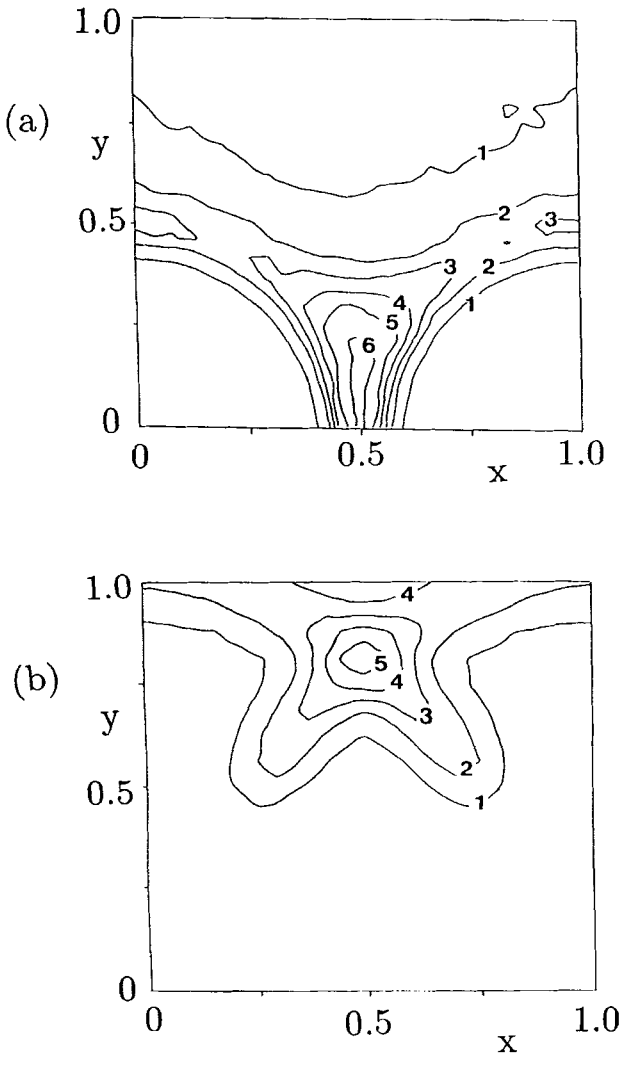

Figure 3 Density profile of (a) counter-ions and (b) monomers for a Coulombic system with $\rho = 0.65$. All adjacent monomer pairs of the polymer chains are mapped with relative scales of the length into two corners in this figure, (0,0) and (1,0). The density is proportional to the numbers attached to each curve.

into consideration. This can be reasonably interpreted as the effects of the Coulombic repulsive force between monomers.

In Figure 5, we show $g(r)$ for the counter-ions. Here, in a marked contrast to the case of the monomers that was shown above, the presence of the Coulombic interactions changes the results drastically. Without the Coulombic interaction, $g(r)$ has a peak at about $r = 0.25\sigma_a$. Remembering that $\sigma_b = 0.25\sigma_a$ in the present model, this result indicates that the counter-ions make clusters in close contact to

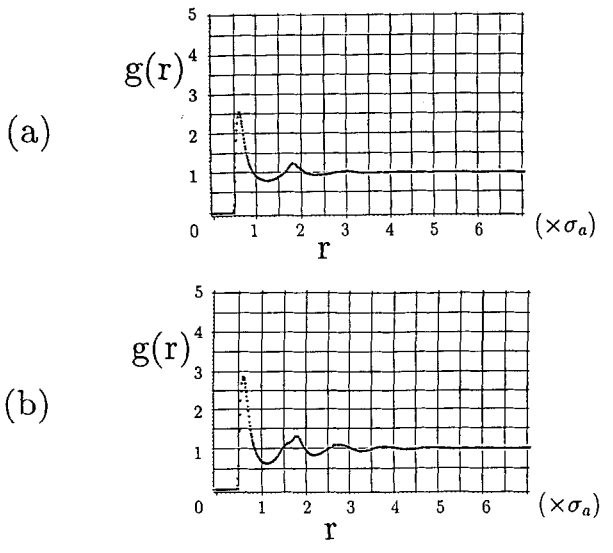

Figure 4 Radial distribution function for monomers with Coulombic interactions. (a) $\rho = 0.4$, (b) $\rho = 0.65$.

each other. On the other hand, with Coulombic interactions, $g(r)$ has a peak at $r = 1.250\sigma_a$, which is the same as the equilibrium distance between an adjacent monomer pair. This suggests that the counter-ions condense on any of the monomers so that the peak in $g(r)$ for counter-ions appears in such a distance.

In Figure 6, we show $g(r)$ for monomers and counter-ions. The peak at around $r = 0.60\sigma_a$ corresponds to the distance when a counter-ion and a monomer are in close contact. The peak at around $r = 1.8\sigma_a$ corresponds to a pair of a counter-ion and the second nearest neighbour monomers.

Note that in all the results for $g(r)$ shown in Figure 4, no distinction is made between different chains of the melt. To see a spatial correlation between different polymer chains, we have tried to compute the $g(r)$ between the centers of the polymer chains, where a center is defined as the midpoint between the 10th and 11th monomers, and not as the center of gravity. We obtained the results in Figure 7. $g(r)$ is zero for short distances. It increases monotonically with r, until it reaches a maximum at around $r = 6\sigma_a$. Then it gradually decreases with further increasing r. We see that the features of all curves obtained here appear almost independent of the density. As an important conclusion from these analyses, we do not see appreciable entanglement effects between different polymer chains in condensed melts irrespective of charged or uncharged.

3.2 *Velocity auto-correlation functions*

To investigate the motions of monomers and counter-ions, we have calculated the velocity auto-correlation function:

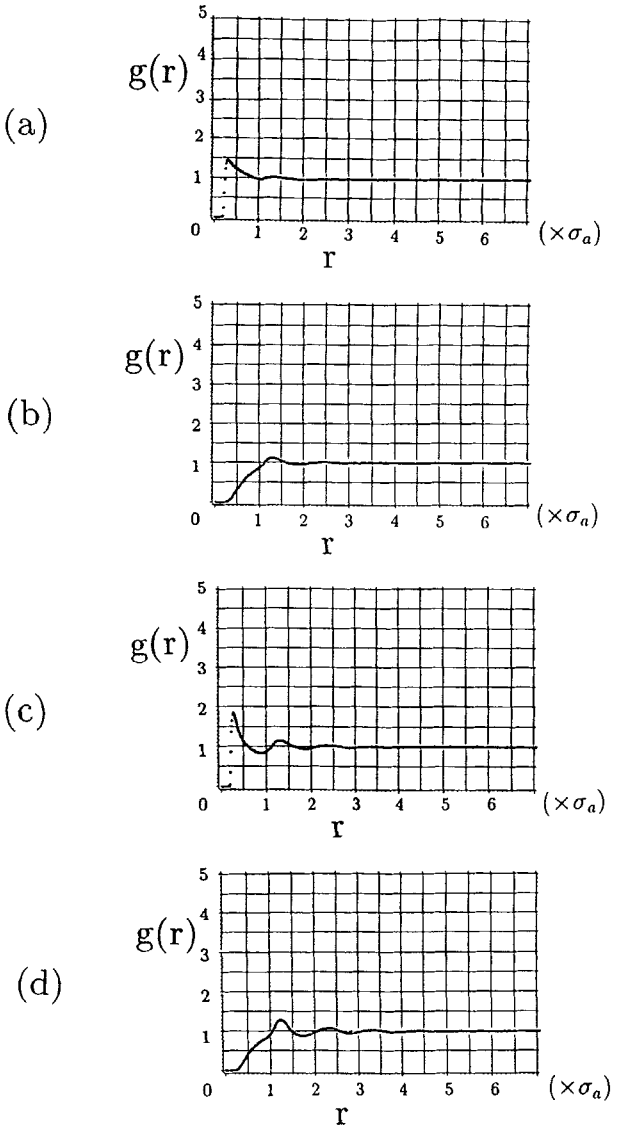

Figure 5 Radial distribution function for counter-ions. The parameters in (a), (b), (c) and (d) are the same as in Figure 2.

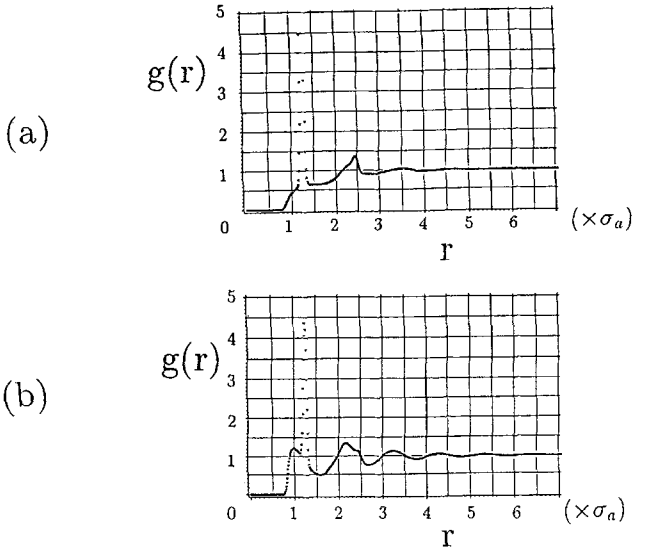

Figure 6 Radial distribution function for monomers and counter-ions. The parameters in (a), (b) are the same as in Figure 4.

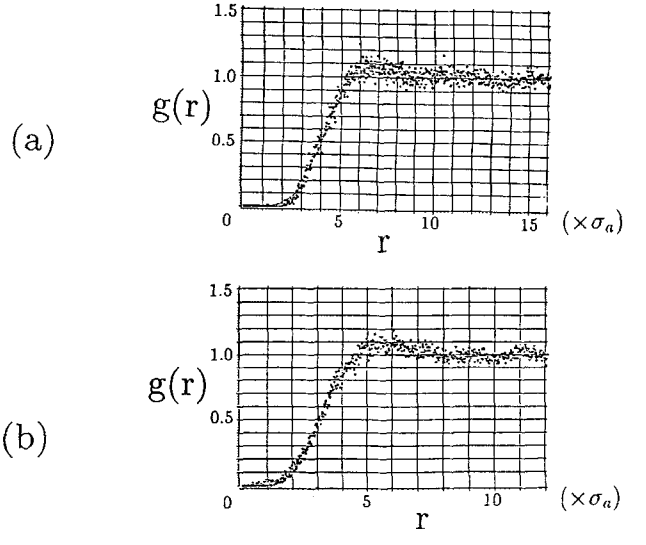

Figure 7 Radial distribution function for the center monomers of each polymer chain. The parameters in (a), (b) are the same as in Figure 4.

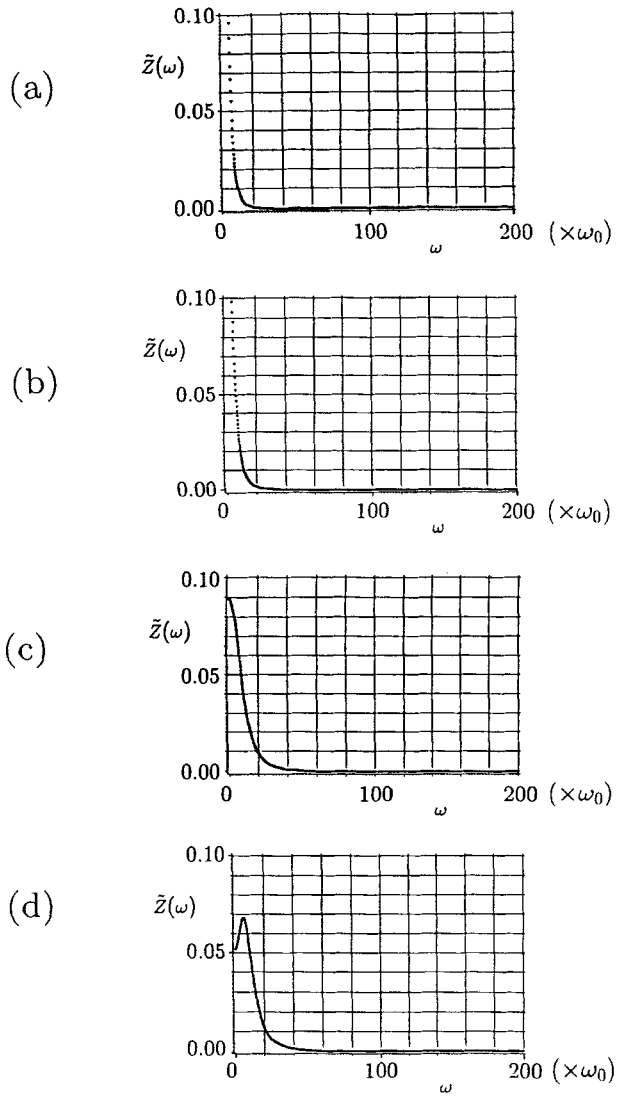

Figure 8 Power spectrum for counter-ions. The parameters in (a), (b), (c) and (d) are the same as in Figure 2.

$$Z(t) = \frac{\langle \vec{v}(t + t_0) \cdot \vec{v}(t_0) \rangle}{\langle \vec{v}(t_0) \cdot \vec{v}(t_0) \rangle} . \tag{5}$$

We obtained the power spectrum $\tilde{Z}(\omega)$ by Fourier transforming $Z(t)$. Figure 8 shows $\tilde{Z}(\omega)$ for the counter-ions.

$\tilde{Z}(\omega)$'s for monomers are remarkably different from those for counter-ions. For the monomers, $Z(t)$ shows oscillations; the corresponding Fourier transforms are

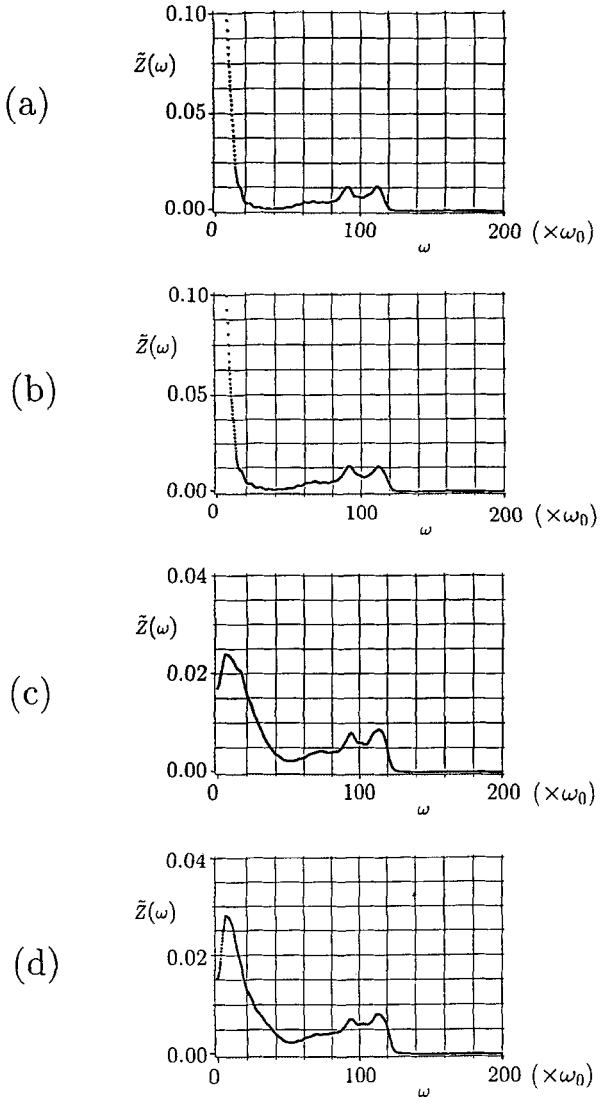

Figure 9 Power spectrum for monomers. The parameters in (a), (b), (c) and (d) are the same as in Figure 2.

shown in Figure 9, indicating weak but clear peaks in the region of about $\omega = 100\omega_0$. These frequencies definitely correspond to the vibrational frequencies of the springs connecting the monomers. We also see a peak in a much smaller frequency region at about $\omega = 10\omega_0$ for $\rho = 0.65$. This peak is caused by a liquid-like behaviour of polymer chains at high density. For the counter-ions, the peak at $\omega = 10\omega_0$ appears only in the case of the Coulombic interaction (Figure 8(d)). In the case of the non-Coulombic interaction (Figure 8(c)), the counter-ions do not

show liquid-like behaviour even at $\rho = 0.65$, because the counter-ions are much smaller in size than monomers and thus the counter-ions move more freely than the monomers do. In the presence of the Coulombic interaction, the counter-ions, attracted by the monomers, follow the liquid-like behaviour of monomers.

3.3 *Diffusion properties*

In this subsection, we study the diffusion properties of the monomers and counter-ions. We have calculated the mean square displacement as defined by:

$$\langle R^2(t) \rangle = \langle |\vec{r}(t + t_0) - \vec{r}(t_0)|^2 \rangle. \tag{6}$$

For the mean square displacement of polymers, we have computed $\langle R^2(t) \rangle$ with only four innermost monomers of each polymer chain, namely, 9th, 10th, 11th and 12th monomers. We show the results in Figure 10. $\langle R^2 \rangle$ of the counter-ions shows almost a straight line already in the time region as shown here, implying the usual behaviour of self diffusion. As the density is increased, the self diffusion constant, which is proportional to the slopes estimated from the straight lines shown in Figure 10, becomes smaller as usual. Comparing Figure 10(a) with (b), we can observe that the presence of the Coulombic interactions significantly reduces the diffusion of the counter-ions, while the diffusion of monomers is much slower than that of counter-ions, as seen from Figure 10(c) and (d). The density dependence of the diffusion of monomers seems to be stronger than that of the counter-ions, so that it rapidly saturates and becomes too small to make an accurate estimate in the range of high densities.

The mean square displacement for monomers is replotted in logarithmic scale in Figure 11. The average slope is around 1/2. According to the reptation model [8, 9], the diffusion should slow down due to the entanglement effect, and the exponent of the mean square displacement should reach 1/4 after some time. Our result obtained from Figure 11 implies that such prediction of the reptation model does not hold for our two-dimensional model. This is consistent with the Monte Carlo results [13, 14].

In Figure 12, we show the radius of gyration as a function of density. We see that the Coulombic interaction makes the gyration length of the polymer chains slightly smaller. This is mainly due to the effect of the attractive interaction between counter-ions and monomers. The density dependence of the gyration radius is clear: as the density becomes larger, the gyration radius becomes smaller.

Finally, in Figure 13, we show examples of polymer configurations to see how monomers move in the course of some elapsed time. For both the Coulombic and non-Coulombic cases, the polymer chains do not seem to show a reptation-modellike motion, such as self diffusion of a chain along the contour or the axis of a tube made up of other neighbouring chains. Thus, our conclusion for this point is that our two-dimensional model for a condensed charged polymer melt does not meet the reptation picture.

4 DISCUSSION

We have investigated a two-dimensional model for a condensed charged polymer melt with a classical molecular dynamics simulation. We have found that the

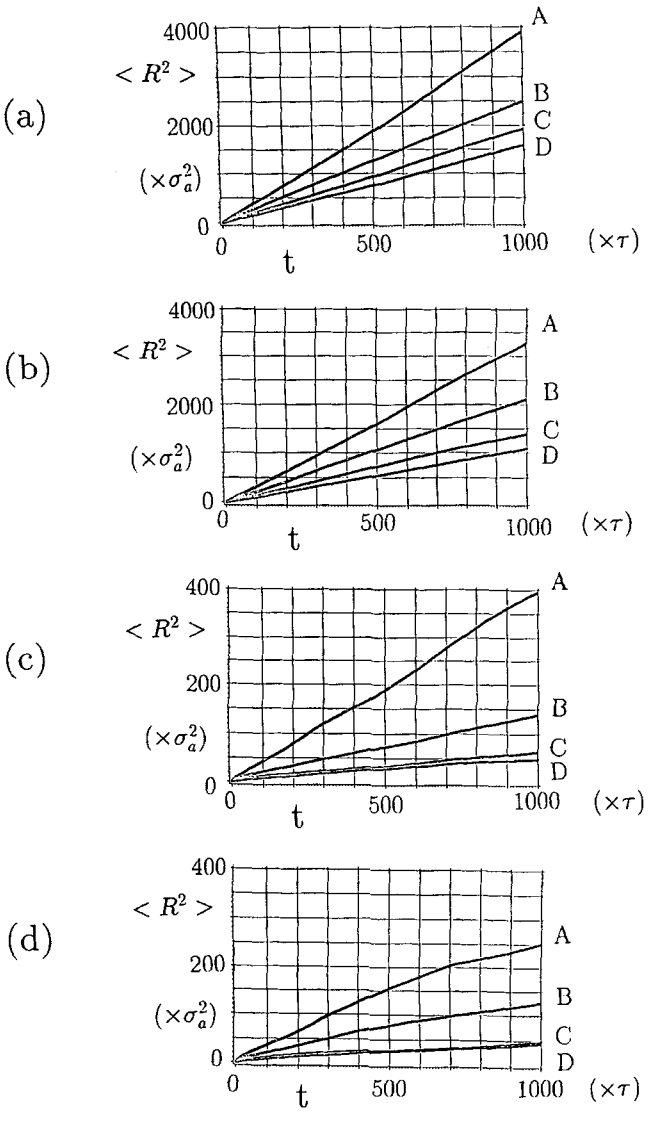

Figure 10 Mean squared displacement for (a) counter-ions without Coulombic interactions, (b) counter-ions with Coulombic interactions, (c) innermost monomers without Coulombic interactions, and (d) innermost monomers with Coulombic interactions. The curves A, B, C, and D are for ρ = 0.4, 0.5, 0.6 and 0.65, respectively.

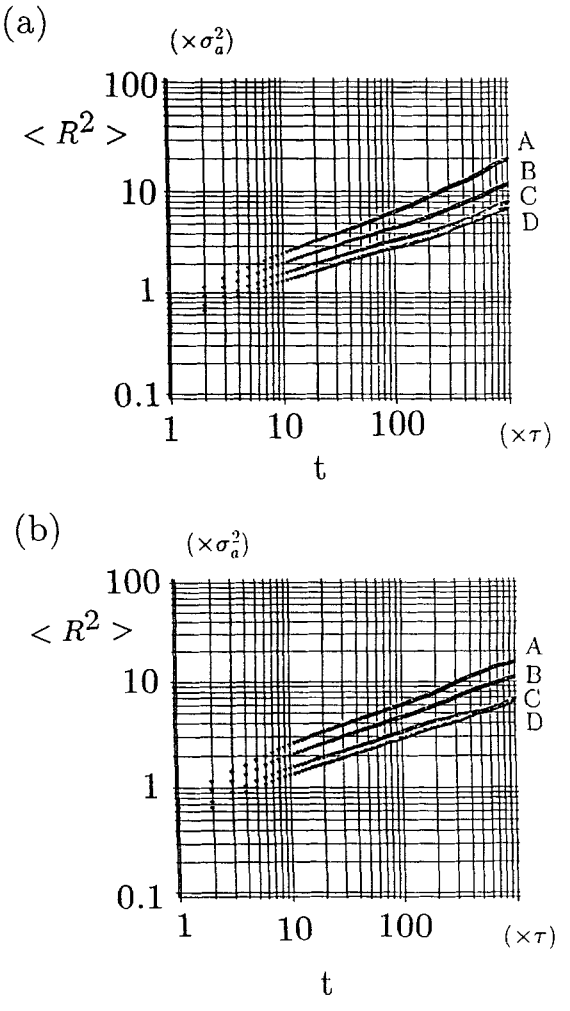

Figure 11 Logarithmic plot of the mean square displacement for monomers. (a) and (b) are replotted with Figure 12 (c) and (d), respectively.

monomers tend to form a local triangular structure, whereas counter-ions mostly populate around the mid-point of the adjacent monomer pairs of the polymer chains. The behaviour of the pair distribution function $g(r)$ for the central monomers of the polymer chains (see Figure 7) shows little density dependence. On the other hand, the gyration radius exhibits a much stronger density dependence, as shown in Figure 14. For an increasing density, the gyration radius monotonically decreases in the density range between $\rho = 0.4$ to 0.65. The conclusion is made that the reptation picture provides us with no physically reasonable model to the self diffusion of the polymer chains in a two-dimensional system. This conclusion may be verified by an experiment for a very thin polymer film. However, there still

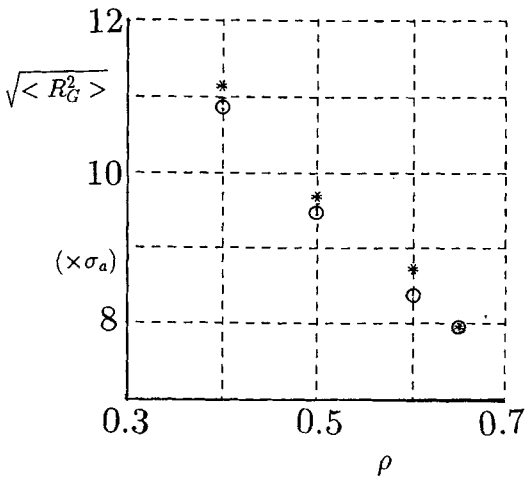

Figure 12 The density variation of the averaged gyration radius for the case of non-Coulombic interactions (*) and for the case of Coulombic interactions (○).

remains a problem as to whether the chain length $N = 20$ used in the present work was not long enough to observe the reptation dynamics. This is a future problem of interest. The effects of Coulombic interactions for the monomers are observed on the gyration size of the polymer chains and on the self diffusion: in the presence of Coulombic interaction, there is a slight decrease of the gyration length, while there is a remarkable reduction of the self diffusion. The counter-ions are much affected by the Coulombic interaction; at high density, the counter-ions follow the motions of the monomers because of the attractive force.

In the present model we have assumed that the monomers and counter-ions all have the same mass. It should be more realistic to use different masses for them, the formers have a substantially lighter mass than the latters.

We have studied uniformly charged polymer melts. The present model can easily be extended to a more general case such as monomers having different charges, positively and negatively, and with or without counter-ions to neutralize the whole system. Such systems are known as polyampholyte solutions [15], the properties of which are particularly of interest. An interesting example is studied recently by Victor *et al.*, in which charges of opposite signs are placed alternatively on a single polymer chain [16]. Both static and dynamical properties of polyampholyte solutions, which greatly differ from those of polyelectrolytes, but some similar to them, are also of great interest.

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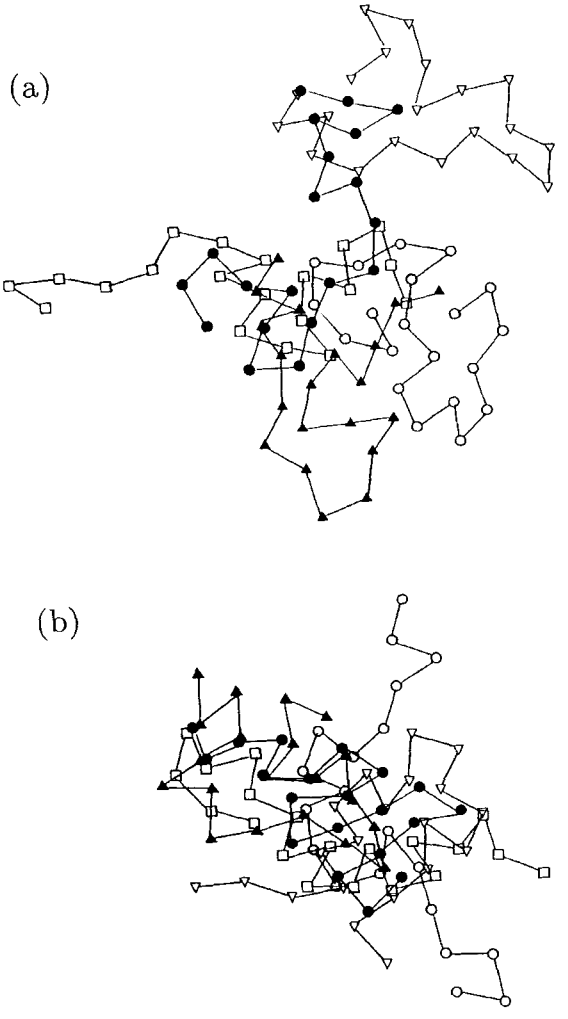

Figure 13 Snapshots of a single polymer chain in a melt in the course of some times for $\rho = 0.65$; the snapshots were taken with the time interval 200 τ. In the figure, the time increases with ○, ▲, □, ●, △, in this order. (a) without Coulombic interactions and (b) with Coulombic interactions.

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