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SHORT COMMUNICATION

Computer Simulation of Polymer Chain Statistics

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Many methods for the Monte Carlo simulation have been developed[1] in regard to the excluded volume of a flexible chain. The self-avoiding-walk on a lattice is one of these. The method presented here is rather primitive but realistic. We have removed the constraint of walks on the lattice and hence can take any interactions between segments into the simulation.

When a flexible chain consists of linearly linked N segments of length a and interacting each other, its "partition" function Z_N is given by

$$Z_N=\sum_{\text{path }\{\boldsymbol{r}_i\}}\exp\left\{-\beta\left[\sum_{i=1}^{N}(\Delta\boldsymbol{r}_i)^2+U(\{\boldsymbol{r}_i\})\right]\right\} \quad (1)$$

where $\{\boldsymbol{r}_i\}$ is a set of position vectors of successive segments ($i=0, 1, 2, \cdots, N$) $\boldsymbol{r}_i=\boldsymbol{r}_i-\boldsymbol{r}_{i-1}$, and $U(\{\boldsymbol{r}_i\})$ is the interaction potential between segments. Path $\{\boldsymbol{r}_i\}$ stands for a set of all allowable paths.

Our special interest is the root-mean-square $\langle\boldsymbol{R}^2\rangle$ of the end-to-end vector $\boldsymbol{R}=\boldsymbol{r}_N-\boldsymbol{r}_0$, *i.e.*,

$$\langle\boldsymbol{R}^2\rangle=\sum_{\text{path }\{\boldsymbol{r}_i\}}\left(\sum_{i=1}^{N}\Delta\boldsymbol{r}_i\right)^2\times\exp\left\{-\beta\left[\sum_{i=1}^{N}(\Delta\boldsymbol{r}_i)^2+U(\{\boldsymbol{r}_i\})\right]\right\}\Big/Z_N \quad (2)$$

In this note, attention has been directed to the calculation of $\langle\boldsymbol{R}^2\rangle$ by the Monte Carlo simulation.

METHOD

We replace $(\Delta\boldsymbol{r}_i)_\mu$ ($\mu=1, 2, \cdots, d$; d is the dimentional number) by the Gaussian number, $(\Delta\tilde{\boldsymbol{r}}_i)_\mu$. This makes the contour length $\tilde{L}=N\tilde{a}$ which has no definite value, where $\tilde{a}=[\sum_{\mu=1}^{d}(\Delta\tilde{\boldsymbol{r}}_i)_\mu^2]^{1/2}$. Similarly we replace R by $\tilde{R}$, $\{\boldsymbol{r}_i\}$ by $\{\tilde{\boldsymbol{r}}_i\}$ and $U(\{\boldsymbol{r}_i\})$ by $\tilde{U}(\{\tilde{\boldsymbol{r}}_i\})$. By repeating these replacements, we finally obtain a set of paths. This is very similar to the concept underlying the renormalization group method in which the short-range correlation is replaced by a Gaussian-type function.

As a result of these replacements, i) $\Delta\tilde{\boldsymbol{r}}_i$ represents a set of segments belonging to a small region, ii) $\tilde{L}$ and hence $\tilde{\boldsymbol{R}}$ have no definite values but distribute in Gaussian form, iii) the interaction potential $\tilde{U}$ is not bare but renormalized. Thus, our method of simulation may be expected to give reasonably realistic results.

For simplicity, we assume the interaction potential $\tilde{U}$ to be represented by

$$\tilde{U}(\{\tilde{\boldsymbol{r}}_i\})=\frac{1}{2}\sum_{i\neq j}\phi(|\tilde{\boldsymbol{r}}_i-\tilde{\boldsymbol{r}}_j|) \quad (3)$$

with

$$\beta\phi(|\tilde{\boldsymbol{r}}_i-\tilde{\boldsymbol{r}}_j|)=\begin{cases}\alpha\ (=\text{const.}) & \text{for } |\tilde{\boldsymbol{r}}_i-\tilde{\boldsymbol{r}}_j|\leqq r_0\\ 0 & \text{for } |\tilde{\boldsymbol{r}}_i-\tilde{\boldsymbol{r}}_j|>r_0\end{cases} \quad (4)$$

Thus, with the interaction parameter α, the effective range r_0, and the standard deviation of $(\Delta\tilde{\boldsymbol{r}}_i)_\mu$, we can generate a path whose weight is $\exp[-\{\sum(\Delta\tilde{\boldsymbol{r}}_i)^2+\tilde{U}(\{\tilde{\boldsymbol{r}}_i\})\}]$ and then the square of

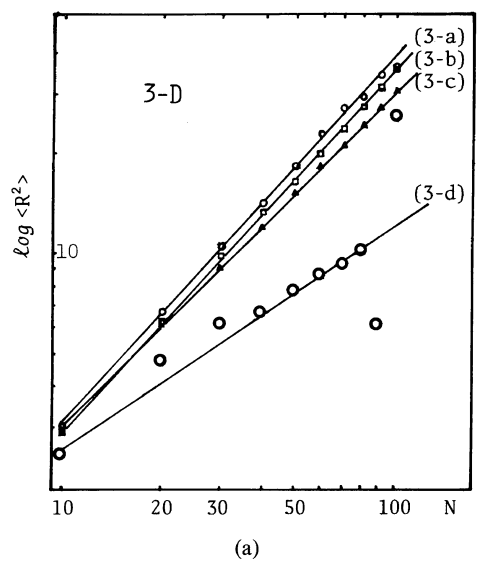
the end-to-end vector for the path. By summing up all these paths, we can evaluate eq 2.

RESULTS

We have simulated eq 2 for $d=2$, 3, and 4, choosing, for each d, the values of r_0 and α as given in Table I. The standard deviation of $(\Delta\tilde{r}_i)_\mu$ is taken as $\beta^{-1/2}$ in every case. The scale of r_0 is $\beta^{-1/2}$. For each simulation, we have generated about 10^4 paths.

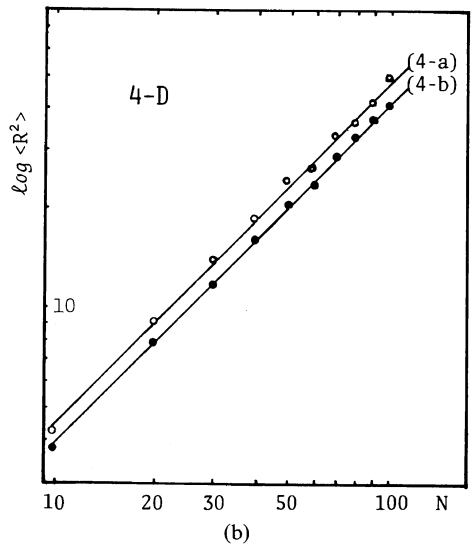
Table I. Simulation results for 2ν chosen for the best fit from the relation of $\langle \boldsymbol{R}^2 \rangle \propto N^{2\nu}$, d is the dimensional number of the space, r_0 and α are the interaction parameters given in eq 4, and the last column refers to Figures 1a—c. r_0 is scaled by $\beta^{-1/2}$

d	r_0	α	2ν	
3	0.5	2.0	1.13	(3-a)
		0.8	1.11	(3-b)
		0	1.00	(3-c)
		−0.8	2/3	(3-d)
4	1.0	2.0	1.00	(4-a)
		0	1.00	(4-b)
2	0.5	0.5	1.35	(2-a)
		0	1.00	(2-b)

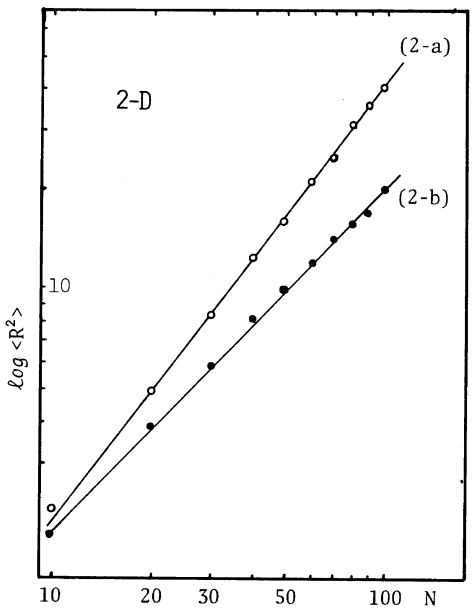


(a)

The results are shown in Figure 1a—2. In these figures, the dots are the simulated results, and the lines indicate the relations between $\langle \boldsymbol{R}^2 \rangle$ and $N^{2\nu}$.



(b)



(c)

Figure 1a—c. a, b, and c are log-log plots of $\langle \boldsymbol{R}^2 \rangle$ *vs.* N for various values of α in 3-, 4-, and 2-dimentional space, respectively: a, $\alpha=2.0$ (small circle), 0.8 (square), 0 (triangle), and -0.8 (large circle); b, $\alpha=2.0$ (circle) and 0 (dot), and c, $\alpha=0.5$ (circle) and 0 (dot), respectively. Each straight line is plotted to make the best fit for $\langle \boldsymbol{R}^2 \rangle \propto N^{2\nu}$ with ν given in Table I.

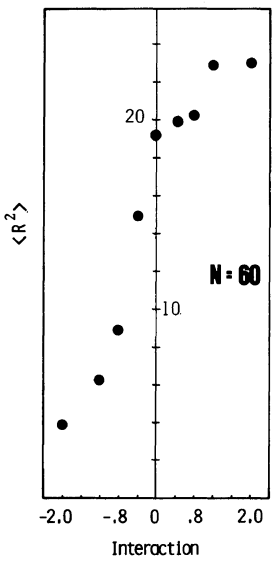


Figure 2. $\langle R^2 \rangle$ *vs.* interaction parameter α for $N=60$. Certainly, the chain is obviously collapsed below $\alpha = -0.8$ because $\langle R^2 \rangle \propto N^{2/3}$ (see Figure 1a).

The best-fit values of ν are given in Table I. In particular our attention was focused on the case in which attractive interactions are present in 3-dimensional space (see Figure 1a and Figure 2). We can see a globule-coil transition,[2,3] although a definite conclusion is necessary in order to carry out a much more extensive and detailed simulation[4] than that done in this work. It should be mentioned that the collapse to zero size cannot occur in spite of the lack of the core part in the effective potential. This is due to the condition such that the finite deviation of the elements is greater than the effective range r_0.

Simulations were carried out at the Computer Center of the University of Tokyo.

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