Renormalization group theory of transport properties of polymer solutions. I. Dilute solutions

2 **AUTHORS**, INCLUDING:

M. Kohmoto

The University of Tokyo

183 PUBLICATIONS **7,137** CITATIONS

Renormalization group theory of transport properties of polymer solutions. I. Dilute solutions

Y. Oono and M. Kohmoto

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

The (Gell–Mann–Low type) renormalization group theory is applied to frictional properties of dilute polymer solutions for the first time. The universal ratios such as Flory's intrinsic viscosity constant, the Flory–Scheraga–Mandelkern parameter, etc., are estimated from the first order ϵ-expansion theory ($\epsilon = 4 - d$, d being the spatial dimensionality). The results are in satisfactory agreement with experimental results in both the nondraining Gaussian and nondraining self-avoiding limits. Preaveraging the Oseen tensor makes the value of the intrinsic viscosity about 10% larger according to the first order ϵ-expansion calculation.

I. INTRODUCTION

The frictional properties such as viscosity, sedimentation coefficient, and diffusion coefficient of dilute polymer solutions are important in experimental characterization of polymers. Indeed, the intrinsic viscosity $[\eta]$ played a crucial role in establishing the existence of macromolecules by Staudinger.[1]

In the present paper, the renormalization group theory[2] is, for the first time, applied to calculate $[\eta]$ and translational diffusion constant D (or, equivalently, translational friction coefficient f) to order $\epsilon = 4 - d$ (d is the spatial dimensionality) in the Kirkwood–Riseman scheme[3] *without preaveraging* the Oseen tensor. Our calculation gives asymptotic values of the universal ratios such as $A_2 M/[\eta]$, $M[\eta]/N_A \langle S^2 \rangle^{3/2}$, etc., in good agreement with experimentally obtained values (see Tables I and II in Sec. V), where A_2 is the osmotic second virial coefficient, $\langle S^2 \rangle$ the mean square radius of gyration, M the molecular weight, and N_A Avogadro's constant.

The frictional properties are given by ensemble averages of quantities containing the force F_i exerted on the ith chain unit by the solvent. In the Kirkwood–Riseman scheme, F_i obeys

$$\mathbf{F}_i = \zeta(\mathbf{u}_i - \mathbf{v}_i) - \zeta \sum_{i \neq j} \mathbf{T}_{ij} \mathbf{F}_j , \qquad (1.1)$$

where ζ is the friction coefficient of the chain unit, $\mathbf{u}_i$ the velocity of the ith unit, $\mathbf{v}_i$ the original solvent velocity at the position of the ith unit without the polymer chain, and $\mathbf{T}_{ij}$ the Oseen tensor representing the hydrodynamic interaction between chain units [see Eq. (2.4)]. Thus, there are two essential steps in calculating frictional properties in this scheme: the first is to solve Eq. (1.1) for $\mathbf{F}_i$, and the second is to calculate the ensemble average of quantities containing $\mathbf{F}_i$. The first step requires the solution to Eq. (1.1) for *each conformation* of the chain, because $\mathbf{T}_{ij}$ depends explicitly on the conformation.

Due to this difficulty, all the conventional analytic approaches[4] in the Kirkwood–Riseman scheme perform certain kinds of preaveraging; the Oseen tensor is averaged (often approximately) with respect to the equilibrium ensemble. Then, Eq. (1.1) turns out to be a Fredholm type equation. Thus, even the calculations for a Gaussian chain have not been carried out systematically. The excluded volume effect has been taken into account by choosing an appropriate ensemble to average the Oseen tensor. Kurata and Yamakawa[5] developed an approximate bare perturbation theory to perform this ensemble average. Ptitsyn, Tschoegl, Zimm, et al[6] have used the Peterlin approximation[7] which replaces the preaveraged Oseen tensor with the approximate form which takes into account the swelling of the chain. Thus, all the existing theories suffer from their *ad hoc* approximations.

The crucial observation in the present approach is that near the fixed point of the renormalization group transformation[2] the strength of the hydrodynamic interaction becomes of order ϵ in $(4 - \epsilon)$-space.[8–10] Hence, the Kirkwood–Riseman equation (1.1) can be solved iteratively without any preaveraging. In the second step, the ensemble average of quantities containing $\mathbf{F}_i$ can also be performed perturbatively, because the excluded volume interaction becomes of order ϵ as well.[11]

The estimate of the effect of preaveraging the Oseen tensor can also be obtained. To order ϵ the preaveraging makes the intrinsic viscosity about 10% higher. This is the first analytic estimate of the effect of preaveraging, and is in agreement with the Monte Carlo result by Zimm.[12]

The effects of the quality of solvents (or temperature) and of polymer concentration will be studied in the forthcoming papers of the present series.

In Sec. II, the friction coefficient f is calculated, and our renormalization group approach is explained in detail. The calculation of $[\eta]$ is given in Sec. III. It is technically more complicated, but the basic renormalization group method is the same as Sec. II. In Sec. IV the effect on $[\eta]$ of preaveraging of the Oseen tensor is studied.

Section V summarizes the results obtained and gives two tables of universal ratios. The first order ϵ-expansion estimates of universal ratios such as viscosity factor, Flory–Scheraga–Mandelkern parameter, etc.,

are in satisfactory agreement with (real or numerical) experimental results.

II. TRANSLATIONAL FRICTION COEFFICIENT AND DIFFUSION CONSTANT

A. Perturbation calculation

Consider a chain whose static properties are given by the Hamiltonian

$$H_a = \frac{1}{2} \int_0^{N_0} \left(\frac{d\mathbf{c}(\tau)}{d\tau}\right)^2$$
$$+ \frac{v_0}{2} \int_0^{N_0} d\tau \int_{\substack{0 \\ |\tau-\tau'|>a}}^{N_0} d\tau' \, \delta(\mathbf{c}(\tau) - \mathbf{c}(\tau')) \, , \qquad (2.1)$$

where $\mathbf{c}(\tau)$ is the conformation of the chain parametrized by the contour variable $\tau \epsilon [0, N_0]$, N_0 is the bare chain length, v_0 is the bare excluded volume parameter, and a is the cutoff to eliminate the self-interaction of the unit of the chain.

The drift velocity response of the chain to the force exerted on it is described by the translational friction coefficient f, i.e.,[4]

$$f\mathbf{u} = \int_0^{N_0} d\tau \langle \mathbf{F}(\tau) \rangle \, , \qquad (2.2)$$

where $\mathbf{u}$ is the drift velocity of the chain and $\mathbf{F}(\tau)$ is the force per unit contour variable exerted on the point at τ on the chain. A very small $\mathbf{u}$ is considered, so the average $\langle \, \rangle$ may be taken over the equilibrium ensemble given by the Hamiltonian (2.1). [As in Eqs. (2.1) and (2.2), the model with continuous contour variable will be used.] According to the Kirkwood–Riseman scheme,[3,4] $\mathbf{F}(\tau)$ obeys a linear equation,

$$\mathbf{F}(\tau) = \zeta_0 \mathbf{u} - \zeta_0 \int_{\substack{0 \\ |\tau-\tau'|>a}}^{N_0} d\tau' \, \mathbf{T}(\tau, \tau') \mathbf{F}(\tau') \, , \qquad (2.3)$$

where ζ_0 is the bare friction coefficient. The hydrodynamic interaction is represented by the Oseen tensor,

$$T_{\alpha\beta}(\tau, \tau') = (2\pi)^{-d} \int d^d k \, \frac{1}{\eta_e k^2}$$
$$\times \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right) \exp\{i\mathbf{k} \cdot [\mathbf{c}(\tau) - \mathbf{c}(\tau')]\} \, , \qquad (2.4)$$

where η_e is the effective viscosity, which is not necessarily equal to the solvent viscosity η_s.[13]

As is known,[11,14,15] the excluded-volume parameter v_0 in the Hamiltonian (2.1) for the static polymer problem becomes order of $\epsilon = 4 - d$ at the fixed point of the renormalization group transformation. Therefore, in the ϵ-expansion method the excluded-volume interaction has been treated perturbatively. Also as is known[8-10] and will be seen later, ζ_0/η_e becomes of order ϵ so that the hydrodynamic interaction can be treated perturbatively as well. From Eqs. (2.2) and (2.3), the translational friction coefficient f is given up to the lowest nontrivial order as

$$f = N_0 \zeta_0 - \zeta_0^2 \int_0^{N_0} d\tau \int_{\substack{0 \\ |\tau-\tau'|>a}}^{N_0} d\tau' \left\langle \frac{1}{d} \sum_\alpha T_{\alpha\alpha}(\tau, \tau') \right\rangle \, . \qquad (2.5)$$

The equilibrium ensemble average in the second term is calculated by using the Hamiltonian (2.1). Up to this order, however, it is sufficient to use the Hamiltonian without the excluded-volume interaction. The resulting Gaussian average is easily performed to give

$$f = N_0 \zeta_0 - \frac{1}{(2\pi)^2} N_0 \zeta_0^2 \frac{1}{\eta_e} (2\pi N_0)^{\epsilon/2} \left(\frac{3}{2} \frac{1}{\epsilon} - \frac{1}{8}\right) \, . \qquad (2.6)$$

The presence of a singularity at $\epsilon = 0$ in this expression necessitates the renormalization treatment, which will be discussed in the next subsection.

B. Renormalization

The original theory contains the bare quantities N_0, v_0, and ζ_0. In the renormalization scheme, singularities appearing in the results of bare calculations are absorbed in the relation between the bare and the renormalized quantities.[16] To this end, it is convenient to use dimensionless quantities. Let L be a quantity which has the same dimensionality as N_0. Then dimensionless quantities are defined by

$$u_0 = v_0 L^{\epsilon/2} \, , \qquad (2.7)$$

and

$$\xi_0 = (\zeta_0/\eta_e) L^{\epsilon/2} \, . \qquad (2.8)$$

The dimensionless nature of ξ_0 is seen from Eq. (2.6).

The renormalized dimensionless coupling constant u corresponding to u_0 has been the expansion parameter in the static problems and the relations between the bare and the renormalized quantities which appear in the static Hamiltonian have been obtained perturbatively as[16]

$$u_0 = u \left[1 + \frac{2}{\pi^2 \epsilon} u + O(u^2)\right] \, , \qquad (2.9)$$

$$N = Z_2 N_0 \, , \qquad (2.10)$$

where

$$Z_2 = 1 + \frac{1}{2\pi^2 \epsilon} u + O(u^2) \, . \qquad (2.11)$$

In the present problem of evaluating the translational friction coefficient,[3,4] there is an additional parameter ξ_0 which represents the strength of the hydrodynamic interaction. The renormalized quantity corresponding to ξ_0 becomes of order ϵ at the fixed point, so that ξ is an expansion parameter as well as u. The relation between ξ_0 and ξ is written as

$$\xi_0 = \xi (1 + E_1 \xi + E_2 u + \cdots) \, . \qquad (2.12)$$

The singularity in Eq. (2.6) must disappear if f is rewritten in terms of the renormalized quantities, N, u, and ξ. This requirement determines the relation between ξ_0 and ξ. First, Eq. (2.6) is rewritten in terms of the dimensionless coupling constant ξ_0.

$$\frac{L^{\epsilon/2}}{\eta_e} f = Z_2^{-1} N \xi_0 - \frac{1}{(2\pi)^2} N \xi^2 \left(\frac{2\pi N}{L}\right)^{\epsilon/2} \left(\frac{3}{2} \frac{1}{\epsilon} - \frac{1}{8}\right) \, . \qquad (2.13)$$

Here, the second term is of higher order in ξ, so that the bare quantities ξ_0 and N_0 have been simply replaced by the renormalized quantities ξ and N, because the bare and the renormalized quantities coincide in the

lowest order. From Eqs. (2.11), (2.12), and (2.13), E_1 and E_2 are determined to yield

$$\xi_0 = \xi\left(1 + \frac{3}{8\pi^2\epsilon}\xi + \frac{1}{2\pi^2\epsilon}u + \cdots\right) . \qquad (2.14)$$

Thus, the translational friction coefficient is written in terms of the renormalized quantities as

$$f = N\zeta\left\{1 - \frac{1}{(2\pi)^2}\xi\left[\frac{3}{4}\log\left(\frac{2\pi N}{L}\right) - \frac{1}{8}\right]\right\} , \qquad (2.15)$$

where ζ is the renormalized version of ζ_0 and is defined by

$$\zeta = \eta_e\xi L^{-\epsilon/2} . \qquad (2.16)$$

C. Renormalization group equation, fixed points, and universal form

In the previous section, the renormalized perturbation result has been obtained to the lowest nontrivial order. However, the scaling property cannot be seen explicitly in the result. To elucidate the universal properties it is essential to have the concept of the renormalization group and its fixed points. A solution to the renormalization group equation combined with the dimensional analysis gives[2,16] the scaling form of the translational friction coefficient f. The renormalization group equation for f is obtained by using the fact that the bare f is independent of L which has been introduced to make the dimensionless quantities. However, note that the renormalized quantities N, u, and ξ may depend on L. The chain rule of differentiation gives

$$\left(L\frac{\partial}{\partial L} + \beta_u\frac{\partial}{\partial u} + \beta_\eta\frac{\partial}{\partial \xi} + \gamma N\frac{\partial}{\partial N}\right)f = 0 , \qquad (2.17)$$

where

$$\beta_u \equiv L\frac{\partial u}{\partial L}\bigg|_{\text{bare quantities}} , \qquad (2.18)$$

$$\beta_\xi \equiv L\frac{\partial \xi}{\partial L}\bigg|_{\text{bare quantities}} , \qquad (2.19)$$

and

$$\gamma \equiv L\frac{\partial \log Z_2}{\partial L}\bigg|_{\text{bare quantities}} . \qquad (2.20)$$

These functions are calculated from Eqs. (2.9), (2.11), and (2.14) as

$$\beta_u(u) = u\left(\frac{\epsilon}{2} - \frac{1}{\pi^2}u\right) + O(u^3) , \qquad (2.21)$$

$$\beta_\xi(\xi, u) = \xi\left(\frac{\epsilon}{2} - \frac{3}{16\pi^2}\xi - \frac{1}{4\pi^2}u\right)$$

$$+ \text{higher order terms} , \qquad (2.22)$$

and

$$\gamma(u) = \frac{u}{(2\pi)^2} + O(u^2) . \qquad (2.23)$$

The coupling constants $u = u^*$ and $\xi = \xi^*$ which give zeros of the β functions β_u and β_ξ are called fixed points. Four fixed points[8,9,18,19] are found from Eqs. (2.21) and (2.22) as

(A) $u^* = 0$, $\xi^* = 0$,

(B) $u^* = \frac{\pi^2}{2}\epsilon$, $\xi^* = 0$,

(C) $u^* = 0$, $\xi^* = \frac{8}{3}\pi^2\epsilon$,

and

(D) $u^* = \frac{\pi^2}{2}\epsilon$, $\xi^* = 2\pi^2\epsilon$.

The fixed points (A) and (B) represent the free-draining cases and (C) and (D) the nondraining cases. The fixed points with $u^* = 0$ approximately correspond to the theta state and $u^* = \frac{1}{2}\pi^2\epsilon$ to the self-avoiding limit. At the fixed points, the renormalization group equation (2.17) becomes

$$\left(L\frac{\partial}{\partial L} + \gamma^* N\frac{\partial}{\partial N}\right)f = 0 , \qquad (2.24)$$

where γ^* is the fixed point value of γ, and is related to the exponent ν by[16]

$$\gamma^* = 1 - 1/2\nu . \qquad (2.25)$$

Equation (2.24) restricts the functional form of f to be

$$f^* = f(L, N, u^*, \xi^*) = f_1(LN^{-1/\gamma^*}, u^*, \xi^*) , \qquad (2.26)$$

where f_1 is a well-behaved function. On the other hand, there is a simple scaling property

$$f(SL, SN, u, \xi) = S^{(d/2)-1}f(L, N, u, \xi) , \qquad (2.27)$$

where S is an arbitrary positive number. This property is most easily seen from Eq. (2.15) with Eq. (2.16). Combining Eqs. (2.26) and (2.27) fixes the functional form of the friction coefficient as

$$f^* = \left[\frac{1}{L}\left(\frac{N}{L}\right)^{-2\nu}\right]^{1-d/2}f_2(u^*, \xi^*) \qquad (2.28)$$

where f_2 is a well-behaved function. The result agrees with the scaling argument.[20,21]

At the fixed points, the renormalized perturbation result, Eq. (2.15), is rewritten to conform with Eq. (2.28)

$$f^* = \frac{\eta_e}{2\pi}\xi^* \exp\left[\frac{1}{(2\pi)^2}\frac{\xi^*}{8}\right]L^{(d/2)-1}\left(\frac{2\pi N}{L}\right)^{1-(3/4)[\xi^*/(2\pi)^2]}$$

$$= \frac{\eta_e}{2\pi}\xi^* \exp\left[\frac{1}{(2\pi)^2}\frac{\xi^*}{8}\right]L^{(d/2)-1}\left(\frac{2\pi N}{L}\right)^{(d-2)\nu} . \qquad (2.29)$$

In the case of the nondraining and self-avoiding fixed point (D), $\xi^* = 2\pi^2\epsilon$, so that

$$f^* = \pi\eta_e\epsilon \, e^{\epsilon/16} L^{(d/2)-1}\left(\frac{2\pi N}{L}\right)^{(d-2)\nu} \qquad (2.30)$$

with

$$\nu = \frac{1}{2} + \frac{1}{16}\epsilon . \qquad (2.31)$$

Another interesting fixed point is the nondraining Gaussian case (C) which corresponds to the theta state. In this case, $\xi^* = 8\pi^2\epsilon/3$ and

$$f^* = \frac{4}{3}\pi\epsilon\eta_e \, e^{\epsilon/12}(2\pi N)^{(d-2)\nu} , \qquad (2.32)$$

with

$$\nu = \frac{1}{2} . \qquad (2.33)$$

Usually, η_e has been identified with the solvent viscosity η_s in Eqs. (2.30) and (2.32). Later in Sec. V the usual choice $\eta_s \simeq \eta_e$ is shown to be reasonable.

The dynamical exponent z is defined by[8]

$$f \propto N^{(z-2)\nu} . \tag{2.34}$$

Hence, Eq. (2.28) implies $z = d$. This is a kinematic consequence as has been noted in Ref. 10.[22]

D. Translational diffusion coefficient

The translational diffusion coefficient D is related to f by the Einstein relation

$$D = kT/f . \tag{2.35}$$

Here, no extra calculation is needed to obtain D to order ϵ. Thus the renormalized results can be seen from Eqs. (2.30) and (2.32) as

$$D^* = \frac{kT}{\pi \eta_e \epsilon} e^{-\epsilon/16} L^{1-(d/2)} \left(\frac{2\pi N}{L}\right)^{(2-d)\nu} , \tag{2.36}$$

with $\nu = \frac{1}{2} + \epsilon/16$ in the nondraining self-avoiding limit, and

$$D^* = \frac{\zeta kT}{4\pi \epsilon \eta_e} e^{-\epsilon/12} (2\pi N)^{(2-d)\nu} , \tag{2.37}$$

with $\nu = \frac{1}{2}$ in the nondraining Gaussian case.

Note that Eqs. (2.5) and (2.35) give

$$D = \frac{kT}{N_0 \zeta_0} \left(1 + \frac{\zeta_0}{N_0} \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \left\langle \frac{1}{d} \sum_\alpha T_{\alpha\alpha}(\tau, \tau') \right\rangle \right), \tag{2.38}$$
$$\scriptstyle |\tau - \tau'| > a$$

which is the famous equation of Kirkwood.[25] This formula as well as Eq. (2.5) is a result of the lowest order bare perturbation. Hence, although its practical value has been recognized,[26] Eq. (2.38) should be treated with the renormalization procedure.

III. INTRINSIC VISCOSITY

The calculation of the intrinsic viscosity follows the analogous procedure for that of the translational friction coefficient f in the preceding section. A chain in a shear flow $(v_x, v_y, v_z) = (gy, 0, 0)$ is considered, where g is the shear strength. Kramers formula[27] for the intrinsic viscosity reads

$$[\eta] = -\frac{N_A}{M\eta_s g} \int_0^{N_0} \langle F(\tau_x)\tilde{c}_y(\tau) \rangle \, d\tau , \tag{3.1}$$

where η_s is the solvent viscosity, M is the molecular weight of the polymer, N_A is Avogadro's constant, F_x is the x component of the force exerted by a segment of the chain and $\tilde{c}_y$ is the y component of the conformation of the chain measured from the center of mass of the chain. The linear equation for $\mathbf{F}(\tau)$ due to Kirkwood and Riseman (1.1) in this case is given similarly to Eq. (2.3) by

$$\mathbf{F}(\tau) = -\tfrac{1}{2}\zeta_0 g(\tilde{c}_y(\tau)\hat{e}_x + \tilde{c}_x(\tau)\hat{e}_y)$$
$$- \zeta_0 \int_0^{N_0} d\tau' \, \mathbf{T}(\tau, \tau')\mathbf{F}(\tau') , \tag{3.2}$$
$$\scriptstyle |\tau - \tau'| > a$$

where $\hat{e}_x$ and $\hat{e}_y$ are the unit vectors in the x and y di-

rections and the Oseen tensor $\mathbf{T}$ has been given by Eq. (2.9). As in Sec. II, Eq. (3.2) is solved iteratively up to the lowest nontrivial order as,

$$\mathbf{F}(\tau) = -\tfrac{1}{2}\zeta_0 g(\tilde{c}_y(\tau)\hat{e}_x + \tilde{c}_x(\tau)\hat{e}_y)$$
$$+ \tfrac{1}{2}\zeta_0^2 g \int_0^{N_0} d\tau' \, \mathbf{T}(\tau, \tau')(\tilde{c}_y(\tau')\hat{e}_x + c_x(\tau')\hat{e}_y) . \tag{3.3}$$
$$\scriptstyle |\tau - \tau'| > a$$

Inserting Eq. (3.3) into Eq. (3.1) gives

$$[\eta] = \frac{N_A}{M\eta_s} \frac{\zeta_0}{2} \left[\int_0^{N_0} \langle \tilde{c}_y(\tau)^2 \rangle \, d\tau - \frac{\zeta_0}{\eta_e} \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \int \frac{d^4 k}{(2\pi)^2} \right.$$
$$\scriptstyle |\tau - \tau'| > a$$
$$\times \left\{ \frac{1}{k^2} \left(1 - \frac{k^2}{k^2}\right) \langle \tilde{c}_y(\tau)\tilde{c}_y(\tau') \exp[i\mathbf{k} \cdot (\tilde{c}(\tau) - \tilde{c}(\tau'))] \rangle \right.$$
$$\left. \left. + \left(-\frac{k_x k_y}{k^2}\right) \langle \tilde{c}_y(\tau)\tilde{c}_x(\tau') \exp[i\mathbf{k} \cdot (\tilde{c}(\tau) - \tilde{c}(\tau'))] \rangle \right\} \right]. \tag{3.4}$$

The perturbative calculation for this equation is given in the Appendix. The result is

$$\frac{M\eta_s}{N_A}[\eta] = \frac{\zeta_0 N_0^2}{12} \left[1 - \frac{u_0}{(2\pi)^2}\left(-\frac{2}{\epsilon} + \frac{13}{12} - \log\frac{2\pi N_0}{L}\right) - 12\frac{\zeta_0}{(2\pi)^2}\right.$$
$$\left. \times \left\{\frac{5}{48(d+2)} + \left(1 - \frac{1}{d}\right)\frac{1}{d-2}\left(\frac{1}{3\epsilon} - \frac{4}{9} + \frac{1}{6}\log\frac{2\pi N_0}{L}\right)\right\}\right] , \tag{3.5}$$

where the dimensionless coupling constants u_0 and ξ_0 have been defined in Eqs. (2.7) and (2.8). The renormalization of this expression for $[\eta]$ with the aid of Eqs. (2.9), (2.10), (2.11), and (2.14) yields

$$\frac{M\eta_s}{N_A}[\eta] = \frac{1}{2}\zeta \frac{N^2}{6} \left[1 - \frac{u}{(2\pi)^2}\left(\frac{13}{12} - \log\frac{2\pi N}{L}\right)\right.$$
$$\left. - \frac{\xi}{(2\pi)^2}\left(-\frac{7}{6} + \frac{3}{4}\log\frac{2\pi N}{L}\right)\right] , \tag{3.6}$$

where all d appearing in Eq. (3.5) have been expanded in terms of ϵ.

For convenience, define a function H by

$$H(L, N, u, \xi) \equiv \frac{M\eta_s}{N_A}[\eta] . \tag{3.7}$$

The renormalization group equation for H is exactly the same as that for f. At the fixed points, the general solution is

$$H^* = H(L, N, u^*, \xi^*) = H_1(LN^{-1/r^*}, u^*, \xi^*) , \tag{3.8}$$

where H_1 is a well-behaved function.

The scaling property for H is slightly different from f and is given by

$$H(SL, SN, u, \xi) = S^{d/2} H(L, N, u, \xi) \tag{3.9}$$

as is seen from Eq. (3.6). Combining Eqs. (3.8) and (3.9) gives

$$H^* = \left[\frac{1}{L}\left(\frac{N}{L}\right)^{-2\nu}\right]^{-d/2} H_2(u^*, \xi^*) . \tag{3.10}$$

This is in agreement with the result due to the scaling argument.[20,21] Finally, Eq. (3.6) is rewritten to conform with Eq. (3.10):

$$\frac{M\eta_s}{N_A}[\eta] = \frac{1}{12}\eta_e\xi^*L^{-d/2}N^2$$

$$\times\exp\left[\frac{7}{6}\frac{\xi^*}{(2\pi)^2} - \frac{13}{12}\frac{u^*}{(2\pi)^2}\right]\left(\frac{2\pi N}{L}\right)^{[u^*/(2\pi)^2]-(3/4)[\xi^*/(2\pi)^2]}$$

$$= \frac{1}{12}\frac{1}{(2\pi)^2}\eta_e\xi^*\exp\left[\frac{7}{6}\frac{\xi^*}{(2\pi)^2} - \frac{13}{12}\frac{u^*}{(2\pi)^2}\right]L^{d/2}\left(\frac{2\pi N}{L}\right)^{d\nu}.$$

$$(3.11)$$

In particular, at the nondraining and self-avoiding fixed point (D) Eq. (3.11) reduces to

$$\frac{M\eta_s}{N_A}[\eta] = \frac{\eta_e\epsilon}{24}\exp\left(\frac{43}{96}\epsilon\right)L^{d/2}\left(\frac{2\pi N}{L}\right)^{d\nu}, \qquad (3.12)$$

with

$$\nu = \frac{1}{2} + \frac{1}{16}\epsilon. \qquad (3.13)$$

At the nondraining Gaussian fixed point,

$$\frac{M\eta_s}{N_A}[\eta] = \frac{1}{18}\epsilon\eta_e\exp\left(\frac{7}{9}\epsilon\right)(2\pi N)^{d\nu}, \qquad (3.14)$$

with

$$\nu = \tfrac{1}{2}. \qquad (3.15)$$

IV. PREAVERAGING OF OSEEN TENSOR

As is stressed in the Introduction, in the present systematic formalism, the preaveraging procedure is unnecessary to solve the Kirkwood–Riseman equation (1.1). However, most of the existing analytic theories utilize this procedure.[4] Thus, it is important to estimate the effect of the preaveraging of the Oseen tensor in the present formalism.

The preaveraged Kirkwood–Riseman scheme[3] uses the following equation instead of (1.1):

$$\mathbf{F}_i = \zeta(\mathbf{u}_i - \mathbf{v}_i) - \zeta\sum_{i\neq j}\langle\mathbf{T}_{ij}\rangle\mathbf{F}_j, \qquad (4.1)$$

where $\langle\ \rangle$ is the ensemble average. To the lowest nontrivial order, this average may be taken over the unperturbed Gaussian chain as has been done in previous sections.

In the calculations of the frictional coefficient f, Eq. (4.1) becomes

$$\mathbf{F}(\tau) = \zeta_0\mathbf{u} - \zeta_0\int_0^{N_0}d\tau'\,\langle\mathbf{T}(\tau, \tau')\rangle\mathbf{F}(\tau'), \qquad (4.2)$$
$$|\tau-\tau'|>a$$

which corresponds to Eq. (2.3). Hence, to order ζ_0^2, the bare perturbation result is identical to Eq. (2.5). This implies that to order ϵ, there is no effect of preaveraging in the calculation of f.

On the contrary, the preaveraging affects the intrinsic viscosity to order ϵ. In this case, Eq. (4.1) becomes

$$\mathbf{F}(\tau) = -\tfrac{1}{2}\zeta_0 g(\tilde{c}_y(\tau)\hat{e}_x + \tilde{c}_x(\tau)\hat{e}_y)$$

$$- \zeta_0\int_0^{N_0}d\tau'\,\langle\mathbf{T}(\tau, \tau')\rangle\mathbf{F}(\tau'), \qquad (4.3)$$
$$|\tau-\tau'|>a$$

which is the preaveraged counterpart of Eq. (3.2). The iterative solution to Eq. (4.3) up to the lowest nontrivial order is given by Eq. (3.3) with $\mathbf{T}(\tau, \tau')$ replaced by

$\langle\mathbf{T}(\tau, \tau')\rangle$. Thus, the preaveraging modifies Eq. (3.4) into

$$\frac{M\eta_s}{N_A}[\eta]_{pre} = \frac{\zeta_0}{2}\left[\int_0^{N_0}\langle\tilde{c}_y(\tau)^2\rangle\,d\tau - \frac{\zeta_0}{\eta_e}\int_0^{N_0}d\tau\int_0^{N_0}d\tau'\int\frac{d^dk}{(2\pi)^d}\right.$$

$$\times\left\{\frac{1}{k^2}\left(1 - \frac{k_y^2}{k^2}\right)\langle\tilde{c}_y(\tau)\tilde{c}_y(\tau')\rangle\langle\exp\{i\mathbf{k}[\tilde{c}(\tau) - \tilde{c}(\tau')]\}\rangle\right.$$

$$\left.\left. + \left(-\frac{k_xk_y}{k^2}\right)\langle\tilde{c}_y(\tau)\tilde{c}_x(\tau')\rangle\langle\exp\{i\mathbf{k}\cdot[\tilde{c}(\tau) - \tilde{c}(\tau')]\}\rangle\right\}\right]. \quad (4.4)$$

A similar calculation to the previous section gives

$$\frac{M\eta_s}{N_A}[\eta]_{pre} = \frac{\zeta_0 N_0^2}{12}\left[1 - \frac{u_0}{(2\pi)^2}\left(-\frac{2}{\epsilon} + \frac{13}{12} - \log\frac{2\pi N_0}{L}\right)\right.$$

$$\left. - 12\frac{\zeta_0}{(2\pi)^2}(1 - 1/d)\frac{1}{d-2}\left(\frac{1}{3\epsilon} - \frac{4}{9} + \frac{1}{6}\log\frac{2\pi N_0}{L}\right)\right]. \quad (4.5)$$

A scaling form of $[\eta]_{pre}$ at fixed points is obtained by the same renormalization group method as Sec. III:

$$\frac{M\eta_s}{N_A}[\eta]_{pre} = \frac{1}{12}\frac{1}{(2\pi)^2}\xi^*$$

$$\times\exp\left[\frac{11}{8}\frac{\xi^*}{(2\pi)^2} - \frac{13}{12}\frac{u^*}{(2\pi)^2}\right]L^{d/2}\left(\frac{2\pi N}{L}\right)^{d\nu}. \quad (4.6)$$

Note that to order ϵ, β_ζ, and β_u, and, consequently, all the fixed points are identical with those without preaveraging. Comparison of Eq. (4.6) with Eq. (3.11) yields

$$[\eta]_{pre}/[\eta] = \exp\{(5/24)[\xi^*/(2\pi)^2]\}, \qquad (4.7)$$

$$= \begin{cases} 1.11 & \text{at the nondraining and self-avoiding} \\ & \text{fixed point (D),} \qquad\qquad (4.8a) \\ 1.15 & \text{at the nondraining Gaussian fixed} \\ & \text{point (C).} \qquad\qquad\quad (4.8b) \end{cases}$$

Zimm[12] and, subsequently, de la Torre et al.[28] have estimated the effect of preaveraging using the Monte Carlo method. The asymptotic results for long Gaussian chains suggest that preaveraging makes $[\eta]$ about 10% or more too high. Miyaki et al.[29] have measured $[\eta]$ for polystyrene under the theta condition and have shown that the observed value is 10% lower than the value for a Gaussian chain with the preaveraged Oseen tensor. These results for $[\eta]$ are in conformity with Eq. (4.8b).

V. UNIVERSAL RATIOS

In previous sections, frictional properties have been calculated to order ϵ. These results generally contain the length scale L which is dependent on, for example, chemical species. Therefore, they depend on microscopic details of the polymer chain. On the other hand, if the results without L can be obtained, they are of universal nature,[30] i.e., they are independent of chemical details of the polymer chain. Appropriate combinations of $[\eta]$, f (or D), $\langle S^2\rangle$ and A_2 make ratios without L, the universal ratios, where $\langle S^2\rangle$ is the mean square radius of gyration and A_2 is the osmotic second virial coefficient. For convenience, all the results obtained in previous sections as well as $\langle S^2\rangle$[31,32] and A_2[33-35] are summarized as follows:

TABLE I. Universal ratios containing transport coefficients.

Universal ratios (asymptotic values)	Nontraining self-avoiding chain (subsection A)		Nondraining Gaussian chain (subsection B)	
	Present theory: ϵ-expansion with $\epsilon = 1$	Experimental results	Present theory: ϵ-expansion with $\epsilon = 1$	Experimental results
$U_{\eta S} \equiv \dfrac{M[\eta]}{N_A \langle S^2 \rangle^{3/2}}$, Eq. (5.8)	4.078	~ 4.5[a] ~ 3.5[b]	5.768	~ 6.22[e] ~ 6.12[f]
$U_{A\eta} \equiv \left(\dfrac{A_2 M}{[\eta]}\right)$, Eq. (5.10)	1.196	~ 1.3[c,b]	0	0
$U_{fS} \equiv \dfrac{f}{\eta_s \langle S^2 \rangle^{1/2}}$, Eq. (5.11)	12.067	~ 12[d]	15.189	~ 14.7[f] ~ 17[g]
$U_{\eta f} \equiv \left(\dfrac{M[\eta]}{N_A}\right)^{1/3} \eta_S/f$, Eq. (5.14)	0.1297		0.1236	~ 0.126[f] ~ 0.12[g]

[a]Reference 36(a) for poly $(D-\beta$-hydroxybutyrate) in trifluoroethanol (Refs. 39 and 40).
[b]Reference 37 for poly $(D, L-\beta$-methyl-β-propiolactone) in tetrahydrofuran (Ref. 40).
[c]Reference 38 for polystyrene in benzene.
[d]Reference 41 for poly (methylmethacrylate) in acetone.
[e]Reference 29 for polystyrene in cyclohexane.
[f]Asymptotic estimates by Zimm (Ref. 12) with the aid of the Monte Carlo method.
[g]Reference 28 by the Monte Carlo calculation.

In the nondraining self-avoiding limit,

$$\frac{M}{N_A} \frac{\eta_s}{\eta_e}[\eta] = \frac{\epsilon}{24} \exp\left(\frac{43}{96}\epsilon\right) L^{d/2}(2\pi N/L)^{d\nu} , \qquad (5.1)$$

$$\frac{f}{\eta_e} = \pi\epsilon \exp(\epsilon/16) L^{d/2-1}(2\pi N/L)^{(d-2)\nu} , \qquad (5.2)$$

$$\frac{A_2 M^2}{N_A} = \frac{\epsilon}{16} \exp\left[-\frac{\epsilon}{8}(1-4\ln 2)\right] L^{d/2}(2\pi N/L)^{\nu d} ,^{35} \quad (5.3)$$

$$\langle S^2 \rangle = \frac{1}{3\pi} \exp\left(-\frac{37}{96}\epsilon\right) L(2\pi N/L)^{2\nu} . \qquad (5.4)$$

In the nondraining Gaussian limit,

$$\frac{M}{N_A} \frac{\eta_s}{\eta_e}[\eta]_\theta = \frac{\epsilon}{18} \exp\left(\frac{7}{9}\epsilon\right)(2\pi N)^{d/2} , \qquad \text{[from (3.14)]} \quad (5.5)$$

$$\frac{f_\theta}{\eta_e} = \frac{4}{3}\pi\epsilon \exp(\epsilon/12)(2\pi N)^{(d-2)/2} , \qquad \text{[from (2.32)]} \quad (5.6)$$

$$\langle S^2 \rangle_\theta = \frac{2}{3} \exp(-\epsilon/4)N . \qquad (5.7)$$

In the prefactors of Eqs. (5.1)–(5.7), all d's are expanded to first order in ϵ and the results are exponentiated. For example, the formula (5.7) is obtained as

$$\langle S^2 \rangle = dN/6 = 4(1-\epsilon/4)N/6 = 2N\exp(-\epsilon/4)/3 .$$

This procedure is consistent with the transformation of Eq. (A14) in the Appendix to Eq. (4.2).

The asymptotic values of the universal ratios in the nondraining cases in both the Gaussian and the self-avoiding limits are summarized in Tables I and II with experimental results in the literature. The universal ratios in Table I are closely related to the customarily defined ratios in Table II.

A. Universal ratios in the nondraining self-avoiding limit

When the chain is sufficiently long, its behavior above the theta temperature is asymptotically described by

the nondraining self-avoiding fixed point (C) in Sec. II.

The ratio containing $[\eta]$ and $\langle S^2 \rangle$ is

$$U_{\eta s} \equiv \frac{M\eta_s}{N_A \eta_e}[\eta]/\langle S^2 \rangle^{d/2} , \qquad (5.8)$$

the universal nature of which can be seen from $\langle S^2 \rangle \propto N^2 L^{1-2\nu}$ and Eq. (3.10). A conventionally used ratio corresponding to $U_{\eta s}$ is Flory's intrinsic viscosity constant $\Phi^{4,42}$ which is defined by

$$\Phi = N_A U_{\eta s}/6^{1.5} . \qquad (5.9)$$

The present ϵ-expansion estimates for $U_{\eta s}$ and Φ in Table I are consistent with experimental results.

The universal ratio containing A_2 and $[\eta]$ is

$$U_{A\eta} \equiv (A_2 M/[\eta])(\eta_e/\eta_s) . \qquad (5.10)$$

Its universal nature can be seen from Eq. (3.10) and the asymptotic relation $A_2 \propto \langle S^2 \rangle^{d/2}$. Table I shows that the ϵ-expansion result for $U_{A\eta}$ is reasonable also. Both $U_{A\eta}$ and $U_{\eta s}$ suggest that the conventional assumption $\eta_e \simeq \eta_s$ is accurate. The universal ratio containing f and $\langle S^2 \rangle$ is

$$U_{fs} = (f/\eta_e)^{1/(d-2)}/\langle S^2 \rangle^{1/2} = (kT/D\eta_e)^{1/(d-2)}/\langle S^2 \rangle^{1/2} . \qquad (5.11)$$

In 3-space this ratio is related to the ratio of the hydrodynamic radius R_H and the radius of gyration $\langle S^2 \rangle^{1/2}$, where the former is defined by

$$R_H = f/6\pi\eta_s$$

in 3-space. Thus,

$$\langle S^2 \rangle^{1/2}/R_H = 6\pi/U_{fs} \quad \text{(in 3-space)} . \qquad (5.12)$$

A conventional universal ratio related to U_{fs} is Flory's P factor^{4,42} defined in 3-space by

$$P = U_{fs}/\sqrt{6} . \qquad (5.13)$$

The universal ratio containing $[\eta]$ and f is

TABLE II. Universal ratios customarily defined.

Conventional universal ratios (asymptotic values)	Nondraining self-avoiding chain X		Nondraining Gaussian chain X_θ		X/X_θ (Subsection C)
	Present theory	Experimental results	Present theory	Experimental results	
Intrinsic viscosity constant Φ Eq. (5.9)	1.67×10^{23} ($\Phi/N_A = 0.277$)	$\sim 1.8 \times 10^{23}$ [a] $\sim 1.4 \times 10^{23}$ [b]	2.36×10^{23} ($\Phi_\theta/N_A = 0.3917$)	$\sim 2.55 \times 10^{23}$ [e] $\sim 2.51 \times 10^{23}$ [f]	0.707
Flory's P factor Eq. (5.13)	4.926	~ 4.9 [d]	6.201	~ 6 [f] ~ 7 [g]	0.794
Flory–Scheraga–Mandelkern parameter β Eq. (5.15)	2.360×10^6		2.249×10^6	$\sim 2.29 \times 10^6$ [f] $\sim 2.2 \times 10^6$ [g]	1.049
Ratio of gyration and hydrodynamic radii Eq. (5.12)	1.562	1.555 [d]	1.241	1.156 [d]	1.259
Penetration function Ψ Eq. (5.16)	0.219	~ 0.22 [a,b]	0	0	—

[a]Reference 36(a) for poly $(D-\beta$–hydroxybutyrate) in trifluoroethanol (Refs. 39 and 40).
[b]Reference 37 for poly $(D, L-\beta$–methyl–β–propiolactone) in tetrahydrofuran (Ref. 40).
[c]Reference 38 for polystyrene in benzene.
[d]Reference 41 for poly (methylmethacrylate) in acetone.
[e]Reference 29 for polystyrene in cyclohexane.
[f]Asymptotic estimates by Zimm (Ref. 12) with the aid of the Monte Carlo method.
[g]Reference 28 by the Monte Carlo calculation.

$$U_{nf} \equiv \left(\frac{M}{N_A} \frac{\eta_s}{\eta_e} [\eta] \right)^{(d-2)/d} \Big/ (f/\eta_e) \ . \tag{5.14}$$

A conventional universal ratio related to U_{nf} is the Flory–Scheraga–Mandelkern parameter β[43,44] defined in 3-space by

$$\beta = (N_A/100)^{1/3} U_{nf} \ . \tag{5.15}$$

For convenience, a purely static universal ratio Ψ, the penetration function, is entered in Table II,

$$\Psi \equiv A_2 M^2 / 4\pi^{3/2} \langle S^2 \rangle^{d/2} N_A \ . \tag{5.16}$$

Witten and Schäfer[31] estimated $\Psi \simeq 0.26$.

Not all the universal ratios are independent. For example, there is a relation

$$U_{nf} U_{fs} = U_{ns}^{1/d} \ . \tag{5.17}$$

The left-hand side is estimated as 1.565 and the right-hand side 1.597 in 3-space. This discrepancy is due to the expansion of d in terms of ϵ and subsequent exponentiation, and may be regarded as a measure of the reliability of the first order ϵ-expansion results. Tables I and II show that the results of the first order calculation are in reasonably good agreement with various experimental results.

B. Universal ratios in nondraining Gaussian limit

At the θ point, the osmotic second virial coefficient vanishes. Therefore, interesting universal ratios are U_{ns}, U_{fs}, and U_{nf}. The estimates of these ratios and the corresponding experimental results are summarized in Tables I and II. The quantity Q at the θ-point is denoted by Q_θ. In the present case, $U_{nf} U_{fs} = 1.877$ and $U_{ns}^{1/3} = 1.793$.

Akcasu et al.[45] have approximately calculated D from which both P and P_θ can be obtained as $\langle S^2 \rangle^{1/2}/R_H = 1.862$ and $(\langle S^2 \rangle^{1/2}/R_H)_\theta = 1.508$. Comparing these values to their observed results, ter Meer et al.[41] have suggested that the disagreement is ascribed to the Oseen tensor expression of hydrodynamic interaction. However, the Benmouna–Akcasu theory relies on the preaveraging approximation of the Oseen tensor and, moreover, on the approximate ensemble average over the conformation set, so that the quantitative reliability of their theory is open to question. Weill–des Clorzeaux[46] or Benmouna–Akcasu type theories will be discussed in the subsequent paper on the crossover behaviors.

C. The ratios X/X_θ

The ratios of universal ratios in the Gaussian and in the self-avoiding chain limits are given in Table II. An important result is that X_θ/X are finite. There have been no theories which can show this finiteness except approximate theories such as Refs. 45 and 46 or theories[6] with the Peterlin approximation.

The ratio of viscosity constants Φ/Φ_θ can be written as

$$\Phi/\Phi_\theta = \alpha_\eta^3/\alpha_s^3 \ , \tag{5.18}$$

where

$$\alpha_\eta^3 \equiv [\eta]/[\eta]_\theta \ , \tag{5.19}$$

and

$$\alpha_s^2 \equiv \langle S^2 \rangle / \langle S^2 \rangle_\theta \ . \tag{5.20}$$

Note that these expansion factors (5.19) and (5.20) are not universal as has been stressed in Ref. 35. The Flory–Fox theory[47] asserts $\alpha_\eta = \alpha_s$. (This is not the result of a theory but an assumption.) The Kurata–

Yamakawa semiempirical theory[5] asserts $\alpha_\eta^3 = \alpha_s^{2.43}$, giving $\Phi/\Phi_\theta = \alpha_s^{-0.57}$ which vanishes in the long chain limit. According to Yamakawa,[4] it is reasonable to consider Φ/Φ_θ to approach unity asymptotically. However, there is no theoretical reason for this asymptotic behavior. The Fixman–Stidham theory,[48] which seems to be the most systematic approach, also fails to give a finite value to the ratio.

Weill and des Clorzeaux[46] have given an argument to show asymptotically

$$\alpha_\eta^3 = \alpha_s^2 \alpha_H , \qquad (5.21)$$

where

$$\alpha_H = D_\theta/D = f/f_\theta . \qquad (5.22)$$

This implies that

$$\Phi/\Phi_\theta = \alpha_H/\alpha_s = (R_H/\langle S^2 \rangle^{1/2})/(R_H/\langle S^2 \rangle^{1/2})_\theta . \qquad (5.23)$$

According to the present calculation, the rightmost side of Eq. (5.23) is 0.794, while $\Phi/\Phi_\theta = 0.707$.

Tables I and II show that the first-order ϵ-expansion calculation gives satisfactory results to frictional properties such as the intrinsic viscosity.

The renormalization group theory has been successful in calculating not only exponents, but universal functions and ratios in static problems.[16,18,31,32–35,49] The present calculation shows that the renormalization group theory is a powerful tool in transport phenomena as well.

ACKNOWLEDGMENT

APPENDIX

Here the calculation which leads Eqs. (3.4) to (3.5) is sketched. First Eq. (3.4) is written as

$$[\eta] = \frac{N_A}{M\eta_s} \frac{\zeta_0}{2} \left[I_1 - \frac{\zeta_0}{\eta_e} I_2 \right] , \qquad (A1)$$

where

$$I_1 = \int_0^{N_0} \langle \tilde{c}_y(\tau)^2 \rangle \, d\tau \qquad (A2)$$

and

$$I_2 = \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \int_{|\tau-\tau'|>a} \frac{d^d k}{(2\pi)^d}$$
$$\times \left[\frac{1}{k^2} \left(1 - \frac{k_x^2}{k^2} \right) \langle \tilde{c}_y(\tau)\tilde{c}_y(\tau') \exp[i\mathbf{k}\cdot(\tilde{\mathbf{c}}(\tau) - \tilde{\mathbf{c}}(\tau'))] \rangle \right.$$
$$\left. - \frac{k_x k_y}{k^2} \langle \tilde{c}_y(\tau)\tilde{c}_x(\tau') \exp[i\mathbf{k}\cdot(\tilde{\mathbf{c}}(\tau) - \tilde{\mathbf{c}}(\tau'))] \rangle \right] . \qquad (A3)$$

The equilibrium ensemble average $\langle \rangle$ is taken with respect to the Hamiltonian (2.1). The self-avoiding interaction term in the Hamiltonian is treated perturbatively.

The average in I_1 is required up to the first order in u_0. On the other hand, for the average in I_2, it is sufficient to use the Hamiltonian without the interaction

term, because the term involving I_2 is of higher order than I_1.

The spherical symmetry of the equilibrium distribution function allows Eq. (A2) to be rewritten as

$$I_1 = \frac{1}{d} \int_0^{N_0} \langle \tilde{\mathbf{c}}(\tau) \cdot \tilde{\mathbf{c}}(\tau') \rangle \, d\tau . \qquad (A4)$$

Since $\tilde{\mathbf{c}}(\tau)$ is the position of a unit measured from the center of mass of the chain, $\tilde{\mathbf{c}}(\tau)$ can be expressed in terms of $\mathbf{c}$ as

$$\tilde{\mathbf{c}}(\tau) = \mathbf{c}(\tau) - \frac{1}{N_0} \int_0^{N_0} d\tau' \, \mathbf{c}(\tau')$$
$$= \frac{1}{N_0} \int_0^{N_0} d\tau' (\mathbf{c}(\tau) - \mathbf{c}(\tau')) . \qquad (A5)$$

Substitution of Eq. (A5) into Eq. (A9) and a little algebra give

$$I_1 = \frac{1}{2dN_0} \int_0^{N_0} dx \int_0^{N_0} dy \, \langle (\mathbf{c}(x) - \mathbf{c}(y))^2 \rangle . \qquad (A6)$$

It is convenient to define a generating function

$$G(\mathbf{k}, x, y) \equiv \langle \exp[i\mathbf{k} \cdot (\mathbf{c}(x) - \mathbf{c}(y))] \rangle \qquad (A7)$$

which is calculated by the standard perturbation technique and its Fourier transform has already been published.[50] The average in Eq. (A6) is obtained as

$$\langle (\mathbf{c}(x) - \mathbf{c}(y))^2 \rangle = -d \frac{\partial^2}{\partial k^2} G(\mathbf{k}, x, y)$$
$$= (y - x)\left[1 - \frac{v_0}{(2\pi)^2} \left\{ -\frac{2}{\epsilon} + 1 - \log 2\pi(y - x) - \frac{x}{y-x} \log y/x \right.\right.$$
$$\left.\left. - \frac{N_0 - y}{y - x} \log \frac{N_0 - x}{N_0 - y} + \frac{1}{2}\left(1 - \frac{y-x}{N_0}\right) + O(\epsilon) \right\} \right], \quad \text{for } y > x.$$

$$(A8)$$

Finally, the integration in Eq. (A6) is performed to give

$$I_1 = \frac{N_0^2}{6} \left[1 - \frac{v_0}{(2\pi)^2} \left\{ -\frac{2}{\epsilon} - \log 2\pi N_0 + \frac{13}{12} + O(\epsilon) \right\} \right] . \qquad (A9)$$

Next, in order to calculate I_2, it is convenient to define a generating function

$$J(\mathbf{k}, \mathbf{l}) \equiv \langle \exp\{i[\mathbf{k} \cdot \mathbf{c}(\tau) - \mathbf{l} \cdot \mathbf{c}(\tau')]\} \rangle . \qquad (A10)$$

The average is taken with respect to the unperturbed Gaussian chain and the result is

$$J(\mathbf{k}, \mathbf{l}) = \exp\left(-\frac{1}{2}\right)\left[\frac{1}{3}N_0 \left(1 - \frac{3\tau(N_0 - \tau)}{N_0^2}\right)k^2 \right.$$
$$+ \frac{1}{3}N_0 \left(1 - \frac{3\tau'(N_0 - \tau')}{N_0^2}\right)l^2$$
$$\left. - 2\mathbf{k} \cdot \mathbf{l}\left\{ \frac{\tau^2 + \tau'^2}{2N_0} + \frac{N_0}{3} - \max(\tau, \tau') \right\} \right] . \qquad (A11)$$

With the aid of this generating function, I_2 is written as

$$I_2 = \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \int_{|\tau-\tau'|>a} \frac{d^d k}{(2\pi)^d} \left\{ \frac{1}{k^2}\left(1 - \frac{k_x^2}{k^2}\right)\left[\frac{\partial}{\partial k_y} \frac{\partial}{\partial l_y} J(\mathbf{k}, \mathbf{l})\right]\right\}_{\mathbf{l}=\mathbf{k}}$$
$$- \frac{k_x k_y}{k^2}\left[\frac{\partial}{\partial k_y} \frac{\partial}{\partial l_x} J(\mathbf{k}, \mathbf{l})\right]_{\mathbf{l}=\mathbf{k}} , \qquad (A12)$$

which turns out to be

$$I_2 = 2N_0^{2+\epsilon/2}(2\pi)^{-2+\epsilon/2}$$

$$\times \left[\frac{5}{48(d+2)} + (1-1/d)\frac{1}{d-2}\left(\frac{1}{3\epsilon} - \frac{4}{9}\right) \right]. \qquad (A13)$$

Equations (A1), (A9), and (A12) give

$$[\eta] = \frac{N_A}{M\eta_s}\frac{\zeta_0}{2}\left[\frac{N_0^2}{6}\left\{1 - \frac{v_0}{(2\pi)^2}\left(1 - \frac{2}{\epsilon} - \log 2\pi N_0 + \frac{13}{12}\right)\right\}\right.$$

$$- 2\frac{\zeta_0}{\eta_e}N_0^{2+\epsilon/2}(2\pi)^{-2+\epsilon/2}\left\{\frac{5}{48(d+2)}\right.$$

$$\left.\left. + (1-1/d)\frac{1}{d-2}\left(\frac{1}{3\epsilon} - \frac{4}{9}\right)\right\}\right]. \qquad (A14)$$

The use of the dimensionless coupling constants $u_0 = v_0 L^{-\epsilon/2}$ and $\xi_0 = (\zeta_0/\eta_0)L^{-\epsilon/2}$ leads Eq. (A14) to Eq. (4.2).

[1] H. Staudinger, *Die hochmolekular Verbindungen* (Springer, Heidelberg, 1932).

[2] See, for example, K. G. Wilson and J. Kogut, Phys. Rept. 12C, 75 (1974).

[3] J. G. Kirkwood and J. Riseman, J. Chem. Phys. 16, 565 (1948).

[4] See, for example, H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971); N. Saitô, *Polymer Physics* (Shokabo, Tokyo, 1967) (in Japanese); R. B. Bird, O. Hassager, and C. F. Curtiss, *Dynamics of Polymer Liquids* (Wiley, New York, 1976), Vol. 2.

[5] M. Kurata and H. Yamakawa, J. Chem. Phys. 29, 311 (1958); M. Yamakawa and M. Kurata, J. Phys. Soc. Jpn. 13, 94 (1958).

[6] O. B. Ptitsyn and Yu. E. Eizner, Zh. Fiz. Khim. 32, 2464 (1958); N. W. Tschoegl, J. Chem. Phys. 40, 473 (1964); V. A. Bloomfield and B. H. Zimm, J. Chem. Phys. 44, 315 (1966).

[7] A. Peterlin, J. Chem. Phys. 23, 2464 (1955).

[8] D. Jasnow and M. A. Moore, J. Phys. (Paris) 38, L-467 (1978).

[9] G. F. Al-Noaimi, G. C. Martinez-Mekler and C. A. Wilson, J. Phys. (Paris) 39, L-373 (1978).

[10] Y. Oono and K. F. Freed, J. Chem. Phys. 75, 1009 (1981).

[11] P. G. de Gennes, Phys. Lett. A 38, 339 (1972).

[12] B. Zimm, Macromolecules 13, 592 (1980).

[13] B. J. Alder and W. E. Alley, in *Molecular Structure and Dynamics*, edited by M. Balaban (Balaban International Science Services, Philadelphia, 1980).

[14] M. Gabay and T. Garel, J. Phys. Lett. (Paris) 39, 123 (1978).

[15] Y. Oono, J. Phys. Soc. Jpn. 47, 683 (1979).

[16] See, for example, Y. Oono, T. Ohta, and K. F. Freed, J. Chem. Phys. 74, 6458 (1981).

[17] The renormalization group equation given in Eq. (2.17) does not have the term containing $\zeta(\partial/\partial\zeta)$ in contrast to the equations given in Refs. 18 and 19. In the present model ζ_0 and ξ_0 are not renormalized independently. Therefore, if bare quantities and ξ are fixed, then ζ is completely determined, so the renormalization group equation cannot have the term proportional to $\zeta(\partial/\partial\zeta)$. Consequently, there is no room for the dynamical exponent z independent of static exponents.

[18] K. Yamazaki and T. Ohta, J. Phys. A 15, 287 (1982).

[19] Y. Shiwa and K. Kawasaki, J. Phys. C 15, 5345 (1982).

[20] P. G. de Gennes, Macromolecules 9, 587, 594 (1976).

[21] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell, Ithaca, 1980).

[22] For the existence of z which is not solely the consequence of the kinematic condition of the model, ζ_0 and ξ_0 should be in-

dependently renormalized. This requires an extra divergence which cannot be absorbed in the $(N, \mu, \xi) - (N_0, u_0, \xi_0)$ relation. However, according to the calculation of Oono (Ref. 23) even if the hydrodynamic interaction is fully taken into account without using the Oseen tensor as is in the theories of dynamical critical phenomena (Ref. 24) there is no extra divergence in the present problem. Hence, the z cited above are exact for dilute polymer solutions.

[23] Y. Oono, unpublished (1981).

[24] See, for example, K. Kawasaki and J. D. Gunton, in *Progress in Liquid Physics*, edited by C. A. Croxton (Wiley, New York, 1980).

[25] J. G. Kirkwood, Rec. Trav. Chim. 68, 649 (1949); J. Polymer Sci. 12, 1 (1954).

[26] R. Zwanzig, J. Chem. Phys. 24, 269 (1955).

[27] H. A. Kramers, J. Chem. Phys. 14, 415 (1946).

[28] J. G. de la Torre, A. Jiménez, and J. J. Freire, Macromolecules 15, 148 (1982).

[29] Y. Miyaki, Y. Einaga, H. Fujita, and M. Fukuda, Macromolecules 13, 588 (1980).

[30] In the present approach, the unit of the length is so chosen that $\langle S^2 \rangle = dN/6$ in the unperturbed state. The parameter N is not specified except by the condition that $N \propto M$, the molecular weight. One may arbitrarily choose the proportionality constant of this relation. Once N-M relation is fixed, L cannot be chosen arbitrarily; since in the self-avoiding limit $\langle S^2 \rangle = (d/6)N(2\pi N/L)^{\epsilon/8}\exp(-13\epsilon/96)$ (Ref. 31 and 32) in order to have an agreement with the experimental result L must be duly chosen.

[31] T. A. Witten, Jr., and L. Schäfer, J. Phys. A 11, 1843 (1978).

[32] T. Ohta, Y. Oono, and K. F. Freed, Phys. Rev. A 25, 2801 (1982).

[33] I. D. Lawrie, J. Phys. A 9, 961 (1976).

[34] D. J. Elderfield, J. Phys. A 11, 2483 (1978); J. Phys. C 13, 5883 (1980).

[35] Y. Oono and K. F. Freed, J. Phys. A 15, 1931 (1982). Equation (5.3) is the corrected result erroneously given in this paper.

[36] (a) Y. Miyaki, Y. Einaga, T. Hirosye, and H. Fujita, Macromolecules 10, 1356 (1977). (b) S. Akita, Y. Einaga, Y. Miyaki, and H. Fujita, Macromolecules 9, 774 (1976).

[37] T. Hirosye, Y. Einaga, and H. Fujita, Polymer J. 11, 819 (1979).

[38] Y. Miyaki, Y. Einaga, and H. Fujita, Macromolecules 11, 1180 (1978).

[39] In this case U_{n_s} spreads over ~ 3.4 to ~ 3.8.

[40] In both cases $U_{A\eta}$ spreads over ~ 1.2 to ~ 1.4.

[41] H. U. ter Meer, W. Burchard, and W. Wunderlich, Colloid & Polymer Sci. 258, 675 (1980).

[42] P. J. Flory, *Principle of Polymer Chemistry* (Cornell, Ithaca, 1953).

[43] L. Mandelkern and P. J. Flory, J. Chem. Phys. 20, 212 (1952).

[44] H. A. Scheraga and L. Mandelkern, J. Am. Chem. Soc. 75, 179 (1953).

[45] M. Benmouna and A. Z. Akcasu, Macromolecules 11, 1187 (1978); A. Z. Akcasu and C. C. Han, Macromolecules 12, 276 (1979).

[46] G. Weill and J. des Cloizeaux, J. Phys. (Paris) 40, 99 (1979).

[57] P. J. Flory and T. G. Fox, Jr., J. Am. Chem. Soc. 73, 1904 (1951).

[48] H. D. Stidham and M. Fixman, J. Chem. Phys. 48, 3092 (1968).

[49] L. Schäfer, Macromolecules 15, 652 (1982); L. Schäfer and T. A. Witten, Jr., J. Phys. (Paris) 41, 459 (1980); A. Knoll, L. Schäfer and T. A. Witten, Jr., *ibid.* 42, 767 (1980).

[50] Y. Oono and T. Ohta, Phys. Lett. 85A, 480 (1981).