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Single polymer chain in an extensional flow: $n \to 0$ model

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By formulating the problem of a single polymer chain in a steady extensional flow as a zero-component field theory, the scaling exponent for the flow rate is obtained exactly in terms of known static and linear dynamic exponents.

I. INTRODUCTION

The renormalization-group approach to study the universal behavior of polymer chains has, thus far, taken two different routes, one using the path-integral formulation,[1,2] and the other employing the n-component field theory in the $n \to 0$ limit.[3,4] Both approaches yield identical results for critical exponents and for static properties that are not sensitive to the polydispersity inherent in the latter method. For dynamic properties, the path-integral method is presently the only available technique.

The problem of a polymer chain in a steady extensional flow is one of the dynamic problems that have been studied by using the path-integral method by Yamazaki and Ohta[5] (subsequently referred to as YO) and Puri, Schaub, and Oono.[6] We show that by reformulating the problem as an $n \to 0$ field theory, and using the renormalization-group equation, the scaling exponent for the flow rate can be determined exactly. This exponent has been obtained to $O(\epsilon)$ by YO where $\epsilon = 4-d$, d being the dimensionality.

The two-dimensional extensional flow of interest is described by a velocity field,

$$\mathbf{v} = (Sx, -Sy, 0) , \tag{1.1}$$

in Cartesian coordinates, with S denoting the flow rate. Since the field in Eq. (1.1) can be derived from a potential,

$$U = -\tfrac{1}{2} S (x^2 - y^2) , \tag{1.2}$$

such that $\mathbf{v} = -\nabla U$, the steady-state behavior of a polymer can be described by an effective Hamiltonian that contains U as an external potential. This simplicity in the path-integral formulation was utilized by YO to study the scaling behavior of various single chain properties in good solvents.[5] It has also been used to study the effect of flow on phase separation—a many chain problem in poor solvents.[7] We emphasize that this quasiequilibrium description is possible only if hydrodynamic interactions among monomers are neglected.

We will consider only small flow rates for stability, as has been done in the previous studies.[5–7] For large flow rates, there is a coil-stretch transition in polymers that cannot be studied in the present framework (see Ref. 6 and references therein). The flow rate, in the renormalization-group language, is a relevant variable near the excluded volume fixed point and the crossover is described by the scaling exponent we want to calculate.

The flow rate S is an externally applied quantity and, therefore, in a renormalization-group treatment should not require any renormalization. However, it couples to the internal degrees of freedom of the polymer through the friction coefficient ζ of the monomers in the solvent, which not being an observable, gets renormalized. Since the aforementioned Hamiltonian involves the combination variable $\gamma = s\zeta$, the renormalization of ζ introduces an exponent ω (to be determined) such that the physical properties (e.g., radius of gyration) depend on the scaling variable

$$\hat{\gamma} = \gamma N^{\omega} , \tag{1.3}$$

where N is the polymer length.

One way of guessing ω is to go through a heuristic argument, following YO, that S has the engineering dimension of frequency and, therefore, need be nondimensionalized by a characteristic time scale. Such a time scale is the characteristic relaxation time of the polymer (no flow) $\tau \sim \xi^z$, where z is the dynamic exponent, and the length scale ξ is proportional to the end to end distance, $\xi \sim \langle R^2 \rangle^{1/2}$. The scaling variable is thus $SN^{z\nu}$ giving

$$\omega = z\nu . \tag{1.4}$$

The dynamic exponent z, in the absence of any hydrodynamic interaction, satisfies the equality[8]

$$z = 2 + \nu^{-1} \tag{1.5}$$

exactly. YO showed that Eq. (1.4) for the exponent ω is correct to $O(\epsilon)$. We prove that Eq. (1.4) with Eq. (1.5) is correct to all orders of ϵ.

The proof is carried out in three parts. First, the n-vector Hamiltonian is obtained from the path-integral formulation of YO, following the method of Emery.[9] Next, the renormalization of a general vertex function[10] in the presence of the flow is discussed. Finally, the renormalization-group equation is used to obtain the scaling exponent.

A. The Model

The path-integral formulation, following YO with changes in notation, gives the effective Hamiltonian in the steady-state limit as

$$(k_B T)^{-1}H=\frac{1}{2}\int_0^N\left[\frac{\partial \mathbf{r}}{\partial s}\right]^2 ds-\frac{1}{2}\gamma\int_0^N ds\,(x^2-y^2)+\frac{u}{4!}\int_0^N ds\int_0^N ds'\delta(\mathbf{r}(s)-\mathbf{r}(s'))\ , \tag{2.1}$$

where $\mathbf{r}(s)$ is the position vector of a point on the chain at an arc length s from one end point, and u (>0) is the excluded volume interaction parameter. The three terms in the Hamiltonian in Eq. (2.1) represent, respectively, the elastic energy, the extra "potential energy" due to the flow, and the excluded volume interaction. The Hamiltonian is valid for al $d\geq 2$, the flow affecting only two directions.

For a field theory with global O(n) symmetry, the ϕ^4 term describes the interaction equivalent to the excluded volume term in Eq. (2.1) in the limit $n\to 0$.[3,9] With this in mind, we concentrate on the flow term and see how it can be incorporated in an O(n) symmetric theory.

Following Emery,[9] we note that, in the usual bra-ket notation,

$$\begin{aligned}G_{ij}&=\langle \mathbf{r}_j|\exp\{-N[-\tfrac{1}{2}\nabla^2+V(r)]\}|\mathbf{r}_i\rangle\ ,\\ &=\mathcal{N}\int_{\mathbf{r}(0)=\mathbf{r}_i}^{\mathbf{r}(N)=\mathbf{r}_j}\mathcal{D}r\exp\left[-\frac{1}{2}\int_0^N ds\left[\frac{\partial \mathbf{r}}{\partial s}\right]^2-\int_0^N V(\mathbf{r}(s))ds\right],\end{aligned} \tag{2.2}$$

where $\mathcal{N}$ is a suitable normalization constant, $\mathcal{D}r$ is the integration measure for the path integral, and $V(r)$ is the potential. Taking the Laplace transform of the left-hand side with respect to N, we find

$$\begin{aligned}\mathcal{G}_{ij}&\equiv\int e^{-\mu N/2}G_{ij}dn\\ &=\langle \mathbf{r}_j|(-\tfrac{1}{2}\nabla^2+\tfrac{1}{2}\mu+V)^{-1}|\mathbf{r}_i\rangle\ .\end{aligned} \tag{2.3}$$

This propagator $\mathcal{G}_{ij}$ is the two-point correlation function for the Hamiltonian

$$(k_B T)^{-1}H_0=\int d\mathbf{r}[\tfrac{1}{2}(\nabla\phi)^2+\tfrac{1}{2}\mu\phi^2+V(\mathbf{r})\phi^2]\ . \tag{2.4}$$

By restoring the ϕ^4 term, representing the excluded volume interaction, the resultant Hamiltonian is

$$\frac{H}{k_B T}=\frac{H_0}{k_B T}+\frac{u}{4!}\int d\mathbf{r}(\phi^2)^2\ , \tag{2.5}$$

where now $\phi^2=\sum_i\phi_i^2=n$, and $n\to 0$ is implied. For more details, the reader is referred to Emery.[9] The important point to note is that the "external potential" $V=\frac{1}{2}\gamma(y^2-x^2)$ in the path-integral Hamiltonian multiplies ϕ^2 in the field-theory formulation [Eq. (2.4)] unlike a magnetic problem where external fields generally couple with the field. This is because ϕ^2 is interpreted as the monomer concentration in the $n\to 0$ model.[4]

B. Renormalization

For a renormalization-group analysis, we start with the engineering dimensions of the various quantities appearing in the Hamiltonian, Eqs. (2.4) and (2.5):

$$\begin{aligned}&[\phi]=L^{(2-d)/2},\ \ [\mu]=L^{-2}\ ,\\ &[\gamma]=L^{-4},\ \ [u]=L^{d-4}\ ,\end{aligned} \tag{2.6}$$

where L has the dimension of length. Introducing an arbitrary cutoff length scale a, we define a dimensionless coupling constant

$$g_0=ua^{4-d}\ .$$

To remove the primitive divergences that occur at four dimensions, one needs to renormalize the various parameters.[1,2,10]

Let us take $\Gamma^{(N)}$, the vertex function of N ϕ operators as an example. We choose the "massless" or the "critical point" renormalization ($\mu=0$). Expanding about this massless point, we have (see Sec. 7.7 of Ref. 10)

$$\begin{aligned}&\Gamma_c^{(N)}(r_i,\gamma,g_0,a)\\ &\quad=\sum_{L=1}^{\infty}\frac{1}{L!}\gamma^L\int dy_1\cdots dy_L v(y_1)\cdots v(y_L)\\ &\qquad\times\Gamma_c^{(N,L)}(r_i,y_i,0,g_{0,}a)\ ,\end{aligned} \tag{2.8}$$

where $\Gamma_c^{(N,L)}$ is the composite vertex function for N ϕ-type and $L\phi^2$-type operators, the subscript c denotes the critical point, and $v(r)=V(r)/\gamma$. Both the right- and the left-hand sides are at the critical point, but more importantly the vertex functions on the right-hand side are evaluated in the no flow situation. The renormalization of $\Gamma_c^{(N,L)}$ in the absence of flow is well known:[10]

$$\Gamma_{R,c}^{(N,L)}(r_i,y_j,0,g,\Lambda)=Z_\phi^{N/2}Z_{\phi^2}^{L}\Gamma_c^{(N,L)}(r_i,y_j,0,g_0,a)\ , \tag{2.9}$$

where Z_ϕ and Z_{ϕ^2} are the renormalization factors to remove the divergences that remain after renormalizing g_0 to g. The cutoff length scale a is replaced by Λ in the process. Using Eq. (2.9), $\Gamma_{R,c}^{(N,L)}$ can be renormalized as follows:

$$\begin{aligned}&\Gamma_{R,c}^{(N)}(r_i,\gamma_R,g,\Lambda)\\ &\quad=\sum_{L=1}^{\infty}\frac{1}{L!}\gamma_R^L\int dy_1\cdots dy_L v(y_1)\cdots v(y_L)\\ &\qquad\times\Gamma_{R,c}^{(N,L)}(r_i,y_j,0,g,\Lambda)\ ,\end{aligned} \tag{2.10}$$

where $\gamma_R=Z_{\phi^2}^{-1}\gamma$ is the renormalized flow variable. This shows that no new renormalization constant is needed to treat the flow variable.

Since the bare vertex functions are independent of Λ, the renormalization-group equation for $\Gamma_c^{(N,L)}$ at $\gamma=0$ is

$$\Lambda\frac{d\Gamma_c^{(N,L)}}{d\Lambda}=0 \tag{2.11}$$

or

$$\left[\Lambda\frac{\partial}{\partial\Lambda}+\beta(g)\frac{\partial}{\partial g}-\tfrac{1}{2}N\gamma_\phi(g)-L\gamma_{\phi^2}(g)\right]\Gamma^{(N,L)}_{R,c}=0 \tag{2.12}$$

where

$$\beta(g)=\Lambda\frac{\partial g}{\partial\Lambda},\quad \gamma_\phi=\Lambda\frac{\partial \ln Z_\phi}{\partial\lambda},\quad \gamma_{\phi^2}=\Lambda\frac{\partial \ln Z^2_\phi}{\partial\Lambda}\ . \tag{2.13}$$

By direct substitution, one can verify that the equation satisfied by $\Gamma^{(N)}_{R,c}(r_i,\gamma_R,g,\Lambda)$ is

$$\left[\Lambda\frac{\partial}{\partial\Lambda}+\beta(g)\frac{\partial}{\partial g}-\tfrac{1}{2}N\gamma_\phi(g)-\gamma_R\gamma_{\phi^2}(g)\frac{\partial}{\partial\gamma_R}\right]\Gamma^{(N)}_{R,c}=0\ . \tag{2.14}$$

At the fixed point $g=g^*$, where $\beta(g)=0$, we obtain, by the method of characteristics,

$$\Gamma^{(N)}_{R,c}(r_i,\gamma_R,g^*,\Lambda)=\Lambda^{NB/2}\hat{\Gamma}^{(N)}_{R,c}(r_i,\gamma_R^{1/C}\Lambda)\ , \tag{2.15}$$

where $B=\gamma_\phi(g^*)$, $C=\gamma_{\phi^2}(g^*)$, and $\hat{\Gamma}^{(N)}_{R,c}$ is a function of only two variables. From dimensional analysis, we can also write for an arbitrary scale transformation λ, suppressing g^* in the argument,

$$\Gamma^{(N)}_{R,c}(r_i,\gamma_R,\Lambda)=\lambda^{\delta_N}\Gamma^{(N)}_{R,c}\left[\frac{r_i}{\lambda},\gamma_R\lambda^4,\frac{\Lambda}{\lambda}\right]\ , \tag{2.16}$$

where δ_N is the canonical or engineering dimension of $\Gamma^{(N)}$, the explicit value of which is of no importance in this paper. Combining Eqs. (2.15) and (2.16) for $\Lambda=1$, we find, at $g=g^*$,

$$\Gamma^{(N)}_{R,c}(r_i,\gamma_R)=\lambda^{\delta_N-NB/2}\hat{\Gamma}^{(N)}_{R,c}\left[\frac{r_i}{\lambda},\gamma_R^{1/C}\lambda^{4/C-1}\right]\ . \tag{2.17}$$

An identical analysis with $\gamma=0$ and $\mu\neq0$ would give

$$\Gamma^{(N)}_{R,\mathrm{nf}}(r_i,\mu)=\lambda^{\delta_N-NB/2}\hat{\Gamma}^{(N)}_{R,\mathrm{nf}}\left[\frac{r_i}{\lambda},\mu^{1/C}\lambda^{2/C-1}\right]\ , \tag{2.18}$$

where nf stands for no flow. A comparison of Eqs. (2.17) and (2.18) shows that the scaling variable involving μ and γ_R is

$$\hat{\gamma}_R=\gamma_R\mu^{-(4-C)/(2-C)}\ , \tag{2.19}$$

and for distance, it is

$$\hat{r}_i=r_i\mu^{1/2-C} \tag{2.20}$$

which identifies

$$\nu=\frac{1}{2-C}\ . \tag{2.21}$$

The result, Eq. (2.19), and the Laplace conjugate relation $\mu\sim N^{-1}$ (for which $n\to0$ is needed) give for the scaling exponent ω [cf. Eq. (1.3)]

$$\omega=\frac{4-C}{2-C}=\left[2+\frac{1}{\nu}\right]\nu\ . \tag{2.22}$$

This proves Eq. (1.4) when Eq. (1.5) is invoked.

III. SUMMARY

To summarize, we have developed the $n\to0$ polymer-magnet analogy for studying the properties of a polymer in an extensional flow and obtained the scaling exponent for the flow rate exactly in terms of the length scale exponent ν. The mathematical reason behind this is that *no new renormalization constant* is required to treat the flow. The method developed here is quite general, and can, in fact, be applied to any external potential problem. Using this for potentials that, for example, lead to a collapse transition,[11] is an interesting problem for further study.

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