An investigation of the configurational statistics of a polymer chain in an external field by the dynamical renormalization group method

A. Yu. Grosberg and E. I. Shakhnovich[1)]

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow

(Submitted 21 February 1986)
Zh. Eksp. Teor. Fiz. **91**, 837–850 (September 1986)

The familiar analogy between the configurational statistics of an ideal polymer chain and the random motion of a Brownian particle is expressed in the fact that the recurrence relation that transforms the distribution function of the end of the chain when one link is added has the form of an equation of motion in which the role of the "time" is played by the length of the chain. This equation is analogous to the time-dependent Schrödinger equation or the diffusion equation of a particle in an external field. If a sufficiently strong external field attracts the links of the chain, a phase transition (collapse), i.e., capture of the chain by a potential well, occurs when the chain is infinite. It is shown that the corresponding equation of motion near the phase-transition point possesses the property of critical slowing down and exact renormalizability. On this basis a variant of the method of the dynamical renormalization group is developed in which the dynamical scaling hypothesis is exact. It is shown that an external field concentrated in a vanishingly small region of space is a fixed point of the renormalization-group transformations. Explicit expressions are obtained for the thermodynamic and geometric characteristics of the chain in the region of the transition. The method developed can be applied to the description of any phase transition that occurs in a one-dimensional system when a discrete level is split off from the edge of the continuous spectrum of the transition operator.

1. INTRODUCTION

Compactly coiled states of polymer macromolecules play a central role in most molecular-biological phenomena and, therefore, have been the subject of numerous theoretical investigations (for more detail, see the reviews in Refs. 1 and 2). The simplest (and the fundamental) phenomenon in this area—the collapse of an ideal (i.e., consisting of infinitely thin links) polymer chain under the influence of a compressive external field—was considered systematically in general form by Lifshitz[3] and, for a number of particular cases, by other authors (see the bibliography in Refs. 4 and 5), and the theory constructed in these papers for the simplest globule-coil transition is asymptotically exact in the limit $N \to \infty$, where N is the number of links in the chain. As regards chains of a real finite length, only the statement that their properties change sharply in a narrow temperature range has been made in the literature. The width of the transition region is proportional to N to a certain negative power that depends on the dimensionality of space and tends to zero as $N \to \infty$. The present work is devoted to a systematic analysis of the properties of a polymer finite length in the region of the coil globule transition. The interest in this question is due to the fact that the number of links in real polymer chains, though large, is insignificant in comparison with the number of particles in ordinary thermodynamic systems; as a result, the width of the region of the coil-globule transition can, in reality, reach tens of degrees.

The problem under consideration is similar to the problem of the temporal behavior of a quantum particle in a potential well whose depth is close to the threshold for the appearance or disappearance of a discrete energy level near the edge of the continuous spectrum. This type of problem is also connected with the spiral-coil transition in two-filament macromolecules of the DNA type.[6]

The question under discussion can be posed as the following mathematical problem. It is well known that for the investigation of one-dimensional statistical systems there exists the general Kramers-Wannier matrix method according to which the Green's function of a t-link segment is determined by the recurrence relation

$$G_t = \hat{Q} G_{t-1}, \tag{1}$$

so that the partition function is $Z_N = \mathrm{Tr} G_n = \mathrm{Tr} \hat{Q}^N$, where $\hat{Q}$ is the so-called transition operator (the analog of the time-evolution operator in quantum mechanics). In the simplest cases the transition operator reduces to a matrix, or, at least, has a discrete spectrum because the set of states of each site of a one-dimensional lattice is discrete (the Ising model) or at least compact (the Heisenberg model); the analysis of this situation in the thermodynamic limit reduces to seeking the largest eigenvalue of the transition operator, because as $N \to \infty$ we have $Z_N \cong \Lambda_{\max}^N$ (the so-called ground-state-dominance approximation). The subject of the present paper is the phase transition that occurs in a one-dimensional system in the more complicated situation when the set of states of each link is unbounded, and so the transition operator has a band of continuous spectrum, and from the upper edge of this band a discrete eigenvalue splits off. Here, to describe one of the phases (namely, that in which the discrete level exists), for $N \to \infty$ the ground-state-dominance approximation is applicable, and it is on this approximation that the above-mentioned theory of Lifshitz[3] and other anal-

0038-5646/86/090493-09$04.00

ogous theories of the coil-globule transition are based. Our problem, however, consists in going beyond the framework of this approximation and investigating the behavior of a system of finite length.

The recurrence relation (1) can be interpreted formally as the equation of the dynamical evolution of a quantity G_t, with the length t along the chain playing the role of the time. We shall show that near the phase-transition temperature the "dynamical equation" (1) possesses the property of critical slowing down. For this reason an adequate approach to our problem can be based on the method of the dynamical renormalization group. A feature of the proposed approach in the context of the statistical physics of macromolecules is that what is subjected to renormalization is not the Hamiltonian of some particular field model, as is often the case (e.g., in Ref. 7), but the "dynamical equation" (1), and this makes it possible to consider the renormalization group directly in the t-representation, without going over to the Laplace transform. This approach makes it possible to analyze in a more transparent and natural form the thermodynamic behavior of an individual finite macromolecule in the region of the coil-globule transition as a function of the length of the chain, and to elucidate from a unified point of view the differences in the pattern of this transition in spaces of different dimensionalities. Another merit of the proposed method is that it seems to be more promising in application to the much more complicated (and exceptionally important for biological applications) phenomenon of the collapse of a disordered heteropolymer.

For the particular case of a point potential well the problem posed of the collapse of an infinitely thin homopolymer can be solved exactly. Its solution for different spatial dimensionalities has been discussed repeatedly in the literature (see the bibliography in Refs. 4 and 5), and for arbitrary dimensionality the exact solution is also given in the Appendix. This solution has a cumbersome and rather opaque form. Nevertheless, it can be analyzed numerically, and the analysis is in full agreement with the results of the renormalization-group investigation. For illustration, in Sec. 6 we also give a simple derivation of the principal results (to within factors) using scaling considerations.

2. QUALITATIVE DESCRIPTION OF THE COLLAPSE OF AN IDEAL POLYMER CHAIN AND OF THE RENORMALIZATION-GROUP TRANSFORMATION PROPOSED FOR THE DESCRIPTION OF THE CHAIN

We recall that the state of a polymer chain on whose links a nonuniform external field $\varphi(\mathbf{x})$ acts is determined by the competition between the energy gain from lowering of the links into the potential wells and the entropy loss from the restriction of their fluctuational motions. If the external field has the form of a potential well concentrated in a certain finite region of space, then at a low temperature the entire chain is found to be localized in the region of the well and the volume occupied by the chain does not depend on its length[2] N—this is the globule state. On the other hand, at high temperature, when the role of the energy of the external field is unimportant, a coiled state is realized with characteristic localization volume $\sim a^d N^{d/2}$, where a is the microscopic size of a link and d is the dimensionality of space. Of course, there is an essential difference between the coil and the globule only in the case when the characteristic size D of the region of localization of the potential well is smaller than the size of the coil:

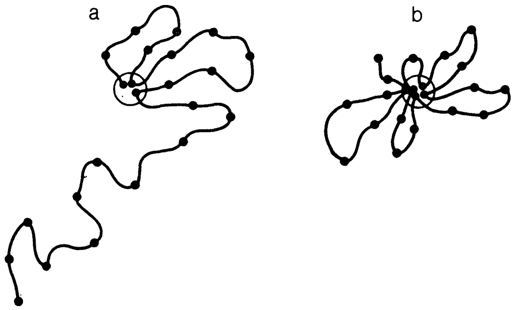

FIG. 1. Typical configurations of a polymer chain interacting with an external field: a) for the coiled state; b) for the globular state.

$$D \ll aN^{1/2}, \qquad (2)$$

i.e., for sufficiently long chains. If this inequality is fulfilled, then between the purely coil region and the purely globule region there exists an intermediate region of temperatures in which a typical instantaneous state of the chain includes parts "anchored" in the potential well and loops of various lengths separating these parts (see Fig. 1). Here the loops, being situated in free space, are, from a local point of view, parts of a Gaussian coil. Of course, in a globule at not too low temperatures fluctuational loops also exist, but their lengths are finite and the number of loops is $\sim N$; for a infinite chain such a situation is preserved right up to the critical temperature of the globule-coil transition. It is clear that our problem in the present work is to investigate a situation when the length of a loop gradually becomes comparable with the length of the chain. In view of the inequality (2), it is clear that in a state with long loops the potential distribution inside the region of the potential well and the details of the microscopic structure of the links of the chain itself should not play any role—just as microscopic details are usually unimportant in the critical region.

The idea of the renormalization-group transformation that must be applied in the long-loop situation described is connected with the decimation procedure proposed by DeGennes[9] in connection with the problem of the excluded volume,—a procedure which is a "variation on the theme" of the well known block construction of Kadanoff.[10] A specific feature of our problem is that its renormalizability [i.e., the fact that when we go over to block variables the functional form of the basic recurrence relation (1) does not change] cannot be established beforehand from any particular *a priori* diagrammatic considerations, but is a directly verifiable fact. Briefly, this follows from the fact that a coil (and, approximately, a loop in a globule) is a fractal object. We must go over to a new way of considering the chain, in which the role of a link is played by a segment of several original (bare) links. Of course, when we do this the profile of the external field distribution is renormalized, and the role of the attractive center is taken not only by the original (bare) potential well itself but also by the short loops surrounding it (see Fig. 1). It is natural to expect, therefore, that as a result of numerous repetitions of such renormalizations the entire chain will be reduced to a one-link "tail" situated near a point potential well, and such a system, of course, can be treated very simply.

We turn now to the task of carrying out the program outlined above.

3. DISCUSSION OF THE ANALOGY WITH CRITICAL SLOWING DOWN, AND CONSTRUCTION OF THE DYNAMICAL RENORMALIZATION GROUP

The transition operator for a polymer chain in an external field $\varphi(\mathbf{x})$ has the form[3]

$$\hat{Q}=(1+f(\mathbf{x}))\hat{g},\ f(\mathbf{x})=\exp[-\varphi(\mathbf{x})/T]-1,$$

where $\hat{g}$ is the so-called "linear-memory operator," which can always be reduced[1] to an integral operator with a spherically symmetric difference kernel $g(\mathbf{x},\mathbf{x}')\equiv g(|\mathbf{x}-\mathbf{x}'|)$. The partition function of a chain of t links with an end clamped at the point $\mathbf{x}$ is equal to[1]

$$G^{(t)}(\mathbf{x})=\hat{Q}^t\delta(\mathbf{x}) \tag{3}$$

[In order not to have to consider the entropy of the translational motions of the chain as a whole, we suppose that the beginning of the chain is clamped at the coordinate origin, and this is reflected by the δ-function in formula (3)]. It is obvious that for $G^{(t)}$ we have a recurrence relation of the form

$$G^{(t+1)}(\mathbf{x})=\hat{Q}G^{(t)}(\mathbf{x}),$$

or, after Fourier transformation,

$$G_{\mathbf{k}}^{(t+1)}=g_{\mathbf{k}}G_{\mathbf{k}}^{(t)}+(2\pi)^{-d}\int f_{\mathbf{k}'-\mathbf{k}}g_{\mathbf{k}'}G_{\mathbf{k}'}^{(t)}\,d^dk'. \tag{4}$$

We can formally regard this recurrence relation as a kind of equation of motion for the field $G^{(t)}(\mathbf{x})$, the label of a link along the chain being regarded as the analog of the time (this is why it has been denoted by the letter t). It is important to emphasize that we are not considering any real dynamics or kinetics in the present paper; we are concerned with the purely formal analogy of the recurrence relations (4) with dynamical equations. The principal difference between Eq. (4) and the usual time-dependent one-particle Schrödinger equation written in terms of the dynamical-evolution operator is due to the nonunitarity of the operator $\hat{Q}$ and is expressed in the fact that the normalization of the function $G^{(t)}(\mathbf{x})$ changes with t. This circumstance has a direct physical meaning, since

$$\int G^{(t)}(\mathbf{x})\,d^dx=G_{\mathbf{k}=0}^{(t)}$$

is the partition function of a t-link chain with a free end, and this function, of course, depends on t. If the largest eigenvalue Λ of the operator $\hat{Q}$ is separated from the next gap, then when t increases by unity the partition function is multipled by Λ (this is the ground-state-dominance approximation; for all the details and justifications, see Refs. 1, 3, and 9). Therefore, to obtain an equation with stationary behavior it is sufficient to divide[3)] the right-hand side of (4) by Λ, when it can be seen immediately that the characteristic "relaxation time" of the mode with wave vector $\mathbf{k}$ is of the order of

$$\tau_{\mathbf{k}}=(1-g_{\mathbf{k}}/\Lambda)^{-1}. \tag{5}$$

The kernel of the operator $\hat{g}$ is a spherically symmetric difference kernel, and, in addition, has the meaning of a probability. It follows from this that $g_{\mathbf{k}}$ depends only on the modulus $|\mathbf{k}|$, $0<g_{\mathbf{k}}\leqslant 1$, $g_{\mathbf{k}=0}=1$, and $g_{\mathbf{k}}\cong 1-(ka)^2/2d$ for $ka\ll 1$, where a is the microscopic length of a link. With regard to the potential $\varphi(\mathbf{x})$ of the external field we assume that both it and the Mayer function $f(\mathbf{x})$ fall off sufficiently rapidly at infinity. From this it is clear that the spectrum of the operator $\hat{Q}$ includes a continuous band—the segment $[0,1]$, and if the quantity f is sufficiently large in the appropriate sense (to be specified below), then the discrete eigenvalue $\Lambda>1$. Consequently, the value of Λ corresponding to the critical temperature, i.e., to the coil-globule transition point in an infinite chain, is $\Lambda=1$. Correspondingly, near the critical temperature the expression (5) gives

$$\tau_{\mathbf{k}}=(\Lambda-1+(ka)^2/2d)^{-1}\ \text{ for } (\Lambda-1)\ll 1 \text{ and } (ka)\ll 1. \tag{6}$$

In view of the importance of this simple formula for what follows, it is worthwhile to discuss its physical meaning in more detail. Putting aside the dynamical analogy, we can say that $\tau_{\mathbf{k}}$ is that number of links (or that length along the chain) which forms a loop with characteristic spatial size $\sim 1/k$. As can be seen, there is a characteristic length $(\Lambda-1)^{-1}$ along the chain, and a characteristic spatial scale $\sim a(\Lambda-1)^{-1/2}$. For shorter segments of the chain we have $\tau_{\mathbf{k}}\sim(ka)^{-2}$; i.e., over short lengths the chain behaves as a Gaussian coil. On the other hand, at large distances, $\tau_{\mathbf{k}}\sim(\Lambda-1)^{-1}$ does not depend on $\mathbf{k}$. In other words, if the whole chain is longer than $(\Lambda-1)^{-1}$, it can be effectively divided into loops of the critical length; i.e., $a(\Lambda-1)^{-1/2}$ is the N-independent size of a globule for $N\gg(\Lambda-1)^{-1}$ [correspondingly, our problem will consist in the analysis of the situation $N\lesssim(\Lambda-1)^{-1}$]. Returning to the dynamical analogy, the above can be summarized as follows: In our system the analog of critical slowing down[11] occurs: As the critical temperature is approached the relaxation times of the longest-wavelength modes increase without bound. This gives us the possibility of applying the dynamical renormalization-group technique,[12] based on the successive elimination of the fast variables.

In order to avoid excessively cumbersome formulas, we shall consider the interaction of a chain with a point potential well

$$\exp(-\varphi(\mathbf{x})/T)=1+\beta\delta(\mathbf{x}), \tag{7}$$

which corresponds to the $\mathbf{k}$-independent quantity $f_{\mathbf{k}}=\beta$. This may appear at this point to be a very important assumption, but we shall show below that under the condition (26) any potential well can be reduced to a point well. Furthermore, to simplify the notation it is convenient to introduce in place of $\mathbf{k}$ the new variable

$$\varkappa^2=1-g_{\mathbf{k}}\ (0\leqslant\varkappa\leqslant 1). \tag{8}$$

Since for us the most interesting region is the region of small **k**, where $\varkappa \sim ka$, for a qualitative understanding we can assume throughout that $\varkappa$ and k are the same. We note that $\varkappa$ is a scalar quantity, because for a point well ($f_{\mathbf{k}} = \beta$) Eq. (4) becomes spherically symmetric. Next, we introduce the function $h_d(\varkappa)$ in accordance with

$$a^d(2\pi)^{-d} g_{\mathbf{k}} d^d k \equiv h_d(\varkappa) d\varkappa. \tag{9}$$

In particular, from (8) it follows that for $\varkappa \ll 1$

$$h_d(\varkappa) \approx h_d^* \varkappa^{d-1}, \tag{10}$$

$$h_d^* \equiv 2\left(\frac{d}{2\pi}\right)^{d/2}\left[\Gamma\left(\frac{d}{2}\right)\right]^{-1}. \tag{11}$$

Using the notation (7)–(11) we can write our basic equation in the form

$$G_\varkappa^{(t+1)} = (1-\varkappa^2) G_\varkappa^{(t)} + (\beta/a^d) \int_0^1 h_d(\varkappa') G_{\varkappa'}^{(t)} d\varkappa'. \tag{12}$$

Our aim is to eliminate, step by step, the modes with large momenta, expressing them in terms of modes with smaller momenta at the cost of a coarsening of the links, i.e., an increase of the scale of t. For this purpose we introduce two parameters: Δ and δ; an elementary renormalization step will consist in the elimination of momenta corresponding to $\varkappa > 1 - \Delta$, and simultaneous combination into an effective $1 + \delta$ bare monomers. Of course, since we shall construct an infinitesimal renormalization-group transformation, we shall let parameters Δ and δ tend to zero in a mutually consistent manner at the end.4)

We shall consider Eq. (12); its formal solution can be written exactly as

$$G_\varkappa^{(t)} = \sum_{\tau=1}^{t} (1-\varkappa^2)^{\tau-1} \int_0^1 h_d(\varkappa') G_{\varkappa'}^{(t-\tau)} d\varkappa' (\beta/a^d). \tag{13}$$

We first discuss the modes with $\varkappa > 1 - \Delta$. For these, in formula (13) we can make three important simplifications: a) In the sum over τ we can omit all terms except the first (corresponding to $\tau = 1$), because they all contain the factor $(1 - \varkappa^2) \lesssim \Delta$ to positive powers; b) we can integrate over $\varkappa'$ from 0 to $1 - \Delta$ only, because the contribution to the integral from the segment $\varkappa' > 1 - \Delta$ is less than or of the order of Δ; c) by virtue of a) and b), $G_{\varkappa'}^{(t-\tau)}$ can be replaced by $G_{\varkappa'}^{(t)}$, because, by virtue of the critical slowing down (6), the change of the "slow" modes with $\varkappa' < 1 - \Delta$ in the time $\tau = 1$ must be neglected. As a result, we have

$$G_\varkappa^{(t)} \approx \frac{\beta}{a^d} \int_0^{1-\Delta} h_d(\varkappa') G_{\varkappa'}^{(t)} d\varkappa' + o(\Delta) \quad \text{for } \varkappa > 1 - \Delta \tag{14}$$

Thus, the modes with "large momenta" $\varkappa > 1 - \Delta$ are expressed in terms of modes with smaller momenta at the same "time." The result (14) must be substituted into the basic equation of motion (12), and a closed relation that includes only modes with $\varkappa < 1 - \Delta$ is then obtained. It follows from the physical considerations discussed above that narrowing the range of momenta requires that the time scale be simultaneously coarsened. For this it is necessary to write $1 + \delta$ equations (12), pertaining to successive links t, and to add them term by term. Here it is again necessary to make use of the property of critical slowing down: Since the change of $G_\varkappa$ in the time from t to $t + \delta$ is itself small (since $\varkappa < 1 - \Delta$), the term $\Sigma_{t'=t}^{t+\delta} G_\varkappa^{(t')}$ can be replaced by $(1 + \delta) G_\varkappa^{(t)}$. As a result we obtain

$$G_\varkappa^{(t+1+\delta)} = [1-(1+\delta)\varkappa^2] G_\varkappa^{(t)}$$
$$+ (1+\delta)\frac{\beta}{a^d}\left\{1 + \frac{\beta}{a^d}\int_{1-\Delta}^{1} h_d(\varkappa'') d\varkappa''\right\} \int_0^{1-\Delta} h_d(\varkappa') G_{\varkappa'}^{(t)} d\varkappa'. \tag{15}$$

It is obvious that this equation can be easily brought to the original form (12) by making the change of variable

$$(1+\delta)\varkappa^2 \to \varkappa_{\text{ren}}^2 \tag{16}$$

and relating the parameters δ and Δ by the condition

$$(1+\delta)(1-\Delta)^2 = 1, \quad \text{i.e.,}\ \theta \approx 2\Delta. \tag{17}$$

The fact that the scales of length and time (in our case, the length along the chain) are connected by a simple power relation of the type (17) constitutes the essence of the dynamical scaling hypothesis.[13] As we shall see, in our problem this hypothesis is exact. We recall that the physical meaning here is very simple and consists in the fact that on small scales all loops look like Gaussian coils, for which the square of the spatial size is of the order of the contour length, and this is what is expressed by formula (17). We cannot explain the renormalizability of our model by any general reference to field-theoretical analogies; however, the calculations described in detail above have shown that coarsening of the scale does indeed lead to an equation [Eq. (12)] that does not differ in structure from the original equation, and the renormalizability is thereby proved.

The difference between this situation and the usual applications of the dynamical renormalization-group method[12,13] is that the analog of the external force (the quantity β) appears in the equation of motion multiplicatively, and not additively as in other cases. Nevertheless, as we shall see, a consistent change of the scales leads, as usual, only to renormalization of the "force":

$$\beta_{\text{ren}} \approx \beta(1+\delta)^{1/2}\left[1 + \frac{\beta}{a^d}\int_{1-\Delta}^{1} h_d(\varkappa'') d\varkappa''\right]. \tag{18}$$

The quantity β_{ren} has the meaning of the virial coefficient of the interaction of the attractive center with a chain segment consisting of $1 + \delta$ monomers.

If we make several (say, l) renormalizations, we obtain a division of the chain into blocks of $(1 + \delta)^l$ monomers. In order to arrive at blocks of a finite length s, it is necessary to go through a sequence of $l \sim (\ln s)/\delta$ infinitesimal renormalization transformations, in which, obviously, $\delta \equiv d \ln s$. Under each succeeding transformation of this kind the quantity $\beta(s)$ obtained in the preceding step is transformed in accordance with formula (18); it is necessary only to remember that now $\varkappa''$ is a quantity that has been renormalized l times in accordance with (16), and therefore the integral term in formula (18) must be replaced by $\Delta h_d(s^{-1/2})$. Therefore, taking (17) into account as well, we can write the law of renormalization of β in the following final form:

$$2d\beta(s)/d\ln s=2\beta(s)+\beta^2(s)h_d(s^{-1/2})a^{-d}s^{-1/2}. \tag{19}$$

We recall that s is the number of monomers in a block. Since an unperturbed block has volume $\sim a^d s^{d/2}$, it is convenient to go over from β to the quantity $b(s)\equiv\beta(s)s^{-d/s}a^{-d}$; for this quantity we have

$$2db(s)/d\ln s=(2-d)b(s)+b^2(s)h_d(s^{-1/2})s^{(d-1)/2}. \tag{20}$$

To aid understanding, it is useful to note at once that the coefficient of $b^2(s)$ in the above equation tends with increase of s, for any dimensionality of space, to a constant h_d^*.

4. ANALYSIS OF THE RENORMALIZATION-GROUP FLOW DIAGRAM

We turn now to the phase portrait of Eq. (20) (see Fig. 2). We see that for $d\neq 2$ the renormalization-group transformation of the quantity $b(s)$ has two fixed points, of which one is stable and the other is unstable. For $d=2$ there exists one fixed point—stable in one direction. The domain of attraction of the stable fixed point is the interval $(-\infty, 0)$ for $d\leqslant 2$ and the interval $(-\infty<b<b_{\rm tr}=(d-2)/h_d^*)$ for $d>2$. As will be explained in detail below, the domain $-\infty<b<b_{\rm tr}$ corresponds to a coiled state of the chain, and the domain $b>b_{\rm tr}$ to a globular state. Thus, the form of the phase protrait of the renormalization-group equation (20) points to the asymptotic universality of the behavior of polymer coils, irrespective of the bare value of $b(0)<b_{\rm tr}$; to put it more simply, for $b(0)<b_{\rm tr}$, with increase in length the chain approaches the state of an unperturbed Gaussian coil. In this region $b(0)$ determines only those values of the chain length N for which the properties of the chain turn out to be universal. On the other hand, the globular state is nonuniversal; its properties depend on $b(0)$, since this state arises for those values of b which lie outside the domain of attraction of the stable fixed point. This implies that in the globular state a finite scale, dependent on $b(0)$, appears. We note that for the coiled state there exists an upper critical dimensionality $d=2$. For $d\geqslant 2$ the stable fixed point of the renormalization-group transformations corresponds to a free coil, while for $d<2$ it corresponds to a coil interacting with a potential "hump" for which $\beta=\varepsilon/h_d^*$, where $\varepsilon=d-2$.

Having discussed the qualitative properties of the solutions of the differential equation (20), we shall integrate it. This is easily done, since it is linear in $1/b(s)$. As a result we obtain

$$b(s)=\left[\frac{a^d}{\beta}-\int\limits_{s^{-1/2}}^{1}h_d(\varkappa)\varkappa^{-2}\,d\varkappa\right]^{-1}s^{-(d-2)/2}, \tag{21}$$

where β is the parameter of the original monomer. The behavior of the integral curves depends in an essential way both on the dimensionality d of space and on the bare parameter b. The corresponding diagrams are given in Fig. 3a for $d>2$ and in Fig. 3b for $d<2$.

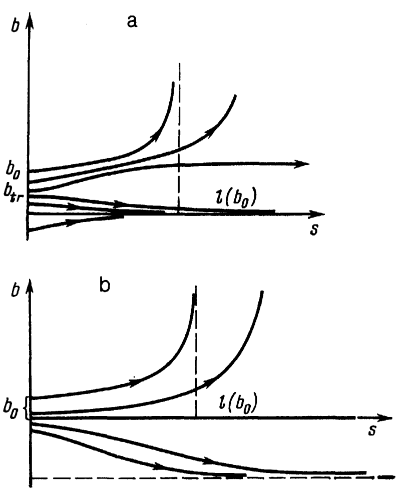

FIG. 3. Renormalization-group flow diagram for $d>2$ (a), and $d<2$ (b).

As we see, in all cases the diagrams contain separatrices, starting from the point

$$\beta_{tr}=0,\quad d\leqslant 2,$$

$$\beta_{tr}=\left[\int\limits_0^1 h_d(\varkappa)\varkappa^{-2}\,d\varkappa\right]^{-1}a^d$$

$$\equiv\left[(2\pi)^{-d}\int(g_k/(1-g_k)d^dk\right]^{-1},\quad d>2. \tag{22}$$

If $\beta>\beta_{\rm tr}$, then $b(s)$ becomes infinite over a finite scale of s (which grows as $\beta-\beta_{\rm tr}$ decreases). But if $\beta<\beta_{\rm tr}$, then with increase of s the quantity $b(s)$ tends to zero for $d>2$ or to a negative constant for $d<2$. What does this mean?

The sharp increase of $b(s)$ at finite s must obviously be interpreted as a manifestation of the globularity of the state. For a long segment of the chain the effective attraction toward the center is so strong that fluctuation detachment from the center becomes essentially impossible. Accordingly, the quantity $b_{\rm tr}$ [the boundary below which $b(s)$ does not increase for any segment length s] must be identified with the critical point of the globule-coil transition in an infinite chain. In fact, it is easy to convince oneself of this by direct calculation, since for the present case of a point well the leading eigenvalue Λ of the operator $\hat{Q}$ is determined by the following exact equation[1]:

$$\frac{1}{\beta}=(2\pi)^{-d}\int\frac{g_k}{\Lambda-g_k}d^dk\equiv\int\limits_0^1\frac{h_d(\varkappa)}{\Lambda-1+\varkappa^2}d\varkappa\,a^{-d}; \tag{23}$$

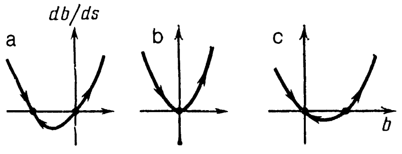

FIG. 2. Phase portrait of the renormalization-group equation (20) for different dimensionalities of space: a) $d<2$; b) $d=2$; c) $d>2$.

but since the transition point in an infinite chain corresponds to $\Lambda = 1$, for the critical value of β we obtain formula[5)] (22). Moreover, the sale s [we call it $l(\beta)$] at which the increase of $b(s)$ occurs for the given bare β should coincide with this characteristic loop length $(\Lambda - 1)^{-1}$; it is easy to convince oneself of this, since the integrals in formulas (21) and (23) are very similar in structure and differ only in the method of elimination of the divergence at small $\varkappa$. In (21) there is a nonzero lower limit, while in (23) there is a positive extra term $\Lambda - 1$ in the denominator; therefore, we obtain

$$l(\beta)\sim(\Lambda(\beta)-1)^{-1}. \tag{24}$$

The region $\beta < \beta_t$ corresponds to the globule regime. Here the difference between the cases $d > 2$ and $d < 2$ calls to mind in an obvious way the well known theorem[14] concerning the probability of the return of a random walk to the starting point. In the three-dimensional case this probability is equal to zero, and therefore a weakly attractive center or a repulsive center has no effect at all on the coil over large scales [$b(s) \to 0$ with increase of s]; on the other hand, in the one-dimensional case this probability is equal to unity, and therefore a repulsive center remains important for the coil on all scales. Incidentally, the same theorem also explains the fact that $\beta_{\rm tr} = 0$ for $d \leqslant 2$ and $\beta_{\rm tr} > 0$ for $d > 2$.

We now discuss the question of the accuracy of the results obtained. We recall that an essential assumption in all the calculations on the route between the original equation and the renormalized equation was that one monomer constitutes a small fraction of the characteristic length $(\Lambda(\beta) - 1)^{-1}$ of a loop. When we are concerned with the next steps in the renormalization, the same condition arises naturally with respect to the block monomer. Consequently, renormalization is possible and is asymptotically exact for $s \ll l(\beta)$. This is the situation for $\beta > \beta_{\rm tr}$. As regards the region $\beta < \beta_{\rm tr}$, here the renormalization is exact for any s and any dimensionality of space—obviously, simply because the coil is a trivial fractal object.

Thus, if $\beta < \beta_{\rm tr}$, the renormalization can be continued up to $s = N$, i.e., we can reduce the problem to the trivial problem of one link in an external field. The same can also be said of the case when β is slightly larger than $\beta_{\rm tr}$ but the length N of the chain is smaller than the length of a loop: $N \ll (\Lambda(\beta) - 1)^{-1}$. We recall that in the case of the opposite inequality $N \gg (\Lambda(\beta) - 1)^{-1}$ the usual theory of Lifshitz[3] becomes asymptotically exact. Thus, as usual, the regions of applicability of the theories of the Landau type and renormalization-group type become joined. We note and stress here one further important fact. The renormalization group makes it possible to carry out the renormalization correctly in order of magnitude up to the loop length (as usual, up to the correlation length), and thereby determine the order of the size of the globule, as was shown above; moreover, on these scales the globule can be regarded crudely as an accumulation of mutually independent loops, and in this sense the renormalization group itself already gives definite information about the globular state as well.

Before implementing (below, in Sec. 5) this program for carrying out the renormalization up to the full chain length $s = N$, we shall also discuss the general case of a nonpoint external field. The starting point here should be an "equation of motion" in the form (4) with a **k**-dependent Mayer function $f_{\mathbf{k}}$. The infinitesimal renormalization-group transformation consists in the elimination of these modes **k** for which $g_{\mathbf{k}} < \Delta$. Performing the calculations, which in all important aspects repeat those described above, one can show that Eq. (4), like the simpler (12), is renormalizable, and one can find the renormalization transformation of the Mayer function $f_{\mathbf{k}}$. We do not write out the corresponding formulas here, because they are rather involved, but the result of analyzing them is easily explained qualitatively. In fact, since in the renormalization the size of an effective monomer increases, in essence we can say that the size of the potential well decreases. More precisely, one can proceed as follows: We expand $f_{\mathbf{k}}$ in powers of **k** and study the renormalization transformations of the corresponding coefficients. It turns out that all contributions from positive powers of **k** tend stably to zero, whereas $f_{\mathbf{k}=0} \equiv \beta$ is transformed in the manner described above for a point well. In the coil situation and at the transition point, when the renormalization can be continued up to the chain length, an external field of any form is renormalized to a δ-function field, provided that the size of the coil is much greater than the size of the region of localization of the well. This also applies to a sufficiently small neighborhood of the transition point, where the characteristic loop length is still much greater than the size of the well. From this, first of all, it follows that for an arbitrary potential $\varphi(\mathbf{x})$ the critical temperature $T_{\rm cr}$ of the coil-globule transition in an infinite chain is determined by the formula

$$\int [\exp(-\varphi(\mathbf{x})/T_{tr})-1]d^dx\sim\beta_{tr}, \tag{25}$$

where $\beta_{\rm tr}$ for each dimensionality d of space is given by the expression (22). Furthermore, it is clear that the immediate neighborhood of the transition temperature can also be described in terms of the single parameter $\beta \equiv f_{\mathbf{k}=0}$; here the condition for applicability of a renormalizability of a renormalization-group approach that operates by approximating the potential well is

$$(D/a)^2\ll N\ll(\Lambda(\beta)-1)^{-1} \tag{26}$$

[D is the size of the well; compare (3)]. If the first inequality is violated, it is not at all appropriate to speak of the coil and globule as different states. If, on the other hand, the second inequality is violated, a theory of the Lifshitz type[3] becomes applicable (ground-state dominance) and, moreover, it becomes meaningless to regard the well as a point well. Thus, the point-well concept, associated with the replacement $f_{\mathbf{k}} \to f_{\mathbf{k}=0} = \beta$, has, in essence, the same region of applicability as the entire renormalization-group approach.

The above is illustrated by the flow diagram given in Fig. 4. In this figure each point represents schematically a certain functional form of the potential $\varphi(\mathbf{x})$ of the external field and a certain value of the temperature T; in other words, each point corresponds to a Mayer function $f(\mathbf{x})$. The flow lines show how different Mayer functions are transformed into each other under the renormalizations.

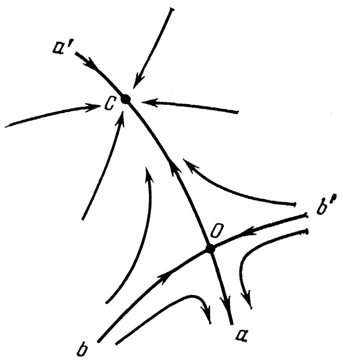

FIG. 4. Schematic representation of the renormalization-group flow diagram in the functional space of potentials of the external field. The line aa' is the hypersurface of potentials concentrated in a vanishingly small region of space, for which $\exp(-\varphi(\mathbf{x})/T) = 1 + \beta\delta(\mathbf{x})$. The line bb' is the hypersurface of potentials for which $\beta = f_{\mathbf{k}=0} = \beta_{\text{tr}}$. The point C is the "coil" stable fixed point; it is the image of the potential $\varphi(\mathbf{x}) = 0$ for $d \geqslant 2$ and $\exp(-\varphi(\mathbf{x})/T) = 1 - [(2-d)/h_d]\delta(\mathbf{x})$ for $d < 2$. The point O is a saddle point for solutions of the renormalization-group equations, for $\exp(-\varphi(\mathbf{x})/T) = 1 + \beta_{\text{tr}}\delta(\mathbf{x})$.

The thick line bb' depicts schematically the hypersurface of all possible potentials at the critical temperature. On this hypersurface there is a stable fixed point O, which corresponds to a δ-function well with $\beta = \beta_{\text{tr}}$. As usual, this point is a saddle point, because in the direction across this hypersurface it is unstable as a fixed point. For example, the flow along the line aa' of point potentials is illustrated by Fig. 3, in which the instability of the point $\beta = \beta_{\text{tr}}$ is clearly visible.

5. CALCULATION OF THE THERMODYNAMIC CHARACTERISTICS

Carrying out (where this is possible—see above) the renormalization up to the full chain length $s = N$, we obtain the possibility, by applying the recurrence transformation (4) once, of finding immediately the distribution of the end link of the chain:

$$\psi^{(N)}(\mathbf{x}) = G^{(N)}(\mathbf{x}) \Big/ \int G^{(N)}(\mathbf{x})\, d^d x.$$

In fact, since the beginning of the chain is clamped at the origin, i.e., $G^{(0)}(\mathbf{x}) = \delta(\mathbf{x})$ or $G_{\varkappa}^{(0)} = 1$, and, according to (10),

$$\int_0^1 h_d(\varkappa N^{-1/2})\, d\varkappa = (h_d^{*}/d) N^{(1-d)/2},$$

normalizing the relation (4) we have

$$\psi_{\varkappa}^{(N)} = \frac{1 - \varkappa^2/N + \beta(s=N) N^{(1-d)/2} (h_d^{*}/d) a^{-d}}{1 + \beta(s=N) N^{(1-d)/2} (h_d^{*}/d) a^{-d}}. \tag{27}$$

In particular, the mean square size of a chain,

$$\overline{R^2} = \int \mathbf{x}^2 \psi^{(N)}(\mathbf{x})\, d^d x = -(\Delta_{\mathbf{k}}\psi)_{\mathbf{k}=0}$$

is found to be simply equal to the coefficient of $\varkappa^2$ in formula (27). Substituting into this the result (21) of the renormalization-group analysis for $\beta(s = N)$, we find

$$\frac{R^2}{Na^2} = \left\{ 1 + \frac{(d-2)}{d} \left[1 - N^{(d-2)/2} a^d \left(\frac{1}{\beta_{tr}} - \frac{1}{\beta} \right) \left(\frac{2\pi}{d} \right)^{d/2} \times \Gamma\left(\frac{d}{2} \right) \frac{d-2}{2} \right]^{-1} \right\}^{-1} \tag{28}$$

for $d > 2$, and

$$\frac{R^2}{Na^2} = \left\{ 1 + \frac{(d-2)}{d} \left[1 - N^{(d-2)/2} \frac{a^d}{\beta} \left(\frac{2\pi}{d} \right)^{d/2} \times \Gamma\left(\frac{d}{2} \right) \frac{2-d}{2} \right]^{-1} \right\}^{-1}$$

for $d < 2$. We recall that these results are applicable for $\beta < \beta_{\text{tr}}$. For $\beta > \beta_{\text{tr}}$ they are applicable for relatively short chains, for which $N(\Lambda(\beta) - 1) \ll 1$. For a point well, Λ for the given β is found from formula (23), and, if β is close to β_{tr}, it is not difficult to obtain

$$a^d \left(\frac{1}{\beta_{tr}} - \frac{1}{\beta} \right) = (\Lambda - 1)^{(d-2)/2} \pi \left(\frac{d}{2\pi} \right)^{d/2} \times \left[\Gamma\left(\frac{d}{2} \right) \sin \frac{\pi(d-2)}{2} \right]^{-1} \quad \text{for } d > 2 \tag{29}$$

(for brevity we do not give here the analogous formula for the case $d < 2$). Comparing (29) with (28), we can see that $\overline{R^2}$ from formula (28) is expressed in terms of just one combination of parameters $N(\Lambda - 1)$. Of course, the general scaling property is manifested in this, inasmuch as the loop length $(\Lambda - 1)^{-1}$ is the only characteristic length along the chain. Taking into account that the result is applicable for $N(\Lambda - 1) \ll 1$, we write it in the form

$$\frac{\overline{R^2}}{Na^2} = \left[\frac{2d-2}{d} + \frac{(d-2)^2}{d} \times \left[2 \sin \frac{\pi(d-2)}{2} \right]^{-1} (N(\Lambda - 1))^{(d-2)/2} \right]^{-1}. \tag{30}$$

Finally, for $\beta > \beta_{\text{tr}}$ and $N(\Lambda - 1) \gg 1$ the usual theory of globules (ground-state dominance), according to which

$$\overline{R^2}/a^2 = (\Lambda - 1)^{-1}, \tag{31}$$

is applicable. We note that in this regime as well $\overline{R^2}/Na^2$ is determined by the combination $N(\Lambda - 1)$. It is not difficult to see that the formulas (30) and (31) match smoothly at $N(\Lambda - 1) \sim 1$.

Besides the mean-square size $\overline{R^2}$ of a chain, we can also calculate all its other thermodynamic characteristics, For example, it is easy to see that the free energy per monomer is equal to $f = -TNa^2/\overline{R^2}$; the degree of absorption (the fraction of particles situation inside the potential well) is equal to $\vartheta = -\beta(\partial/\partial\beta)(Na^2/\overline{R^2})$, and so on.

Thus, the renormalization-group method does indeed make it possible to investigate fully the behavior of finite chains in the region of the coil-globule transition. In fact, however, the problem of a point potential well can be solved exactly, and this is done in the Appendix. Although the solution has a fairly complicated form, the results of a numerical analysis of it are given in Fig. 5, in which they are compared with the results (28)–(30) from this paper. In view of the

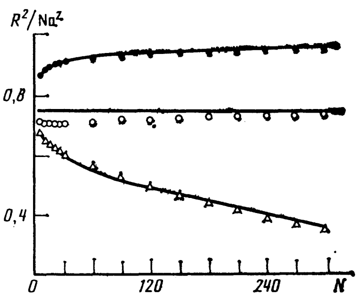

FIG. 5. Comparison of the results of a numerical determination of the contraction coefficient R^2/Na^2 of the chain on the basis of formula (A2) with the results of a calculation of this quantity using formulas (28)–(30) (the solid lines) for $d = 3$ and different values of β: ●) $\beta = 1.0<\beta_{tr}$; ○) $\beta = 1.17 = \beta_{tr}$; △) $\beta = 1.40>\beta_{tr}$.

relatively cumbersome nature of the exact solution and the complexity of the renormalization-group approach described above, it is worthwhile to describe also a qualitative derivation of the principal results.

6. DERIVATION OF THE PRINCIPAL RESULTS FROM SIMPLE SCALING CONSIDERATIONS

We return to the qualitative language of the first section. If the temperature is below the critical temperature, a characteristic loop length should exist; we denote it by l, and the thermodyanamic properties can depend only on the ratio N/l. For example, the ratio of the size of a globule to the unperturbed size of a coil can be written in the form

$$R^2/Na^2=f(N/l). \tag{32}$$

If $N\gg l$, the situation is globular; i.e., R^2 should not depend on N, and, consequently, $f(x)\sim x^{-1}$ for $x\gg 1$, which corresponds to $R^2\sim la^2$ [cf. (31)].

On the other hand, if the exernal field is so weak that it scarcely perturbs the conformation of the coil, the deviation of R^2 from the ideal size Na^2 is easily estimated—it is proportional simply to the number of monomers of the Gaussian coil that are situated by chance in the region of the potential well:

$$R^2/Na^2\approx 1-\text{const}\,N^{-(d-2)/2}\beta/a^d. \tag{33}$$

This result agrees exactly with (28) for small β. Since, finally, the loop length l should depend on the difference $\beta-\beta_{tr}$, comparing (32) and (33) we obtain

$$l\sim(\beta^{-1}-\beta_{tr}^{-1})^{-2/(d-2)}. \tag{34}$$

Hence, $f(x)\approx 1-\text{const}\,x^{-(d-2)/2}$ for $x\ll 1$, and this formula coincides with the result (28). Thus, from scaling considerations we can find not only all three asymptotic forms (28), (30), and (31) for the chain size, but also the order to the transition in an infinite chain.

APPENDIX

Here we shall describe very briefly how the method of generating functions can be used to express exactly in the form of an integral the partition function of a polymer of arbitrary length N is a point external field. Analogous calculations for several other modes are contained, e.g., in Ref. 15.

First of all, it is easily verified that the partition function $Z_t=\int G_t(\mathbf{x})d^dx$ of a t-link chain can be represented in the form

$$Z_t=\sum_{t'=0}^{t}G_{t'}(\mathbf{x}=0). \tag{A1}$$

Next, for the quantities $G_t(\mathbf{x}=0)$ it is easy to set up the following Dyson equation:

$$G_t(\mathbf{x}=0)=\beta\sum_{t'=1}^{t-1}G_{t'}(\mathbf{x}=0)\,G^{(0)}_{t-t'+1}(\mathbf{x}=0)+G^{(0)}_t(\mathbf{x}=0),$$

where $G_t^{(0)}(\mathbf{x})$ is the Green's function of a free coil (for $\beta=0$). If we set up the generating function

$$G(s)=\sum_{t=0}^{\infty}s^tG_t(\mathbf{x}=0),$$

it is easy to obtain a linear algebraic equation for it, and to find, finally,

$$G_t(\mathbf{x}=0)=\oint\frac{G^{(0)}(s)}{1-\beta G^{(0)}(s)}s^{-t+1}\frac{ds}{2\pi i}, \tag{A2}$$

where

$$G^{(0)}(s)=(2\pi)^{-d}\int sg_{\mathbf{k}}/(1-sg_{\mathbf{k}})\,d^dk, \tag{A3}$$

and the contour of integration, as usual, should not enclose any singularities of the function $G(s)$.

For large t the integral (A3) is determined by the pole of $G(s)$, at which $1-\beta G^{(0)}(s)=0$ (the approximation of ground-state dominance). It can be said that in the present work we have carried through an analysis of the integral (A2) for values of t such that a contribution is made to the integral not only by the residue at the indicated pole but also by the integration along the edges of the cut due to the branch point of $G^{(0)}(s)$ at $s=1$.

[1)] Protein Institute, Academy of Sciences of the USSR.

[2)] We recall that we are discussing the collapse of a so-called ideal chain, for which the intrinsic volume of the links is assumed to be equal to zero. A detailed explanation of the meaning of this formulation of the problem is contained in the reviews in Refs. 1 and 8.

[3)] A more rigorous argument consists in the following. We divide both sides of the equality (4) by $G^{(t+1)}_{\mathbf{k}=0}$, and in the right-hand side express this quantity using the same formula (4). We then obtain a nonlinear recurrence relation for the function $\psi^{(t)}(\mathbf{x})$, which has the meaning of the distribution function of the end of a t-link chain. If Q has a discrete spectrum, then $\psi^{(t)}(\mathbf{x})\to\psi(\mathbf{x})$ as $t\to\infty$; by linearizing the recurrence relation $\psi^{(t)}$ near the "fixed point" ψ, we at once obtain the result (5).

[4)] The number of monomers is a discrete quantity, and therefore the passage to the limit $\delta\to 0$ has physical meaning only because of the existence of the large length scale $(\Lambda-1)^{-1}$ along the chain; $\delta\to 0$ means simply $\delta\ll(\Lambda-1)^{-1}$.

[5)] Here it is necessary to explain that in the point-well model only β depends on the temperature, and, therefore, in place of the critical temperature we shall speak of the critical value of β.

---

[1] I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978).

[2] A. Yu. Grosberg and A. R. Khokhlov, in: Problems of Solid State Phys-

ics (eds. A. M. Prokhorov and A. S. Prokhorov, Mir, Moscow (1984), p. 330.

[3] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **55**, 2408 (1968) [Sov. Phys. JETP **28**, 1280 (1969)].

[4] T. M. Birshteĭn, Vysokomol. Soedin., Ser. A **24**, 1828 (1982).

[5] A. Yu. Grosberg, Vysokomol. Soedin., Ser. A **24**, 1194 (1982).

[6] A. A. Vedenov, A. M. Dykhne, and M. D. Frank-Kamenetskiĭ, Usp. Fiz. Nauk **105**, 479 (1971) [Sov. Phys. Usp. **14**, 715 (1972)].

[7] P. G. DeGennes, J. Phys. (Paris) Lett. **36**, L-55 (1975).

[8] A. Yu. Grosberg and E. I. Shakhnovich, Biofizika **31**, 6 (1986).

[9] P. G. DeGennes, Scaling Concepts in Polymer Physics, Cornell University Press, Ithaca, New York (1979) [Russ. transl., Mir, Moscow (1982)].

[10] M. E. Fisher, Rev. Mod. Phys. **46**, 597 (1974).

[11] E. M. Lifshitz and L.P. Pitaevskiĭ, Fizicheskaya kinetika (Physial Kinetics), Nauka, Moscow (1979) [English translation published by Pergamon Press, Oxford (1981)].

[12] S.-K. Ma, Modern Theory of Critical Phenomena, Benjamin, New York (1976) [Russ. transl., Mir, Moscow (1979)].

[13] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, Fluktuatsionnaya teoriya fazovykh perekhodov (Fluctuation Theory of Phase Transitions), Nauka, Moscow (1982) [English translation of 1975 edition) published by Pergamon Press, Oxford (1979)].

[14] A. W. Feller, An Introduction to Probability Theory and its Applications, Wiley, New York (1950) [Russ. transl, Mir, Moscow (1982)], Vol. 2, Ch. XIX.

[15] M. Ya. Azbel, Phys. Rev. A **20**, 1671 (1979).

Translated by P. J. Shepherd