Conformational Entropy of a Branched Polymer

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ABSTRACT: We consider the globular state of a randomly branched polymer macromolecule with an annealed structure of branchings. We extend for a branched polymer the main steps of the Lifshitz theory of the globular phase and arrive at a generalized Lifshitz equation for conformational entropy. Both the ensemble with given density distributions for all types of particles (ends, branch points, linear chains, etc.) and the one with given total density and chemical potentials of different particles are considered. The entropy of a branched polymer confinement up to some scale R is shown to scale as $N(a/R)^4$, contrary to $N(a/R)^2$ for linear polymers; simple scaling arguments are given to explain this difference. The effect of nonlocality, or correlations between ends and branch points, is shown to cause a tendency toward microphase segregation in a branched system.

1. Introduction

Branched polymers, along with linear ones, are the classical object of polymer physics. Since the classical work of Zimm and Stockmayer,[1] the statistical physics of branched structures was studied extensively.[2–6] These investigations are aimed not only at real chemically branched polymers but also at several other systems and theoretical models of very different physical nature but having in essence many common intrinsic features. There are several examples of different physical systems, which have many common features with branched macromolecules: (1) lattice animals;[6] (2) polymer rings in topologically restricted environments;[7] (3) closed vesicle (compressed by external pressure);[8–10] (4) RNA molecules with secondary structure.[11,12] It is interesting, therefore, to explore statistical mechanics of branched polymers to the same degree of detail as was done for linear polymers.

Three different regimes are possible for three-dimensional linear polymer chains, depending on volume interactions or on solvent quality. Namely, the chain is in the swollen coil state with the size $R > aN^{1/2}$ when repulsions dominate in monomer–monomer volume interactions, it is in the Gaussian coil state with $R \sim aN^{1/2}$ at compensation Θ-conditions, and, finally, a condensed globule with $R < aN^{1/2}$ is formed when attractions prevail.

As to branched polymers, the statistics of branchings for an ideal ("Gaussian") system, as well as the swelling phenomenon in a good solvent in various space dimensionalities, are understood rather well at present.[2–6] On the other hand, the compressed globular regime is much less studied. Such a regime, however, is of great importance both from the basic physical point of view and for biological applications. The former is clear, for example, from the fact that collapsed vesicles are equivalent to branched polymers. The latter concerns mainly the clover-leaf structure of RNA. The clover leaf itself can be considered as a kind of secondary structure, but this structure has to be packed in some way in three dimensions. The corresponding structures are not investigated in detail experimentally and also are not understood theoretically. Branched structure discussed below may be the simplest starting model for such a globular RNA. The compressed globular regime for a branched polymer is thus our main concern here.

To begin with, let us make simple estimates of the density of a branched polymer. It is well-known that ideal linear chains are in the Gaussian coil state with size proportional to $N^{1/2}$. Similarly, the characteristic size of an ideal branched macromolecule, in accord with the Zimm–Stockmayer result,[1] scales as $N^{1/4}$. Densities of ideal linear and branched polymers in d dimensions are proportional to $\varrho_{\text{lin}} \sim N/N^{(1/2)d} \sim N^{(2-d)/2}$ and $\varrho_{\text{branched}} \sim N/N^{(1/4)d} \sim N^{(4-d)/4}$, respectively. It is clear even from these simplest estimates that linear and branched polymers behave quite differently in three dimensions; the ideal linear chain is "sparse" in three dimensions so that attraction between monomers causes its collapse but the branched polymer is not. One concludes that the three-dimensional case for a branched polymer has to be in some sense similar to the $d < 2$ case for the linear chain, etc.

Of course, in any case the size of any polymer, linear or branched, must exceed the value of order $N^{1/d}$—simply because of the fact that each monomer has some of its own excluded volume. At the same time, a globular polymer, regardless of linearity or branchings, always has the size of that order. Comparing this with the size $N^{1/2}$ of an ideal linear polymer, one concludes that the usual coil-to-globule transition between swollen and collapsed states can take place in linear polymer at $d > 2$, while at $d < 2$ all the states of the linear chain are necessarily swollen, so that one can expect some unusual transition from the more swollen to the less swollen state. Exactly the same is the situation with the branched polymer at $d < 4$ and, in particular, at $d = 3$. This is the additional reason for us to be interested in the globular states of branched polymers.

Where a branched polymer is concerned, the cases of frozen and annealed disordered branchings have to be distinguished,[13] as is always the case for disordered systems.[14] We stressed in ref 13 that these cases are both of interest for applications in physics and biology, in particular, in the context of different RNA clover-leaf properties. In the present paper we will focus on the annealed case.

Scaling arguments are not readily applicable to annealed branched polymers, because branchings and spatial density distribution are not independent, so that either swelling or collapse of the macromolecule leads

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to a certain (and, of course, different) rearrangement of the branchings. Accordingly, as we show in Appendix 1, one needs to involve some additional heuristic arguments when applying the scaling method. This is why we have to develop the more regular approach. We build here such an approach on two sources: Lifshitz mean-field theory of the condensed globular state of a linear polymer[15-17] and de Gennes theory of an annealed clover-leaf structure.[11] We generalize to the case of branched polymers the Lifshitz equation for conformational entropy as a function of spatial density distribution. This generalization is the main result of our work. We discuss also the applications of this result to the theory of adsorption of branched polymer, the theory of microphase segregation in the melt or solution of branched polymers, etc.

Let us remind everyone that in order to derive the Lifshitz equation we have to do the following:

1. Consider an ideal (i.e., without excluded volume and, in general, volume interactions) polymer in an external potential field $\varphi(x)$, to derive the recursion relation between Green's function of N- and $(N + 1)$-monomer chains, which is similar to a diffusion equation with sources or annihilation proportional to $\varphi(x)$. At this very stage we shall use de Gennes' approach[11] to build up the recursion relations for the branched structure.

2. Find the equilibrium free energy as a function of the imposed external field $F = F\{\varphi(x)\}$.

3. Derive the expression for conformational entropy of a compressed globular polymer in an arbitrary state described by spatial distribution of monomer density $\varrho(x)$, just using the standard relation

$$F = E - TS \tag{1.1}$$

where obviously $E = \int \varrho(x)\varphi(x)\, dx$ plays the role of energy, and, most important, the external field is chosen in such a way that the density distribution $\varrho(x)$ is an equilibrium one under the action of this very external field. We will reproduce in the present paper all the steps 1−3 for the branched polymer.

This work is organized after the introduction as follows:

2. ideal branched polymer in an external field, including the recursion relations and analysis of the analog of the ground-state dominance principle

3. theory of adsorption phase transition for an ideal branched polymer in an external field

4. generalized Lifshitz equation for conformational entropy of a branched polymer

5. analysis of a generalized equation for conformational entropy and of some of its applications

Appendix 1 is devoted to the discussion of scaling estimates of conformational entropy as well as the limitations of the scaling method in the description of branched polymers. Appendix 2 illustrates some technical details.

2. Ideal Branched Polymer in an External Field

2.1. Recurrence Relation for Green's Function. We define Green's function of a *branched* polymer, $G_N(x)$, as the partition function of N-monomer macromolecule with *one* of the ends fixed at the point x. The following recursion relation holds for an *annealed* branched polymer:[11]

$$\begin{aligned} G_{n+1}(x) = {} & \Lambda_2 \int dx' \exp[(-\varphi_1(x))/k_BT] g(x-x') \exp[(-\varphi_2(x') + \\ & \varphi_1(x'))/k_BT] G_N(x') + \\ & \Lambda_3 \int dx' \exp[(-\varphi_1(x))/k_BT] g(x-x') \exp[(-\varphi_3(x') + \\ & 2\varphi_1(x'))/k_BT] \sum_{i_1,i_2=2}^{\infty} \{G_{i_1}(x')\, G_{i_2}(x')\, \Delta(i_1 + i_2 - 1 - N)\} + \\ & \ldots = \sum_{f=2}^{\infty} \Lambda_f \int dx' \exp[(-\varphi_1(x))/k_BT] g(x-x') \times \\ & \exp[(-\varphi_f(x') + (f-1)\varphi_1(x'))/k_BT] \sum_{i_1,i_2,\ldots,i_{f-1}=2}^{\infty} \{G_{i_1}(x') \times \\ & G_{i_2}(x') \ldots G_{i_{f-1}}(x')\, \Delta(i_1 + i_2 + \ldots + i_{f-1} - f + 2 - N)\} \\ & \qquad (\text{for } N \geq 2) \end{aligned} \tag{2.1}$$

where $\varphi_f(x)$ is external field which acts on the monomer units of functionality f placed at the point x; in particular, the φ_1 field acts on the end points of the macromolecule, φ_2 acts on the links of linear chains, included in the branched structure, φ_3 acts on the simplest "triple" branch points, etc. Additional unit number $N + 1$ is an end point of the structure in accord with the definition of Green's function $G_N(x)$. It has to be connected with a previous part of the macromolecule, integral operator

$$\hat{g} \ldots = \int dx'\, g(x-x') \ldots$$

accounts for this fact. $\int dx' \ldots$ denotes integration over all the d-dimensional x-space. The Nth monomer itself, however, which is in connection with added $(N + 1)$th monomer, may be of another type, namely, of arbitrary functionality, f. Accordingly, the partition function G_{N+1} includes the summation over all the possibilities. The factor $\exp(-\varphi_f(x)/k_BT)$ in each term describes the action of the external field on the monomer unit of type f. A simple product of Green's functions $G_{i_1}(x)$, $G_{i_2}(x)$, ..., $G_{i_{f-1}}(x)$ appears in eq 2.1 due to the fact that we consider now an *ideal* macromolecule; i.e., different branches do *not* interact with each other except only the effective interaction through the common branch point; the Kronecker Δ symbol means that the total number of monomer units has to be exactly N, but a branch point is common to all of $f - 1$ "old" branches and one "new" tail. Old branches have not now, however, end points, and this is why the multiplier $\exp[(f-1)\varphi_1(x')/k_BT]$ has to be included. Finally, Λ_f denote activities of different types of monomer units; they appear due to the fact that we consider annealed structure, which is in equilibrium with respect to different ways of branching. Equation 2.1 is applicable for $N \geq 2$ and should be completed with "initial condition", which reads obviously as follows:

$$G_2(x) = \Lambda_1 \int dx' \exp(-\varphi_1(x)/k_BT) g(x-x') \times \exp(-\varphi_1(x')/k_BT) \tag{2.2}$$

In the limiting case of free macromolecule without any external fields, eq 2.1 represents the recursion relation for treelike structures derived by de Gennes.[11] It should be emphasized, however, that different types of statistics are possible for trees depending on symmetry and

distinguishability of branches; we use here the version which corresponds to the case of RNA "clover-leaf" structure.

As usually, we present the generating function

$$G(p,x) = \sum_{N=2}^{\infty} p^{N-1} G_N(x) \tag{2.3}$$

which transforms the relation (2.1) to the following:

$$G(p,x) = \Lambda_1 e^{-\varphi_1}\hat{g}[e^{-\varphi_1}p] + \Lambda_2 e^{-\varphi_1}\hat{g}[e^{-\varphi_2+\varphi_1}pG(p,x)] + \Lambda_3 e^{-\varphi_1}\hat{g}[e^{-\varphi_3+2\varphi_1}pG^2(p,x)] + \ldots = \sum_{f=1}^{\infty}\Lambda_f e^{-\varphi_1}\hat{g}[e^{-\varphi_f+(f-1)\varphi_1}pG^{f-1}(p,x)] \tag{2.4}$$

where we have changed for simplicity $\varphi_f(x)/k_BT$ by φ_f.

2.2. "Ground-State Dominance". For linear polymer, the relation (2.4) is a linear equation for Green's function. It is well-known that the analytical structure of this Green's function on the complex p-plane is determined by the spectrum of linear operator (which plays, in fact, the role of transfer operator) $e^{-\varphi_1}\hat{g}[e^{-\varphi_2+\varphi_1}\ldots]$:

if its largest eigenvalue Λ, which corresponds to the ground state eigenfunction $\Psi(x)$

$$e^{-\varphi_1}\hat{g}[e^{-\varphi_2+\varphi_1}\Psi(x)] = \Lambda\Psi(x) \tag{2.5}$$

belongs to the discrete spectrum, then the main (nearest to origin) singularity of $G(p,x)$ on complex p-plane is a simple pole of the type

$$G(p,x) \simeq \text{const}\cdot\frac{\Psi(x)}{p-p^*} \tag{2.6}$$

Note that eq 2.5 can be rewritten in a simpler form as

$$e^{-\varphi_2}\hat{g}\psi = \Lambda\psi(x) \tag{2.7}$$

where $\psi(x) = e^{-\varphi_2+\varphi_1}\Psi(x)$. We remind everyone that $\psi(x)$ here can be interpreted as an order parameter. We note that one can "guess" eq 2.6, based on physical ideas (decay of correlations in the globular state), and then transform eq 2.4 to eq 2.5 by simply considering it at $p \approx p^*$ and keeping the most singular terms in eq 2.4, where $\Lambda = 1/\Lambda_2 p^*$. This procedure corresponds, of course, to the usual "ground-state dominance" approximation. We will use similar logic for branched polymers as well.

In the case of a branched polymer the relation (2.4) becomes essentially nonlinear; to analyze it, we return for a moment to the case of a free polymer without an external field. It is known[11] that square-root singularity, instead of the simple polelike (2.6), is inherent for Green's function of the branched structure, corresponding to a certain logarithmic term in free energy. Indeed, consider for example eq 2.4 in the case $\varphi = 0$ for the macromolecule with monomers of functionalities $f = 1$ and 3 only (i.e., with $\Lambda_2 = 0$ and $\Lambda_4 = \Lambda_5 = \ldots = 0$):

$$G(p) = p\Lambda_1 + p\Lambda_3 G^2(p)$$

It gives obviously

$$G(p) = \{1 - [[1 - 2p(\Lambda_1\Lambda_3)^{1/2}] \times [1 + 2p(\Lambda_1\Lambda_3)^{1/2}]]^{1/2}\}/2\Lambda_3 p$$

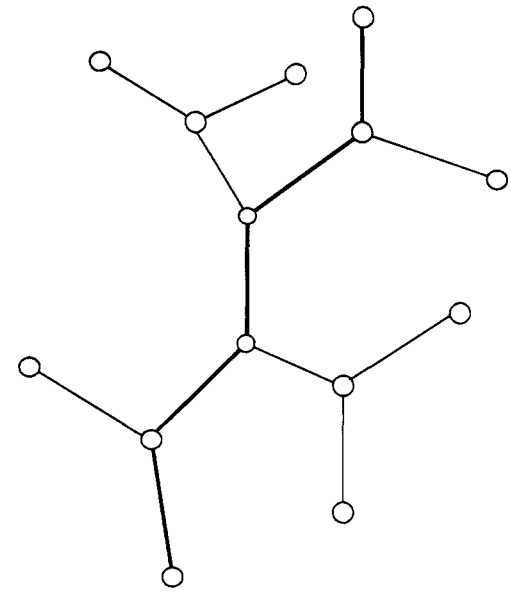

Figure 1. "Probe diameter" of a branched macromolecule. One arbitrarily chosen path from one end to another in the branched structure is shown by a thick solid line. It can be considered as a linear polymer with some length on average of order $N^{1/2}$. Each monomer of it is a root of a tree and feels external or self-consistent field not only directly but also through the effective action of this tree.

i.e., the nearest to the origin singularity is the square-root one at

$$p = p_0^* = 1/[2(\Lambda_1\Lambda_3)^{1/2}] \tag{2.8}$$

This type of singularity is the result of the polynomial nature of eq 2.4, and we expect it to be valid for the case with nonzero external fields φ_f and, accordingly, with nonlocal operators $\hat{g}$.

Therefore, we will seek the solution of eq 2.4 in the form

$$G(p,x) \simeq \Phi(x)\, e^{-\varphi_1} + \Psi(x)\, e^{-\varphi_1}(p^* - p)^{1/2} \tag{2.9}$$

where $\Phi(x)$ and $\Psi(x)$ are expected to determine the spatial structure of the system. The factor $e^{-\varphi_1}$ is not very important; it is involved in the definitions of $\Phi(x)$ and $\Psi(x)$ to simplify the expressions (similar to simplification from eq 2.5 to eq 2.7); $\Phi(x)$ is connected with the value of Green's function at the singular point $p = p^*$; i.e., $\Phi(x) = G(p^*,x)\, e^{\varphi_1}$. Taking the first equation (2.4) precisely at the singular point $p = p^*$, we obtain

$$\Phi(x) = p^*\sum_{f=1}^{\infty}\Lambda_f\hat{g}[e^{-\varphi_f}\Phi^{f-1}(x)] \tag{2.10}$$

Keeping further the most singular terms in the neighborhood of singular point in eq 2.4, we obtain

$$\Psi(x) = p^*\sum_{f=2}^{\infty}\Lambda_f(f-1)\hat{g}[e^{-\varphi_f}\Phi^{f-2}(x)\,\Psi(x)] \tag{2.11}$$

This is the equation for $\Psi(x)$. It is, of course, more complicated than eq 2.5, but it is still *linear*. This is a very important fact, which has a simple physical interpretation. Indeed, let us consider one "diameter" of the branched macromolecule, i.e., some chemical path from one end point to another (Figure 1). It is the linear polymer with the only specifics that each of its monomer

units is on average the root of equilibrium branched tree and, therefore, it "feels" the effective external field given by

$$e^{-\varphi_{eff}(x)} = \sum_{f=2}^{\infty} \Lambda_f (f-1) e^{-\varphi_f(x)} \Phi^{f-2}(x)$$

Taking this into account, we see that eq 2.11 has the same physical meaning as eq 2.5. Accordingly, its solution $\Psi(x)$ is still the spatial distribution of the end points of a macromolecule. It includes, however, the function $\Phi(x)$, which describes the effective, mediated by branches, action of the whole system of external fields on a given monomer unit. This function is determined by the *nonlinear* equation (2.10), which is, therefore, something essentially new compared to the theory of linear chains.

We stress here that eqs 2.10 and 2.11 are in fact essentially coupled with each other in the following way: $1/p^*$ is the eigenvalue of eq 2.11 with "potential" $\Phi(x)$, while this very p^* appears in eq 2.10 for $\Phi(x)$ itself.

As to the free energy of a branched macromolecule in the given external fields, it can be found from formula (2.9): taking the inverse Laplace transform

$$G_N(x) = \frac{1}{2\pi i} \oint dp \, \frac{G(p,x)}{p^N}$$

and keeping the leading exponential term $\sim (p^*)^N$, we obtain

$$\Omega = k_B T N \ln p^* \tag{2.12}$$

where the thermodynamic potential is denoted as Ω because it depends on activities $\{\Lambda_f\}$ (or on chemical potentials).

2.3. Density Distribution in a Branched Polymer. As usually, averaged densities of monomers of different types can be calculated as variational derivatives of free energy with respect to the external fields:

$$\varrho_f(x) = \delta\Omega/\delta\varphi_f$$

Taking a variation of eq 2.10

$$\delta\Phi = (\delta p^*/p^*)\Phi - p^* \sum_{f=1}^{\infty} \Lambda_f \hat{g}[e^{-\varphi_f} \Phi^{f-1} \delta\varphi_f] + p^* \sum_{f=2}^{\infty} \Lambda_f (f-1) \hat{g}[e^{-\varphi_f} \Phi^{f-2} \delta\Phi] \tag{2.13}$$

multiplying both the left- and right-hand sides of this relation by

$$\sum_{f=2}^{\infty} \Lambda_f (f-1) e^{-\varphi_f} \Phi^{f-2}(x) \, \Psi(x)$$

taking the integral over all x-space, and using eq 2.11, we obtain finally

$$\varrho_f(x) = C \Lambda_f e^{-\varphi_f} \Phi^{f-1}(x) \, \Psi(x) \tag{2.14}$$

where C is the normalization constant of the form

$$C = N \Big[\sum_{f=2}^{\infty} (f-1) \Lambda_f \int dx \, e^{-\varphi_f} \Phi^{f-1}(x) \, \Psi(x) \Big]^{-1} \tag{2.15}$$

As was expected, $\Psi(x)$ is proportional to $\varrho_1(x)$, i.e., to the density distribution of end points.

As to the total numbers of particles of different kinds of f, N_f, their calculation is straightforward since $\mu_f = k_B T \ln \Lambda_f$ are the corresponding chemical potentials:

$$N_f = \frac{1}{k_B T} \frac{\partial \Omega}{\partial \ln \Lambda_f} = C \Lambda_f \int dx \, e^{-\varphi_f} \Phi^{f-1}(x) \, \Psi(x) \tag{2.16}$$

where C is the same as in eq 2.14. Comparing eqs 2.14 and 2.16, we obtain the obvious normalization condition

$$\int dx \, \varrho_f(x) = N_f \tag{2.17}$$

Moreover, since $\sum_{f=1}^{\infty} N_f = N$, the important relations follow from these results:

$$\sum_{f=1}^{\infty} f N_f = 2 \sum_{f=1}^{\infty} N_f = 2N \tag{2.18a}$$

$$\sum_{f=1}^{\infty} (f-1) N_f = N \tag{2.18b}$$

$$\sum_{f=1}^{\infty} (f-2) N_f = 0 \tag{2.18c}$$

These identities have a very simple physical meaning, reflecting the fact that the structure created by the recursion procedure (2.1) is treelike; i.e., it has no cycles, so that the number of bonds is simply related to the number of vertices according to eq 2.18.

Using the relation (2.14) for densities $\varrho_f(x)$, we can rewrite eqs 2.10 and 2.11 for $\Phi(x)$ and $\Psi(x)$ in the following simplified form:

$$\Phi(x) = (p^*/C) \hat{g} \left[\frac{\sum_{f=1}^{\infty} \varrho_f(x)}{\Psi(x)} \right] \tag{2.19}$$

$$\Psi(x) = (p^*/C) \hat{g} \left[\frac{\sum_{f=1}^{\infty} (f-1) \varrho_f}{\Phi(x)} \right] \tag{2.20}$$

Equations 2.10, 2.11, 2.12, and 2.14 or 2.19, 2.20, 2.12, and 2.14 represent the complete set of equations for the description of the structure of a branched annealed macromolecule in the given external fields $\{\varphi_f(x)\}$. We have to emphasize, however, that different types of physical situations exist here and, accordingly, different formulations of the problem are of interest depending on the character of thermodynamic equilibrium in the system. Namely, different types of ensembles can be adequate for a branched polymer. In particular, the most natural ensembles correspond (i) to setting the density distributions $\{\varrho_f(x)\}$ for all the types of particles f or (ii) to setting only the total density of the structure and the set of chemical potentials, or activities $\{\Lambda_f\}$, which control the redistribution of a given mass of particles over the effective chemical types.

3. Coil-to-Globule "Adsorption" Transition of an Ideal Branched Polymer in an External Field

Equations 2.10, 2.11, 2.12, and 2.14 or 2.19, 2.20, 2.12, and 2.14 are somewhat complicated, and one may need a sort of prescription on how to use them. It can be done by giving a simple example with a particular choice of

the external field shape. We can use as an example either a parabolic potential well of the type $\varphi \sim x^2$ or a localized potential well; the question of the ideal polymer behavior in these wells is rather academic. Therefore, we consider this example in Appendix 2. On the other hand, the example of a pointlike external field is of much more significance, since even the globular state becomes rather expanded in the vicinity of the transition point, so that the arbitrary potential well can be rescaled to the pointlike one. This example gives, therefore, some physical insight into the system and, moreover, some feeling on how the theory works.

To be more specific and also for the sake of simplicity, we will use for illustration purposes the example of simplest branched polymer with triple branchings only. Let us start with writing the basic equations (2.10) and (2.11) for this very particular case, when $\Lambda_2 = 0$ and $\Lambda_4 = \Lambda_5 = ... = 0$ so that only Λ_1 and Λ_3 are nonzero:

$$(1/p^*)\Phi(x) = \Lambda_1 \hat{g} e^{-\varphi_1} + \Lambda_3 \hat{g}[e^{-\varphi_3}\Phi^2] \quad (3.1)$$

$$(1/p^*)\Psi(x) = 2\Lambda_3 \hat{g}[e^{-\varphi_3}\Phi(x)\,\Psi(x)] \quad (3.2)$$

Let us suppose now that $e^{-\varphi_f} = 1 + \beta_f \delta(x)$. To begin with, we would like to remind everyone briefly of the solution of a similar problem for linear polymer (see, for example, ref 17); it is, of course, the theory of adsorption, or of a coil–globule transition for a linear polymer near the pointlike absorber. Equation 2.5 reads in this case

$$\hat{g}\psi + \beta g(x)\,\psi(0) = \Lambda\psi(x) \quad (3.3)$$

(here $\psi = e^{\varphi_1}\Psi$), it can be easily solved by means of Fourier transformation

$$\psi(x) = (2\pi)^{-d}\int dk\, e^{-ikx}\frac{g_k}{\Lambda - g_k}\beta\psi(0) \quad (3.4)$$

giving at $x = 0$ the equation for an unknown eigenvalue Λ:

$$1 = (2\pi)^{-d}\int dk\, e^{-ikx}\frac{g_k}{\Lambda - g_k}\beta \quad (3.5)$$

For $d \le 2$, this equation has a solution at any positive β, meaning that a linear polymer is captured in the well of arbitrarily small depth. On the other hand, for $d > 2$, in particular, for $d = 3$, a solution, corresponding to polymer captured by the well, exists at $\beta > \beta_{tr}$ only, where β_{tr} is the point of an adsorption coil–globule phase transition. Of course, β_{tr} depends on d. In any case, however, transition takes place at $\Lambda \to 1$, so that a nearly singular function under the integrals (3.4) or (3.5) looks like $g_k/[1 - (1 - \epsilon)g_k]$ with some small ϵ (=$(\Lambda - 1)/\Lambda$).

Let us now return to the branched polymer. As was already mentioned, the three-dimensional situation for a branched polymer is expected to be similar to the $d < 2$ situation for a linear chain. Accordingly, we expect that the transition point for a branched polymer in $d = 3$ will be at $\beta = 0$. This is why we consider from the very beginning the $\beta \to 0$ limiting case.

Note first that some nonzero value Φ_∞ is predicted for the $|x| \to \infty$ limit of $\Phi(x)$ by eq 3.1:

$$(1/p^*)\Phi_\infty = \Lambda_1 + \Lambda_3\Phi_\infty^2 \quad (3.6)$$

(smallest root of the equation has to be chosen, since $G(p) \to 0$ at $p \to 0$ by definition (2.3)). Further, we shall seek a solution in the form

$$\Phi(x) = \Phi_\infty[1 + \chi(x)] \quad (3.7)$$

where $\chi(x)$ is expected to be small in the $\beta \to 0$ limit. Using eq 3.7, one obtains instead of eq 3.1 the following *linear* equation for $\chi(x)$:

$$\hat{g}\chi \times 2\Lambda_3\Phi_\infty^2 + g(x)\,[\Lambda_1\beta_1 + \Lambda_3\beta_3\Phi_\infty^2] = (1/p^*)\chi(x)\,\Phi_\infty \quad (3.8)$$

It is similar to eq 3.3 for a linear polymer and can be solved accordingly:

$$\chi(x) = (2\pi)^{-3}p^*[\Lambda_1\beta_1/\Phi_\infty + \Lambda_3\beta_3\Phi_\infty]\int dk\, e^{-ikx}\frac{g_k}{1 - (1 - \epsilon)g_k} \quad (3.9)$$

where ϵ is defined via the relation

$$1 - \epsilon = 2p^*\Lambda_3\Phi_\infty \quad (3.10)$$

Equation 3.10 defines the smooth function $\chi(x)$ which decays at the length scale of order $a/\sqrt{\epsilon}(\chi(x)|_{|x|\to\infty} \sim (1/x)\exp(-x\sqrt{\epsilon}/a)$.

Now, having the solution $\Phi(x)$ of eq 3.1 for an arbitrary p^*, we return to eq 3.2 for $\Psi(x)$. The important fact is that φ_3 can be neglected in this equation in the vicinity of the $\beta = 0$ point, since pointlike potential with $\beta < \beta_{tr}$ does not affect the linear chain behavior in three dimensions or, in other words, does not affect the discrete spectrum of eq 2.7 or eq 3.2 for a linear polymer. This approximation is, of course, very simple physically: it means that direct action of an external field on the links of "probe diameter" (see Figure 2) is negligibly small in comparison with the effective action mediated by polymer branches. Thus, using definitions(3.7) and (3.10), we obtain

$$\hat{g}[(1 - \epsilon)(1 + \chi(x))\Psi] = \Psi(x) \quad (3.11)$$

Since β is small, and accordingly the characteristic length scale $a/\sqrt{\epsilon}$ is expected to be large, we can replace $\hat{g}$ with the Laplacian operator $\hat{g} \simeq 1 + (a^2/6)\Delta$, therefore transforming eq 3.11 into the usual Schroedinger-type one

$$(a^2/6)\Delta\Psi - [\epsilon - \chi(x)]\Psi(x) = 0 \quad (3.12)$$

(see also ref 17 for further details). Since we are working near the capture threshold, we can estimate the energetic level as[18]

$$\epsilon \sim \frac{a^2}{(a/\sqrt{\epsilon})^2}\left[\frac{\chi(0)}{\chi_{min}} - 1\right]^2$$

where $a/\sqrt{\epsilon}$ is the size of the potential well, $\chi(0)$ is its depth, and χ_{min} is the threshold depth of the well corresponding to creation of a discrete level of energy in eq 3.12; $\chi_{min} \sim a^2/(a/\sqrt{\epsilon})^2$ (see again ref 18). Taking the value of $\chi(0)$ from eq 3.9, one obtains therefore

$$p^*[\Lambda_1\beta_1/\Phi_\infty + \Lambda_3\beta_3\Phi_\infty]a^{-3} \sim \epsilon \quad (3.13)$$

It defines, of course, the eigenvalue of eq 3.2. Since the effective potential in this equation (see $\chi(x)$ in eq 3.12) depends in turn on p^*, we have to consider consistently eqs 3.6, 3.10, and 3.13 for the unknown values p^*, Φ_∞, and ϵ. This leads to the following results:

$$p^*/p_0^* - 1 \sim (\beta_1 + \beta_3)^2$$

where, as usually, $p_0^* = 1/2(\Lambda_1\Lambda_3)^{1/2}$ is the value of p^* in the absence of any external fields (see eq 2.8); in other words, according to eq 2.12, free energy of adsorption scales as

$$\delta F/k_BTN = \ln(p^*/p_0^*) \sim (\beta_1 + \beta_3)^2 \qquad (3.14)$$

i.e., in this sense adsorption is the second-order phase transition. The characteristic length scale of the confined globular state is given by:

$$R \sim a/\sqrt{\epsilon} \sim a/(\beta_1 + \beta_3)^{1/2} \qquad (3.15)$$

or

$$\delta F \sim k_BTN(a/R)^4 \qquad (3.16)$$

These results can also be interpreted in terms of simple scaling estimations (see below).

Note that β_1 and β_3 enter eqs 3.14 and 3.15 as a sum only. This is due to the existence of a large space scale near the transition point: since numbers of ends and of branch points are the same in the polymer considered (see eq 2.18), a typical branched structure is designed in such a way that an end point always can be found near any branch point (closer than the characteristic scale $a/\sqrt{\epsilon}$). This is why all types of monomers give the same contribution to the adsorption free energy near the transition point.

4. Conformational Entropy of a Branched Polymer: Generalized Lifshitz Equation

Let us return to the general consideration of section 2. Following the logic of ref 15 on linear polymers, we shall derive now the equation for the conformational entropy of a branched polymer by simply using the relation $F = E - TS$, since (i) free energy F or Ω of a branched polymer in an external field was derived before (eq 2.12), (ii) energy E of a branched polymer in an external field is

$$E = \sum_{f=1}^{\infty}\int dx\ \varphi_f(x)\ \varrho_f(x) \qquad (4.1)$$

and, the most important, (iii) conformational entropy S of the macrostate does not depend on the way of preparation and fixation of this state and, therefore, we can suppose the fields $\{\varphi_f(x)\}$ to be determined in such a way that given macrostates occur as equilibrium ones in these very fields.

There are a few possibilities depending on the type of macrostate concerned. Indeed, we will consider two cases: (a) a macrostate with a given set of distributions $\{\varrho_f(x)\}$ for all types of particles $\{f\}$; (b) a macrostate with a given distribution of the *total* density $\varrho(x) = \sum_{f=1}^{\infty}\varrho_f$ and with given activities $\{\Lambda_f\}$. These cases are both of interest for different physical realizations. The first case (a) pertains to various phenomena like segregation, when different types of monomers in a branched polymer (for example, branch points and end points) are localized mainly in different space regions; for example, it may be the result of some selective adsorption or the result of a tendency toward microphase separation (this last possibility is investigated in detail in ref 20). On the other hand, the second case (b) is adequate, for example, for the problem of the overall compression of a branched polymer in some confined geometry, and in such a case the values of $\{\Lambda_f\}$ control the distribution of particles over the functionalities $\{f\}$. We will consider both cases (a) and (b) in turn.

4a. Entropy of a Macrostate with Given Distributions of Densities. Using the general scheme described above, we start with the free energy which is the thermodynamic potential of the branched macromolecule with given fixed densities $\{\varrho_f(x)\}$ and, in particular, with fixed numbers of particles $\{N_f\}$ instead of activities $\{\Lambda_f\}$ or chemical potentials. This thermodynamic potential can be easily found from eq 2.12 by means of the usual Legendre transformation:

$$F\{\varrho_f\} = \Omega + \sum_{f=1}^{\infty}k_BTN_f \ln \Lambda_f = \sum_{f=1}^{\infty}k_BTN_f \ln(p^*\Lambda_f) \qquad (4.2)$$

In other words, we write

$$S\{\varrho_f(x)\} = \frac{E - F}{k_BT} = \sum_{f=1}^{\infty}\int dx\ \varrho_f[\varphi_f - \ln(p^*\Lambda_f)] \qquad (4.3)$$

and have to consider now the relations (2.14), (2.19), and (2.20) as the equations for $\{\varphi_f\}$, $\Phi(x)$, and $\Psi(x)$ with given $\{\varrho_f\}$. Defining densities

$$\varrho^{(l)}(x) \equiv \varrho(x) = \sum_{f=1}^{\infty}\varrho_f(x) \qquad (4.4)$$

and

$$\varrho^{(b)}(x) = \sum_{f=1}^{\infty}(f-1)\varrho_f(x) \qquad (4.5)$$

("l" and "b" denote "links" and "bonds", respectively), and defining new functions $\phi(x)$ and $\psi(x)$ instead of $\Phi(x)$ and $\Psi(x)$ according to

$$\psi(x) = \varrho^{(b)}(x)/\Phi(x) \qquad (4.6)$$

and

$$\phi(x) = (p^*/C)\varrho^{(l)}(x)/\Psi(x) \qquad (4.7)$$

we obtain the relations

$$\varrho^{(l)}(x) = \phi\hat{g}\psi \qquad (4.8)$$

$$\varrho^{(b)}(x) = \psi\hat{g}\phi \qquad (4.9)$$

which do not contain the values of fields $\{\varphi_f\}$. We can now find φ_f from eq 2.14 and substitute it in eq 4.3, and, taking into account also eq 2.18c, we obtain

$$S\{\varrho_f(x)\} = \int dx\ \{\varrho^{(l)} \ln \hat{g}\psi + \varrho^{(b)} \ln \hat{g}\phi - \sum_{f=1}^{\infty}\varrho_f \ln \varrho_f\} \qquad (4.10)$$

or

$$S\{\varrho_f(x)\} = \int dx \sum_{f=1}^{\infty} \varrho_f \ln \frac{\hat{g}\psi(\hat{g}\phi)^{f-1}}{\varrho_f} \quad (4.11)$$

where $\phi(x)$ and $\psi(x)$ have to be expressed through densities $\{\varrho_f\}$ by eqs 4.8 and 4.9.

Note that there is a sort of gauge invariance in eqs 4.8–11, determining the conformational entropy: nothing changes under the transformation $\phi \to c\phi$, $\psi \to c^{-1}\psi$, because $\int dx \{\varrho^{(l)} - \varrho^{(b)}\} = 0$ due to the identities (2.18).

4b. Entropy of a Macrostate with a Given Total Density. Using the same general scheme, we have (i) to consider from the very beginning such a case, when every monomer is subjected to the same external field φ independently on its type or functionality f, i.e., $\varphi_f = \varphi$, and (ii) to start with the thermodynamic potential Ω (rather than free energy F above). Thus, according to eqs 2.12 and 4.1, conformational entropy equals to

$$S\{\varrho(x),\Lambda_f\} = \frac{E - \Omega}{k_B T} = \int dx\, \varrho(x)\,[\varphi(x) - \ln p^*] \quad (4.12)$$

(compare to eq 4.3). As to our eqs 2.14, 2.19, and 2.20, it is convenient to write them in terms of neither $\Phi(x)$ and $\Psi(x)$ (like eqs 2.19 and 2.20) nor $\phi(x)$ and $\psi(x)$ (like eqs 4.8 and 4.9), but using $\Phi(x)$ and $\psi(x)$. Rewriting definitions eqs 4.6 and 4.5 with eq 2.14

$$\psi(x) = \Psi(x)\, C e^{-\varphi_1} \sum_{f=1}^{\infty} (f-1)\Lambda_f \Phi^{f-2}(x) \quad (4.13)$$

or

$$\Psi(x) = (p^*/C)\hat{g}\psi \quad (4.14)$$

we can transform eq 2.11 into the following equation (since $\varphi_f = \varphi_1 = \varphi$)

$$p^* e^{-\varphi}[\sum_{f=1}^{\infty} (f-1)\Lambda_f \Phi^{f-2}(x)]\hat{g}\psi = \psi(x) \quad (4.15)$$

We can now determine $p^* e^{-\varphi}$, or $\ln p^* - \varphi$, from eq 4.15 and substitute it into the relation for entropy (4.12)

$$S\{\varrho(x),\Lambda_f\} = \int dx\, \varrho(x) \ln\left\{\frac{\hat{g}\psi}{\psi}[\sum_{f=1}^{\infty} (f-1)\Lambda_f \Phi^{f-2}(x)]\right\} \quad (4.16)$$

where $\Phi(x)$ and $\psi(x)$ have to be expressed through the density $\varrho(x)$ by means of the equations

$$\Phi(x) = \hat{g}\frac{\varrho(x)}{\hat{g}\psi} \quad (4.17)$$

and

$$\varrho(x) = \psi(x) \frac{\sum_{f=1}^{\infty} \Lambda_f \Phi^{f-1}(x)}{\sum_{f=1}^{\infty} (f-1)\Lambda_f \Phi^{f-2}(x)} \quad (4.18)$$

(Equation 4.17 is obtained by substituting eq 4.14 into eq 2.19, and eq 4.18 can be derived from eq 2.14 by taking into account eq 4.13.) Equations 4.16–4.18 give the solution of the problem, since they do not contain the auxiliary external field φ.

Note that, opposite to the first case (eqs 4.18–4.11), there is not any gauge invariance in eqs 4.16–4.18, since Φ and ψ are completely defined by eqs 4.17 and 4.18.

Equations 4.8–4.11 and 4.16–4.18 are two different generalizations of the Lifshitz equation for the conformational entropy of a linear polymer. These are the main results of the present work.

5. Specific Cases

5a. Linear Chain. First of all, let us show how the usual Lifshitz equation for a long linear polymer can be recovered from our generalizations. Let us start with the first version (eqs 4.8–4.11). In the case of a linear polymer, $\varrho^{(l)} = \varrho_1 + \varrho_2$ (see eq 4.4) and $\varrho^{(b)} = \varrho_2$ (see eq 4.5). Since the limit of *long* polymers is taken, the density of end points ϱ_1 is negligibly small, so that in fact $\varrho^{(l)} = \varrho^{(b)} = \varrho = \psi\hat{g}\phi = \phi\hat{g}\psi$ (see eqs 4.8 and 4.9). Due to the gauge invariance we can take $\phi = \psi$ then obtaining

$$\varrho = \psi\hat{g}\psi \quad (5.1)$$

and from eq 2.10

$$S = \int dx\, \varrho(x) \ln \frac{(\hat{g}\psi)^2}{\varrho} = \int dx\, \varrho(x) \ln \frac{\hat{g}\psi}{\psi} \quad (5.2)$$

This coincides with the Lifshitz equation for the entropy of linear chains.[15-17]

Let us consider now the second variant of our generalization. For the case of a linear chain $\Lambda_3 = \Lambda_4 = ... = \Lambda_f = ... = 0$, and for a *long* chain Λ_1 is negligibly small compared to Λ_2. In this case eq 4.18 gives $\varrho = \psi\Phi$, and then eq 4.17 means $\Phi = \hat{g}\psi$, thus converging back to eqs 5.1 and 5.2.

5b. Spatially-Uniform State. Returning to branched polymers, let us start with the simplest spatial distribution of polymer density, namely, with uniform structure. This is the case for the corresponding melt or concentrated solution and also for a large polymeric globule in volume approximation.[17]

Ensemble with Fixed Numbers of Particles. In the uniform state $\varrho^{(l)} = \varrho^{(b)}$ due to eq 2.18. We have therefore

$$\varrho^{(l)} = \varrho^{(b)} = \phi\psi$$

and

$$S = \sum_{f=1}^{\infty} N_f \ln \frac{N}{N_f} \quad (5.3)$$

It is, of course, the usual Boltzmann entropy associated with redistribution of N particles over different types f, with population N_f each.

Ensemble with Fixed Activities. Considering the spatially-uniform state where ϱ, ψ, and Φ do not depend on x at all, so that $\hat{g}\psi = \psi$ etc., we have $\varrho = \Phi\psi$ from eq 4.17, and therefore according to eq 4.18 Φ, independently of the given value of uniform density, has to be equal to Φ_0, the solution of the following equation:

$$\sum_{f=1}^{\infty} (f-2)\Lambda_f \Phi_0^{f-1} = -\Lambda_1 + \Lambda_3 \Phi_0^2 + ... = 0 \quad (5.4)$$

Note that for positive $\{\Lambda_f\}$ this equation always has some positive solution, and only one. Accordingly,

$$S = N \ln \sum_{f=1}^{\infty} \Lambda_f \Phi_0^{f-2} \tag{5.5}$$

Note that eq 5.5 looks a little more complicated and less transparent compared to eq 5.3. New constant, Φ_0, determined by eq 5.4, appears in eq 5.5. It is a manifestation of the complex character of the ensemble considered. In particular, the value of Φ_0 characterizes the redistribution of the given number of particles over the different "states" controlled by chemical potentials $\{\ln \Lambda_f\}$. To understand it, let us return for a moment to eqs 2.8 and 2.9. Since we are considering the spatially-uniform state, we can omit the x-dependence in eq 2.8. In this approximation Φ_0 is the value of Green function $G(p)$ exactly at the singular point $p = p_0^*$. According to eq 2.8 and the equation just before eq 2.8, it is $(\Lambda_1/\Lambda_3)^{1/2}$, in clear correspondence with eq 5.4.

5c. Smooth Limit. We would like to remind everyone that the most known version of eqs 5.1 and 5.2 for the entropy of a linear polymer looks like

$$S = (a^2/2d) \int dx\, \psi(x)\, \Delta\psi, \quad \varrho(x) = \psi^2 \tag{5.6}$$

From the point of view of the more general Lifshitz equation (5.2), it can be called a "smooth" approximation since it is valid in the case $a \ll R$, where R is the characteristic size of space nonuniformity, or of change of external fields, or densities, or order parameter $\psi(x)$.

Let us reproduce a similar simplification for a branched polymer with fixed activities $\{\Lambda_f\}$.

Since in the uniform case $\Phi(x) = \Phi_0$ (eq 5.4), we expect only a small deviation of $\Phi(x)$ from Φ_0 in the case of the smooth density distribution. Accordingly, we seek a solution in the form

$$\Phi(x) = \Phi_0(1 + \chi) \tag{5.7}$$

where $\chi(x)$ is small. Taking into account that

$$\hat{g} \simeq 1 + (a^2/2d)\Delta + (b^4/8d^2)\Delta^2 \tag{5.8}$$

where $b \sim a$ ($b = a$ for Gaussian connectors), and performing expansion up to χ^2 and a^4 terms in eqs 4.17 and 4.18, we find

$$S - S_0 \simeq -\frac{1}{2}\left(\frac{a^2}{2d}\right)^2 Q \int dx\, \frac{(\Delta\varrho)^2}{\varrho} \sim N\left(\frac{a}{R}\right)^4 \tag{5.9}$$

where

$$Q = \frac{\sum_{f=1}^{\infty}(f-1)\Lambda_f \Phi_0^{f-2}}{\sum_{f=1}^{\infty}(f-1)(f-2)\Lambda_f \Phi_0^{f-2}} \tag{5.10}$$

$Q = 1$ for polymer with three-functional and one-functional units only. The result (5.9) differs dramatically from eq 5.6 for a linear polymer, being proportional to $(a/R)^4$ in agreement with scaling arguments described below.

Note that entropy does not depend on b, so that the Δ^2 term in eq 5.8 is actually irrelevant.

Equation 5.9 is applicable independently of space dimensionality and therefore can be generalized to the replica space in order to analyze a polymer with a frozen structure of branchings. We have applied it in this way in ref 19.

We would like to explain here also the following. We considered the situation when $\Phi(x)$ does not deviate too much from the constant Φ_0. It does not imply, however, that density has the same property. Φ characterize redistribution of particles over the "chemical" types and, accordingly, it feels the gradient of density and not the density itself. This is why the result (5.9) is indeed applicable to realistic structures, for example, of globular type, with large but smooth variations of density from zero at the periphery to some considerably large value in the central core.

5d. Microdomain Structure. The phenomenon of microphase segregation in a concentrated solution or melt of a branched polymer has been investigated theoretically in ref 20. Here we give only some comments on the application of the generalized Lifshitz equation to this particular problem.

Consider an ensemble with given densities $\{\varrho_f\}$. One may try to investigate a smooth limit for this ensemble. If gradients are small, then $\varrho^{(1)}$ is nearly equal to $\varrho^{(b)}$ (see eqs 4.8 and 4.9), meaning the identities (2.18) are valid nearly locally. It does not mean, however, that the structure cannot be essentially stretched. This conjecture is extremely important for understanding the situation. Indeed, on large enough space scales the elements of a branched structure can be moved relative to each other to an arbitrarily large distance—and with conservation of the local balance between densities. Roughly speaking, there may be the same number of branch points and of ends in some space region, but the ends may be attached to different branches placed far from this point. It shows the important nonlocality in the system.

To consider the mentioned nonlocal effect, let us consider an incompressible system with

$$\varrho_1(x) + \varrho_2(x) + \varrho_3(x) + \ldots = \varrho^{(1)} = \varrho = \text{const} \tag{5.11}$$

It does not mean, of course, that all the components are distributed uniformly. Moreover, we can expect some regimes in this system with a strong tendency toward microphase segregation similar to the one known for block copolymers.[21] Accordingly, we will suppose some small deviations of component densities from averaged uniform values $\bar{\varrho}_f = N_f/V$, V being the whole volume of the system. Thus, we write

$$\varrho_f(x) = \bar{\varrho}_f + \delta_f(x) \tag{5.12}$$

and, accordingly,

$$\varrho^{(b)}(x) = \varrho + \delta(x), \quad \delta(x) = \sum (f-1)\delta_f \tag{5.13}$$

where δ_f and δ are small. Considering now eqs 4.8 and 4.9, it is natural to look for a solution of the form $\psi(x) = \sqrt{\varrho}[1 + \xi(x)]$, $\phi(x) = \sqrt{\varrho}[1 + \eta(x)]$. Linearizing, one obtains immediately the solution

$$\xi(x) = (\hat{g} - \hat{g}^{-1})^{-1}\delta(x)/\varrho + O(\delta^2);$$
$$\eta(x) = (1 - \hat{g}^2)^{-1}\delta(x)/\varrho + O(\delta^2) \tag{5.14}$$

Nonrestricted operators $(\hat{g} - \hat{g}^{-1})^{-1}$ and $(1 - \hat{g}^2)^{-1}$ here have very simple physical meaning, and this is the main

point we would like to stress here: behaving as $1/k^2$ in small wave vector $k \to 0$ limit, they are just describing the polymer link-induced correlations, which become of dramatic importance for long-wavelengths perturbations of densities δ.

In fact, however, linear terms (5.14) do not contribute to the conformational entropy, and one has to keep also quadratic terms. Omitting the corresponding rather complicated expressions, we write the final equation for the conformational entropy:

$$S = -(1/2\varrho)\int dx\ \delta(x)\,\hat{g}^2(1-\hat{g}^2)^{-1}\delta(x) - \sum_{f=1}^{\infty}(1/2\bar{\varrho}_f)\int dx\ \delta_f^2(x) \quad (5.15)$$

or in terms of Fourier k-representation

$$S = -\frac{1}{2\varrho}\int dk\ \frac{g_k^2}{1-g_k^2}\delta_k^2 - \sum_{f=1}^{\infty}\frac{1}{2\bar{\varrho}_f}\int dk\ \delta_{f,k}^2 \quad (5.16)$$

where δ_k is related to the set of $\{\delta_{f,k}\}$ by

$$\delta_k = \sum_{f=1}^{\infty}(f-1)\delta_{f,k} \quad (5.17)$$

We would like to remind everyone that a typical g_k looks like $\exp(-k^2a^2)$, so that the singularity of the $1/k^2$ type is presented in the expression (5.16) for conformational entropy. This is of the same type as the well-known behavior of the conformational entropy for block copolymers.[21] Therefore, this analogy leads immediately to the prediction of the possibility of microphase segregation in the melt, or concentrated solution, or a large globule of a branched polymer, as was investigated in detail elsewhere.[20]

6. Conclusion

We have studied many properties of collapsed globular states of a branched macromolecule with an annealed structure of branchings. Our main results are generalizations (4.10) and (4.16) of the Lifshitz equation for the conformational entropy. We hope these results will be useful for many various applications. Some of them are described above, like the theory of branched polymer adsorption, of microphase segregation, etc. Other applications were described elsewhere.[19,20]

From the point of view of biological applications, where a branched polymer is RNA with a secondary structure of the clover-leaf type, the problem of the unique globule structure is of utmost interest. This problem is very similar to the one for linear chains applied for protein folding. We hope that the results of the present work may be used as a first step toward understanding the fascinating problem of RNA folding.

Appendix 1: Scaling Estimations for Adsorption and the Collapsed State of a Branched Polymer

Here we provide a simple estimate of the conformational entropy loss due to the confinement of a branched polymer in some restricted volume of size R. Let us remind everyone that for a linear polymer this entropy scales as Na^2/R^2 [22] (instead of R^2/Na^2 for a stretched chain) and this result can be obtained by means of simple scaling arguments (see, for example, ref 17). Similar arguments are applicable to the case of a branched polymer. Indeed, consider a branched polymer confined in some hole with impenetrable walls. Let us start from some monomer positioned at the moment somewhere inside the cavity far from the walls and let us walk along the backbone of our polymer. Up to the nearest contact to the wall we shall see monomers whose conformations are not affected by the fact of confinement. Therefore, entropy loss due to confinement is of order 1 per each unperturbed blob with a size of order R. The number of steps of our walk g can be defined, therefore, via the relation $ag^{1/4} \sim R$, or $g \sim (R/a)^4$. Accordingly, the number of blobs per entire chain is $\sim N/g$ and entropy loss scales as

$$S \sim N(a/R)^4 \quad (A1.1)$$

Let us apply this result for the physical question of branched polymer adsorption on the potential well. Following de Gennes,[23] we can write for the free energy of an adsorbed macromolecule

$$F/k_BT \sim \delta N f_b - N(a/R)^4 \quad (A1.2)$$

where f_b is fraction adsorbed among the monomers and δ characterizes the deviation from the adsorption threshold; it is *not* generally the depth of the potential well; it is rather some effective value which takes into account the local effects of monomers packing in the attractive region (for example, near the impenetrable wall). Estimate of f_b is the most delicate step here. The simplest estimate like $f_b \sim r/R$ is valid in the one-dimensional case considered in ref 23 since the density distribution is exponential. In other dimensions density has usually some power decay outside the region of the potential well. It is this very point which makes it impossible to restrict consideration with the framework of the scaling approach. Therefore, we assume that density decays as $1/x$, which can be easily obtained from the rigorous theory (see eq 3.9) but, to the best of our knowledge, cannot be obtained from qualitative arguments. Supposing this type of decay, one gets immediately $f_b \sim (r/R)^2$ and, minimizing the free energy (A1.2) with respect to R, obtains

$$R \sim \delta^{-1/2} \quad \text{and} \quad F/k_BTN \sim \delta^2 \quad (A1.3)$$

the results of which are consistent with eqs 3.15 and 3.16 obtained in a more rigorous theory.

Appendix 2: Parabolic Potential

According to the general scheme, we start with eq 3.1 for an arbitrary value of p^*. Since $\Phi(x)$ goes to zero in the regions where $\varphi(x)$ tends to infinity, the quadratic term can be neglected in the asymptotic region:

$$\Phi(x)|_{|x|\to\infty} \simeq p^*\Lambda_1\hat{g}e^{-\varphi_1} \quad (A2.1)$$

Approximation (A2.1) has very simple physical meaning: neglecting the second term (and, in general, the subsequent ones) in eq 3.1 (or eq 2.10) means that only nearly linear chains, or comblike structures with the smallest side groups, can reach the periphery of the structure and contribute the large $|x|$ asymptotic.

To be more specific, let us restrict ourselves with the simplest Gaussian connectors between polymer links

$$\hat{g}\psi = \int dx' \, (2\pi a^2/d)^{-d/2} \exp[-d(x - x')^2/2a^2]\psi(x') \tag{A2.2a}$$

or

$$\hat{g} = \exp[(a^2/2d)\Delta] \tag{A2.2b}$$

where Δ is Laplacian operator.

In our example potentials φ_f are parabolic, i.e.

$$\varphi_f = dx^2/2\eta_f^2 \tag{A2.3}$$

where r_f are the corresponding length scales, factor $d/2$ is included in their definition for simplicity. Corresponding approximation (A2.1) for $\Phi(x)$ in this case is Gaussian. Substituting it in eq 3.2, we obtain a *linear* equation for $\Psi(x)$:

$$(1/p^{*2})\Psi(x) = 2\Lambda_1\Lambda_3\hat{g}[e^{-\varphi_3}\hat{g}[e^{-\varphi_1}\Psi(x)]] \tag{A2.4}$$

where p^{*2} plays the role of an eigenvalue. Being considered in the entire x-space, this equation has an obvious Gaussian solution of the form

$$\Psi(x) = \exp(-dx^2/2R^2) \tag{A2.5}$$

and can be, therefore, easily solved exactly. This result is applicable, however, for the case of a narrow potential well with $r_3 \ll a$, since in this situation only approximation (A2.1) is valid almost everywhere. Performing integration, one then obtains

$$R^2 = \frac{a^2}{2} + \frac{1}{2}\left(a^4 + \frac{a^2}{\dfrac{1}{r_3^2} + \dfrac{1}{a^2 + r_1^2}}\right)^{1/2} \simeq a^2 + \frac{r_3^2}{4} \tag{A2.6}$$

and

$$p^* = \sqrt{2}\{[1 + a^2/r_1^2][R^2/(R^2 - a^2)]\}^{d/4} p_0^* \simeq \sqrt{2}(a^2/r_1 r_3)^{d/2} \tag{A2.7}$$

where $p_0^* = 1/2(\Lambda_1\Lambda_3)^{1/2}$ is the value of p^* for the free polymer without any external fields, i.e., with $r_f \to \infty$ (see eq 2.8), so that $\ln(p^*/p_0^*)$ is proportional to the change of the free energy of a macromolecule in the external fields—see eq 2.12. Note that the characteristic size of the globule, R, is basically $\sim a$, meaning monomers are confined inside the well while polymer bonds of length a form a sort of fringe outside. At the same time correction in the size R is mainly due to r_3 and not r_1, even if $r_1 \gg r_3$, meaning that confinement of branch points is much more crucial for the polymer as a whole than the same event with end points.

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