Dynamics of Gaussian chain with topological constraints

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Conformational relaxation of a long polymer chain ($N \gg 1$ links) without volume interactions and with nonintersecting parts is investigated. It is shown that the maximum relaxation time of such a chain is $\tau_{\max} \geqslant t(N)$, where $t(N)$ increases in the presence of hydrodynamic interaction in proportion to $N^2(\ln N)^{-2}$ ($N \gg 1$). It is thus proved rigorously that topological constraints lead to a substantial (in the sense of the influence of these constraints on the critical exponents) slowing down of the conformational relaxation of a macromolecule even in a very highly diluted solution.

1. INTRODUCTION

Topological constraints, as understood in polymer physics, indicate that moving parts of a macromolecule cannot intersect. In accord with their meaning, topological constraints influence just dynamic rather than equilibrium properties of polymer systems. The very important role of these constraints for the dynamics of concentrated polymer solutions and melts is well known.[1,2] At the same time, the importance of topological constraints (in other words—of the entanglement effect) to the dynamics of an isolated polymer chain (in a dilute solution) is less obvious. Most investigators tend to assume that the entanglement effect is inessential for an arbitrary long isolated polymer chain in a good solvent.[3] Topological constraints can be expected, however, to influence noticeably the dynamics of a polymer chain under theta-conditions (i.e., in a Gaussian chain, whose spatial conformations are more compact).[3,4]

It is known that the maximum time τ of conformational relaxation for a phantom Gaussian chain (i.e., for a chain without topological constraints) with hydrodynamic interaction depends on the number N of links in accordance with the law[3]

$$\tau_H \propto N^{3/2}. \qquad (1.1)$$

For a chain with topological constraints one should expect a slower relaxation [4,5]

$$\tau_{top} \propto N^z, \qquad (1.2)$$

where $z > 3/2$. It is proposed in Refs. 3 and 4 to take topological constraints into account by a method based on certain physically plausible assumptions. The dynamic exponent z was calculated, and a number of important dynamic effects, whose onset is based entirely on the fact that $z > 3/2$, was predicted. It is therefore very important to prove the inequality $z > 3$ rigorously. This is the aim of this paper.

Our plan is the following: In the next section we describe a variational principle that yields a rigorous lower-bound for the maximum relaxation time. In Sec. 3 we obtain specific estimates using the very simple trial function (2.19). We describe and employ in this section a scaling model for the calculations, based on the derivation, for the investigated quantities, of recurrence equations generated by a procedure of enhancing the polymer-chain link. The results of this section (rigorous lower bounds for the maximum relaxation time) turn out to be trivial. The causes of this failure are considered at the end of the section, where additional criteria that the trial function must meet are proposed. In Sec. 4 we determine a new, modified trial function and analyze its properties. In the final Sec. 5 we obtain, by synthesis of a scaling method and using a modified trial function, a nontrivial lower bound of the dynamic exponent z. The remainder of the section is devoted to a brief description of the models used in investigations of the dynamics of nonlinear molecules.

The macroscopic equilibrium properties of a Gaussian polymer chain are described by a model of beads and springs[6]—a sequence $\mathbf{r}_0, \mathbf{r}_1, \ldots, \mathbf{r}_N$ of pointlike beads connected by weightless links (springs) having an elastic energy

$$U_{el} = \sum_{n=1}^{N} \frac{T}{4a^2} (\mathbf{r}_n - \mathbf{r}_{n-1})^2, \qquad (1.3)$$

where a is the characteristic dimension of the link. The Brownian dynamics of such a chain is described by the standard equations

$$\frac{\partial r_{\alpha n}}{\partial t} = T^{-1} \sum_{m,\beta} D_{nm}^{\alpha\beta} \left(-\frac{\partial U_{el}}{\partial r_{\beta m}} + \xi_{\beta m} \right),$$

$$n = 0, 1, \ldots, N, \qquad \alpha = 1, 2, 3, \qquad (1.4)$$

where the superscripts α and β number the Cartesian components of the vectors, $D_{nm}^{\alpha\beta}$ is the matrix of the generalized diffusion coefficients, and $\xi_{\beta m}(t)$ is a δ-correlated random force exerted on the mth bead by the solvent. The Rouse model, which presupposes complete absence of hydrodynamic interaction between the beads, corresponds to a very simple diffusion-coefficient matrix

$$D_{nm}{}^{\alpha\beta} = D_0 \delta_{nm} \delta_{\alpha\beta}, \qquad (1.5)$$

where D_0 is the bead diffusion coefficient. For a chain of beads with hydrodynamic interaction (the Zimm model), this matrix takes the form

$$D_{nm}{}^{\alpha\beta} = D_0 \delta_{nm} \delta_{\alpha\beta} + (1 - \delta_{nm}) (T/8\pi\eta_s r) (\delta_{\alpha\beta} + r_\alpha r_\beta / r^2), \quad (1.6)$$

where $\mathbf{r} = \mathbf{r}_n - \mathbf{r}_m$ and η_s is the solvent viscosity.

The maximum time of conformational relaxation for the Rouse phantom chain is [3]

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$$\tau_R=\text{const}\, a^2N^2/D_0, \qquad N\gg 1. \tag{1.7}$$

The analogous quantity for the phantom Zimm chain is [cf. Eq. (1.1)]:

$$\tau_H=\text{const}(\eta_s a^3/T)N^{3/2}, \qquad N\gg(aD_0\eta_s/T)^2. \tag{1.8}$$

2. VARIATIONAL PRINCIPLE

In the absence of volume interactions, the topological constraints can be specified as follows: we consider a broken line $\mathbf{r}_0\mathbf{r}_1...\mathbf{r}_N$ with beads as the vertices (Fig. 1) and stipulate that the segments of this broken line (which we shall call the chain trajectory) cannot intersect one another as they move. Most trajectories with self-intersection form a certain hypersurface Σ_Ω in the space Ω of all the chain conformations, which we shall call the forbidden surface. Forbiddenness of self-intersection can be ensured if each trajectory

$$\Gamma\equiv(\mathbf{r}_0,\ \mathbf{r}_1,\dots,\mathbf{r}_N), \tag{2.1}$$

belonging to the forbidden surface is set formally in correspondence with an infinite potential energy.[1)]

The total energyy $U(\Gamma)$ of the beam interaction consists thus of two parts: regular $U_{el}(\Gamma)$ and singular $U_s(\Gamma)$:

$$U(\Gamma)=U_{el}(\Gamma)+U_s(\Gamma). \tag{2.2}$$

The regular part [see (1.3)] describes the connection of the beads to form a polymer chain; the singular part

$$U_s(\Gamma)=\begin{cases}\infty, & \Gamma\in\Sigma_\Omega\\ 0, & \Gamma\notin\Sigma_\Omega\end{cases} \tag{2.3}$$

describes the topological constraints.

Let $f(\Gamma)$ be the density of the distribution over the polymer-chain conformations. The evolution of this function is described by the diffusion equation

$$\partial f/\partial t=-\hat{L}f, \tag{2.4}$$

$$\hat{L}f=-\sum_{n\alpha,m\beta}\frac{\partial}{\partial r_{\alpha n}}D^{\alpha\beta}_{nm}\left(\frac{\partial}{\partial r_{\beta m}}f+f\frac{\partial}{\partial r_{\beta m}}U\right). \tag{2.5}$$

The general solution of this equation is

$$f(t)=\sum_s f_s\exp(-\gamma_s t), \tag{2.6}$$

where γ_s are the eigenvalues of the diffusion operator $\hat{L}$,

$$\hat{L}f_s=\gamma_s f_s. \tag{2.7}$$

We stipulate that the distribution function $f(\Gamma)$ be invariant to parallel transports of the chain as a whole in space (since we shall hereafter be interested just in conformational relaxation, and not in diffusion of the chain as a whole). After imposing this condition, the spectrum of the operator $\hat{L}$ becomes discrete. The zeroth eigenvalue of this operator correspond to the equilibrium distribution function

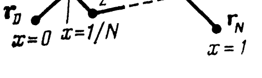

FIG. 1. Model of polymer chain in the form of beads $\mathbf{r}_n$, $n=0,1,2,...,N$, joined by straight-line segments; x is the continuous coordinate along the chain, $x_n=n/N$.

$$f_0(\Gamma)=\text{const}\exp[-U(\Gamma)]\equiv P(\Gamma). \tag{2.8}$$

The operator $\hat{L}$ becomes Hermitian if the scalar product of two functions, $f(\Gamma)$ and $g(\Gamma)$, is defined as

$$(f,g)=\int f(\Gamma)g(\Gamma)P^{-1}(\Gamma)D(\Gamma), \tag{2.9}$$

where the integral of $D(\Gamma)$ means the integral over all the conformations of the chain. We can therefore formulate the following variational principle for the smallest nonzero (positive) eigenvalue γ_1:

$$\gamma_1=\min_f\{(f,\hat{L}f)/(f,f)\}, \tag{2.10}$$

under the condition

$$(f,\ f_0)=0. \tag{2.11}$$

After simple transformations, Eqs. (2.10) and (2.11) take the form

$$\gamma_1=\min_\varphi\left\{\left\langle\sum_{n\alpha,m\beta}D^{\alpha\beta}_{nm}\frac{\partial\varphi}{\partial r_{\alpha n}}\frac{\partial\varphi}{\partial r_{\beta m}}\right\rangle\Big/\langle\varphi^2\rangle\right\}, \tag{2.12}$$

under the condition

$$\langle\varphi\rangle=0. \tag{2.13}$$

The angle brackets denote here averaging over the equilibrium distribution:

$$\langle\dots\rangle=\int P(\Gamma)\dots D(\Gamma). \tag{2.14}$$

The weighting function $P(\Gamma)$ vanishes identically in the forbidden layer (see footnote 1), so that an arbitrarily fast change of the "trial" function $\varphi(\Gamma)$ within the confines of the forbidden layer makes no contribution whatever to the numerator of the right-hand side of (2.12). This function can therefore (in the limit 0) have discontinuities on the forbidden surface.

Equation (2.12) can be rewritten by introducing the maximum relaxation time $\tau_{\text{top}}\equiv 1/\gamma_1$

$$\tau_{top}=\min_\varphi t[\varphi], \tag{2.15}$$

where

$$t[\varphi]\equiv\sigma_\varphi{}^2/D_\varphi, \tag{2.16}$$

$$\sigma_\varphi{}^2\equiv\langle\varphi^2\rangle, \tag{2.17}$$

$$D_\varphi\equiv\left\langle\sum_{n\alpha,m\beta}D^{\alpha\beta}_{nm}\frac{\partial\varphi}{\partial r_{\alpha n}}\frac{\partial\varphi}{\partial r_{\beta m}}\right\rangle. \tag{2.18}$$

We have thus $t[\varphi]\leqslant\tau_{\text{top}}$ for any function $\varphi=\varphi(\Gamma)$ that satisfies condition (2.13), i.e., the value of the functional $t[\varphi]$ is a rigorous lower bound of the maximum relaxation time. The remainder of this paper is devoted to an investigation of this functional and to obtaining a (nontrivial) estimate for τ_{top}.

The function $\varphi(\Gamma)$ can be regarded as a coordinate in conformation space Ω. Obviously, σ_φ [see (2.17) and (2.13)] can be interpreted here as the mean squared change of this coordinate (in the course of the relaxation), and D_φ as the average diffusion coefficient along this coordinate. (It is easy to show that the mean squared displacement along the coordinate φ over a short time δt is equal to

$\langle \delta\varphi^2\rangle = 2D_\varphi \delta t$.) In the upshot, Eq. (2.16) acquires a clear physical meaning: the diffusion-relaxation time (along the coordinate φ) is the squared change of the coordinate, divided by the effective diffusion coefficient.

A polymer chain, having a large number of degrees of freedom, is characterized by both fast and slow variables. Obviously, to obtain a good estimate of the relaxation time it is necessary to choose φ to be as slow a variable as possible. (We emphasize that even a small addition of a fast variable to the function φ can immediately spoil the estimate, i.e., decrease substantially the value of $t[\varphi]$.) The function φ must essentially have then discontinuities on the forbidden surface Σ_Ω, for in the absence of such discontinuities the estimate (2.16) becomes directly related also to the problem of phantom-chain relaxation, and can therefore not discern the "topological slowing down" of the relaxation process.

The simplest function with discontinuities on the forbidden surface can be obtained as a generalization of the known Gauss topological invariant[7]

$$\varphi(\Gamma)=\int_0^1 dx\int_0^1 dy\, Q(x,y)\left[\frac{\partial\mathbf{r}(x)}{\partial x}\,\frac{\partial\mathbf{r}(y)}{\partial y}\right]$$

$$\times(\mathbf{r}(x)-\mathbf{r}(y))\,|\mathbf{r}(x)-\mathbf{r}(y)|^{-3}, \quad (2.19)$$

where $\mathbf{r}(x)$, $0\leqslant x\leqslant 1$, is a vector function that specifies the polymer-chain trajectory; x (or y) is a coordinate along the trajectory, such that the nth bead corresponds to $x_n = n/N$ (see Fig. 1), i.e.,

$$\mathbf{r}_n\equiv\mathbf{r}(n/N). \quad (2.20)$$

It is convenient to choose the function $Q(x,y)$ in factorized form:

$$Q(x,y)=q_1(x)q_2(y), \quad (2.21)$$

where $q_1(x)$ and $q_2(x)$ differ from zero only inside the respective intervals $(0, 1/2)$ and $(1/2, 1)$. The specific form of these functions is immaterial in what follows; we put for the sake of argument

$$\begin{aligned} &q_1(x)=x(1-2x), \quad 0\leqslant x\leqslant {}^1/_2;\\ &q_2(y)=(1-y)(2y-1), \quad {}^1/_2\leqslant y\leqslant 1. \end{aligned} \quad (2.22)$$

So defined, the function $\varphi(\Gamma)$ is approximately equal to the number of turns of one half of the chain around the other.

The functional $t[\varphi]$ with the "trial" function (2.19) can be calculated directly, without any approximations. The results of the corresponding (most laborious) calculations for both models (Rouse and Zimm) yields little: the value of $t[\varphi]$ turns out to be smaller than the longest relaxation time in the absence of topological constraints. A new, modified trial function φ^M, defined in Sec. 4, is such that direct calculation of the functional $t[\varphi^M]$ is already impossible. In Sec. 5 $t[\varphi^M]$ is calculated by the more effective scaling method. The gist of this method, which makes it possible to find $t[\varphi]$ apart from a numerical coefficient (in the limit as $N\to\infty$) is described in the next section. By way of illustration, the scaling method is used in this section to calculate $t[\varphi]$ with the trial function (2.19).

3. THE SCALING METHOD

The scaling approach is based on an investigation of the laws that govern the conversion of the quantities of interest to us by renormalization transformations. For the system considered, these transformations correspond to the procedure of thickening the links of a polymer chain, such that g links of the initial chain are joined to form one renormalized link (the initial-chain section corresponding to the renormalized link will hereafter be called a blob). Thus, the initial trajectory of the polymer chain $\Gamma\equiv\{\mathbf{r}(x),\ 0\leqslant x\leqslant 1\}$ goes over into a renormalized trajectory $\Gamma\equiv\{\mathbf{r}'(x),\ 0\leqslant x\leqslant 1\}$, which is a broken line with vertices at the points

$$\mathbf{r}_n'\equiv\mathbf{r}'(n/N')=\mathbf{r}(ng/N), \qquad n=0,1,\ldots,N', \quad (3.1)$$

where N' is the number of links in the renormalized chain (Fig. 2). The link dimension a is increased by renormalization[3]:

$$N\to N'=N/g, \quad a\to a'=g^{1/2}a. \quad (3.2)$$

Obviously, the macroscopic equilibrium properties of the initial and renormalized chains coincide: at the same time, the topological properties of these chains are, of course, different. It is natural nevertheless to expect a sufficiently simple common connection between their topological characteristics. As shown below, one can obtain definite recurrence relations (i.e., in fact renormalization-group equations) for the dimensionless functions in terms of which $t[\varphi]$ is expressed. Analysis of these equations will reveal the asymptotic behavior of these functions (and hence of $t[\varphi]$) as $N\to\infty$.

Let us explain these basic principles using as an example the calculation of the function

$$s(N)\equiv\sigma_\varphi^2\equiv\langle\varphi^2\rangle, \quad (3.3)$$

where $\varphi=\varphi(\Gamma)$ is defined by Eq. (2.19). It is easy to verify that the function $s(N)$ is in itself dimensionless in the sense that it does not depend on the dimensional properties of the polymer chain (such as a or D_0, i.e., it depends only on the number N of the links.

Let $\varphi'=\varphi(\Gamma')$ be the value of the trial function for the renormalized (smoothened) trajectory. We express the connection between φ and φ' in the form

$$\varphi=\varphi'+\tilde{\varphi}, \quad (3.4)$$

where $\tilde{\varphi}$ is defined by (3.4). Obviously, the main contribution to $\tilde{\varphi}$ is made by the integration [see (2.19)] over those pairs of blobs that approached each other to a distance of the order of their size $a'=g^{1/2}a$; integration over trajectory seg-

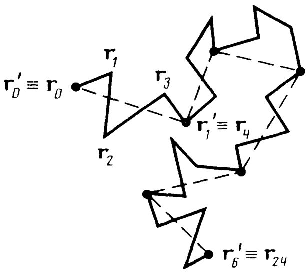

FIG. 2. Trajectories of a chain of $N=24$ links (solid line) and of a renormalized chain of $N'=N/g=6$ links (dashed line).

ments that are far from one another is not very sensitive to the renormalization procedure (smoothening of the trajectory) and makes no noticeable contribution to $\tilde{\varphi}$. (This and the similar statements that follow can, of course be rigorously proven.) Thus, apart from inessential corrections,

$$\tilde{\varphi}=\sum_{\nu=1}^{M}\tilde{\varphi}_\nu, \tag{3.5}$$

where the subscript ν numbers the "contacting" (i.e., approaching in space) pair of blobs. By virtue of (2.22), the blobs in each pair should belong to different halves of the chain. (Note that $\tilde{\varphi}$ can be roughly regarded as the number of turns of each half of the chain around the other, a number lost upon renormalization. It is quite obvious that these additional turns can appear only at contacts between chain sections belonging to different halves. Consequently $\tilde{\varphi}_\nu$ is the number of turns of one of the contacting blobs around the other.)

The quantities $\tilde{\varphi}_\nu$ are determined by the (local) conformations of the contacting sections of the chain, and are therefore independent. Consequently,

$$\langle\varphi^2\rangle_0=\langle\varphi'^2\rangle_1+\left\langle\varphi'\sum_\nu\langle\tilde{\varphi}_\nu\rangle_\phi\right\rangle_1$$
$$+\left\langle\sum_{\nu\neq\mu}\langle\tilde{\varphi}_\nu\rangle_\phi\langle\tilde{\varphi}_\mu\rangle_\phi\right\rangle_1+\left\langle\sum_\nu\langle\tilde{\varphi}_\nu^2\rangle_\phi\right\rangle_1, \tag{3.6}$$

where the angle brackets with zero and unity subscripts denote averaging over the trajectories of the initial and renormalized chains, respectively, while the subscript ϕ denotes averaging over (unrenormalized) links that were crossed out in the renormalization (the averaging is carried out for a fixed renormalized trajectory). Obviously (for $g\gg 1$),

$$\langle\varphi^2\rangle_0=s(N),\quad \langle\varphi'^2\rangle_1=s(N/g),\quad \langle\tilde{\varphi}_\nu^2\rangle_\phi=\text{const}\,s(g). \tag{3.7}$$

It is also easy to show that $\langle\tilde{\varphi}_\nu\rangle_\phi$ is of the order of unity and is independent of g (for $g\gg 1$). Consequently, the second and third terms in the right-hand side of (3.6) depend (for $g\gg 1$) only on the number N/g of links in the renormalized chain:

$$\left\langle\varphi'\sum_\nu\langle\tilde{\varphi}_\nu\rangle_\phi\right\rangle_1+\left\langle\sum_{\nu\neq\mu}\langle\tilde{\varphi}_\nu\rangle_\phi\langle\tilde{\varphi}_\mu\rangle_\phi\right\rangle_1=f(N/g). \tag{3.8}$$

Substituting (3.7) and (3.8) in (3.6) we get

$$s(N)=s(N/g)+\text{const}\langle M\rangle_1 s(g)+f(N/g),\quad g\gg1,$$

where M is the number of terms in the sum over ν, i.e., the number of contacts between the halves of the renormalized chain. Since the chain is Gaussian, we have

$$\langle M\rangle_1=\text{const}(N/g)^{1/2}. \tag{3.9}$$

Thus,

$$s(N)=s(N/g)+\text{const}(N/g)^{1/2}s(g)+f(N/g),\quad g\gg1. \tag{3.10}$$

The recurrence equation (3.10) contains an additional unknown function f, which can be eliminated by differentiating (3.10) with respect g for a fixed N/g. As a result we obtain

$$N^{1/2}ds(N)/dN=\text{const}\,g^{1/2}ds(g)/dg,\quad g\gg1,\quad N\gg1. \tag{3.11}$$

Consequently

$$N^{1/2}ds(N)/dN=\text{const},\quad N\gg1,$$

i.e.,

$$s(N)=\text{const}\,N^{1/2},\quad N\gg1. \tag{3.12}$$

We proceed now to calculate the effective diffusion coefficient D_φ for the Rouse model. Substituting (1.5) in (2.18), we write[2)]

$$D_\varphi=(D_0/N^2a^2)\,w_R, \tag{3.13}$$

where

$$w_R=N^2a^2\left\langle\sum_{n,\alpha}(\partial\varphi/\partial r_{\alpha n})^2\right\rangle \tag{3.14}$$

is a dimensionless function: $w_R = w_R(N)$. The problem consists thus of investigating the dependence of w_R on N.

Differentiating the function φ [see (219)] with respect to the coordinates of the nth bead, we get

$$\frac{\partial\varphi}{\partial\mathbf{r}_n}=N^{-1}\frac{\partial q_\sigma(x)}{\partial x}\mathbf{H}_n+q_\sigma(x)\left[\frac{\partial\mathbf{r}_n}{\partial n}\mathbf{E}_n\right], \tag{3.15}$$

where

$$\sigma=\sigma(n)=\begin{cases}1, & n<N/2\\ 2, & n>N/2\end{cases},$$
$$x=x_n\equiv n/N,\quad \partial\mathbf{r}_n/\partial n\equiv(\mathbf{r}_{n+1}-\mathbf{r}_{n-1})/2,$$
$$\mathbf{H}_n=\mathbf{H}^{(\sigma)}(\mathbf{r}_n),\quad \mathbf{E}_n=\text{rot}\,\mathbf{H}^{(\sigma)}(\mathbf{r}_n).$$

The field $\mathbf{H}^{(\sigma)}(\mathbf{r})$ induced by one half of the chain at the other (by the second at the first for $\sigma = 1$ and by the first at the second for $\sigma = 2$) is defined by the equation

$$\mathbf{H}^{(\sigma)}(\mathbf{r})=\int_0^1\frac{dy\,q_{3-\sigma}(y)}{|\mathbf{r}(y)-\mathbf{r}|^3}\left[\frac{\partial\mathbf{r}(y)}{\partial y}(\mathbf{r}(y)-\mathbf{r})\right]. \tag{3.16}$$

Substituting (3.15) in (3.14), we obtain (we omit the subscript R in the intermediate expressions)

$$w(N)=u(N)+v(N), \tag{3.17}$$

where

$$u(N)=a^2\left\langle\sum_n\left(\frac{\partial q_\sigma}{\partial x}\right)^2\mathbf{H}_n^2\right\rangle, \tag{3.18}$$

$$v(N)=a^2N^2\left\langle\sum_n q_\sigma^2(x_n)\left[\frac{\partial\mathbf{r}_n}{\partial n}\mathbf{E}_n\right]^2\right\rangle$$
$$=4(a^2N)^2\left\langle\sum_n q_\sigma^2(x_n)\mathbf{E}_n^2\right\rangle. \tag{3.19}$$

The cross terms produced when the right-hand side of (3.15) is squared vanish after averaging, since the direction of the random vector $\partial\mathbf{r}_n/\partial n$ is independent of the direction of the vector $\mathbf{H}(\mathbf{r}_n)$ or $\nabla\times\mathbf{H}(\mathbf{r}_n)$; for the same reason, the relation

$$\left\langle\left[\frac{\partial\mathbf{r}_n}{\partial n}\text{rot}\,\mathbf{H}_n\right]^2\right\rangle=\frac{2}{3}\left\langle\left(\frac{\partial\mathbf{r}_n}{\partial n}\right)^2\right\rangle\langle|\text{rot}\,\mathbf{H}_n|^2\rangle$$
$$=4a^2\langle|\text{rot}\,\mathbf{H}_n|^2\rangle,$$

used in (3.19) is valid.

We consider now the functions $u(N)$ and $v(N)$ in turn. We introduce the quantity u' for the renormalized chain

$$u'=a'^2\left\langle\sum_{n'}\left(\frac{\partial q_\sigma}{\partial x}\right)^2\mathbf{H}_{n'}'^2\right\rangle,\qquad x\equiv\frac{n'}{N'},\tag{3.20}$$

where $\mathbf{H}_{n'}'\equiv\mathbf{H}'(\mathbf{r}_{n'}')$ is given by Eq. (3.16) in which the trajectory $r(y)$ should be replaced by $\mathbf{r}'(y)$. If all the links of one half of the renormalized chain are far enough from all the links of the other half (i.e., at a distance than a'), replacement of $\mathbf{r}(y)$ by $\mathbf{r}'(y)$ hardly affects the value of the integral in (3.16), i.e., in this case we have

$$\mathbf{H}_{n'}'\equiv\mathbf{H}'(\mathbf{r}_{n'}')=\mathbf{H}(\mathbf{r}_{n'}')\equiv\mathbf{H}(\mathbf{r}_{n'g}).\tag{3.21}$$

In addition, under this condition the vector $\mathbf{H}_{n'}'$ changes little on going from n' to $n'+1$, so that the sum over n' can be replaced by an integral. Substituting (3.21) in (3.20) and changing to integration over $x=n'/N'$, we get

$$u'=(a'^2N')\left\langle\int_0^1 dx\left(\frac{\partial q_\sigma}{\partial x}\right)^2(\mathbf{H}^{(\sigma)})^2(\mathbf{r}(x))\right\rangle.\tag{3.22}$$

Similarly, transforming (3.18) under the same conditions, we write

$$u=(a^2N)\left\langle\int_0^1 dx\left(\frac{\partial q_\sigma}{\partial x}\right)^2(\mathbf{H}^{(\sigma)})^2(\mathbf{r}(x))\right\rangle.\tag{3.23}$$

Comparing (3.22) with (3.23) and taking (3.2) into account, we verify that $u\approx u'$ in the absence of contacts between the chain halves. In the general case

$$u=u'+\langle\tilde{u}\rangle_1,\tag{3.24}$$

where u is the contribution due to the contacts between blobs belonging to different halves of the chain, we have

$$\tilde{u}=\sum_\nu\tilde{u}_\nu.\tag{3.25}$$

The contribution from one contact is equal to

$$\tilde{u}_\nu=a^2\left\langle\sum_{n|\nu}\left(\frac{\partial q}{\partial x}\right)^2\mathbf{H}_n{}^2\right\rangle_\varphi,\tag{3.26}$$

where the summation is over all (nonrenormalized) links n belonging to the νth contacting blob. Comparing (3.26) and (3.18) and recognizing that $(\partial q/\partial x)^2\sim 1$, we arrive at the relation

$$a^2\left\langle\sum_{n|\nu}\left(\frac{\partial q_\sigma}{\partial x}\right)^2\mathbf{H}_n{}^2\right\rangle_\varphi=\mathrm{const}\,u(g),\qquad g\gg 1.\tag{3.27}$$

Substituting (3.25)–(3.27) in (3.24) and averaging over the trajectories of the renormalized chain, we get

$$u=u'+\mathrm{const}\,u(g)\langle M\rangle_1\tag{3.28}$$

[$\langle M\rangle_1$ is the average number of terms in the sum over ν, see (3.9)]. Recognizing that

$$u=u(N),\qquad u'=u(N/g),$$

we obtain the following recurrence equation:

$$u(N)=u(N/g)+\mathrm{const}(N/g)^{1/2}u(g),\qquad g\gg 1.\tag{3.29}$$

The asymptotic solution of (3.29) is [cf. (3.10)–(3.12)]

$$u(N)=\mathrm{const}\,N^{1/2},\qquad N\gg 1.\tag{3.30}$$

The value of $v(N)$ can be calculated in exactly the same manner. First, assuming the absence of contacts, we obtain the renormalization law for the "regular" part. The result is:

$$v=gv'.$$

Adding the "irregular" term due to contacts between the blobs, we write

$$v=gv'+\langle\tilde{v}\rangle_1.\tag{3.31}$$

Calculating the value of $\langle v\rangle$ by analogy with $\langle u\rangle_1$, we obtain the relation

$$v(N)=gv(N/g)+\mathrm{const}(N/g)^{1/2}v(g),\qquad g\gg 1.\tag{3.32}$$

The asymptotic solution of Eq. (3.52) is

$$v(N)=\mathrm{const}\,N,\qquad N\gg 1.\tag{3.33}$$

Substituting (3.33), (3.30), (3.17), and (3.12) in (2.16), we get ultimately

$$t[\varphi]=\mathrm{const}(a^2/D_0)N^{3/2},\qquad N\gg 1.\tag{3.34}$$

The lower bound of the maximum relaxation time for the Zimm model can be calculated in exactly the same way as for the Rouse model. The result of the scaling calculations for the Zimm model is the following: the main contribution to D_φ is made as before by the term due to the curl of the field $\mathbf{H}$ [see (3.1)]; in the limit $N\gg 1$ the difference from the Rouse model reduces only to an insignificant renormalization of the unrenormalizd diffusion coefficient:

$$D_0\to D_0^*=D_0+\mathrm{const}\,T/\eta_s a,\qquad \mathrm{const}>0.\tag{3.35}$$

The value of $t[\varphi]$ for the Zimm model is thus determined by Eq. (3.34) with D_0 replaced by D_0^*.

We emphasize once more that the estimate (3.34) does not reveal a slowing down of the conformational relaxation due to topological constraints. The lower value of $t[\varphi]$ is obviously due to the fact that the contribution of the second term, v, to the value of w turned out to be too large. The high value of v, in turn, is obviously to the "incorrect" law (3.31) of renormalization of this quantity, in contrast to the "correct" law (3.24) for the quantity u (or the law (34) for φ). The posited incorrect behavior is supported by the following consideration. Consider the right-hand sides of the recurrence equations (3.10), (3.29), and (3.32). In all cases the first terms correspond to the contribution from the spatially remote sections of the chain, whereas the second terms are due to the contacts (between the two halves of the chain). Comparison of these terms shows that the main contributions to s and u are indeed made by the contacts; at the same time, the quantity v is due mainly to the contribution from the spatially remote sections of the chain. It is natural to assume that this contribution (and hence the value of v) can be decreased by appropriately modifying (smoothening) the trial function.

4. MODIFIED TRIAL FUNCTION

Thus, the trial function must be altered so as to ensure a correct renormalization of the regular contribution to v (i.e., the contribution from the remote sections of the chain). The simplest way is to replace the true trajectory $r(x)$ of the chain by the smoothened one $R(x)$ (the smoothing method will be considered below):

$$\varphi^M[\mathbf{r}]\equiv\varphi[\mathbf{R}]=\int Q(x,y)\,\frac{[d\mathbf{R}(x)\,d\mathbf{R}(y)]\,(\mathbf{R}(x)-\mathbf{R}(y))}{|\mathbf{R}(x)-\mathbf{R}(y)|^3}. \tag{4.1}$$

The smoothing procedure must meet the following two conditions: 1) the fact that self-intersection of the true trajectories is forbidden should automatically apply also to the smoothened trajectories; 2) the smoothening radius should not be changed (noticeably) by the renormalization (far from the contacts). It follows directly from these conditions that the smoothening radius should be variable, i.e., dependent on x.

That the first condition is necessary is obvious. Let us show that the second condition ensures a correct renormalization of the regular part of D_φ. The radius vector $\mathbf{R}(x_0)$ of the smoothened trajectory is determined by averaging over the section $\mathbf{r}(x)$ of the unrenormalized trajectory of the chain, in the vicinity of x_0: $|x-x_0|\lesssim\rho$, where ρ is the smoothening radius. Following the renormalization ($N\to N'=N/g$), the number of links that determine the vector $\mathbf{R}(x_0)$ should decrease by g times: $\Delta n\sim\rho N\to\Delta n'\sim\rho N'$, since the smoothening radius ρ remains unchanged. Consequently, the derivative $\partial\mathbf{R}(x_0)/\partial\mathbf{r}_n$ should increase by a factor g. The derivative $\partial\varphi/\partial\mathbf{r}_0$ should increase by the same factor:

$$\partial\varphi/\partial\mathbf{r}_n\to\partial\varphi/\partial\mathbf{r}_{n'}'=g\partial\varphi/\partial\mathbf{r}_n. \tag{4.2}$$

In addition, obviously,

$$\sum_n\to\sum_{n'}\approx g^{-1}\sum_n. \tag{4.3}$$

Substituting (4.2) and (4.3) in (3.14) and taking (3.2) into account, we obtain (for the regular part)

$$w_R\to w_R'=w_R,$$

i.e., the regular part of w_R is not altered by the renormalization. Taking footnote 2 into account, we conclude that the regular part of the effective diffusion coefficient for the Rouse model is invariant to renormalization transformations.

The effective diffusion coefficient for the Zimm model is given by [see (1.6) and (2.18)]

$$D_\varphi=(D_0/N^2a^2)\,w_R+(T/8\pi\eta_sN^{3/2}a)\,w_H, \tag{4.4}$$

where

$$w_h=a^3N^{3/2}\left\langle\sum_{n\alpha,m\beta}\frac{1}{r}\left(\delta_{\alpha\beta}+\frac{r_\alpha r_\beta}{r^2}\right)\frac{\partial\varphi}{\partial r_{\alpha n}}\frac{\partial\varphi}{\partial r_{\beta m}}\right\rangle,\qquad\mathbf{r}\equiv\mathbf{r}_n-\mathbf{r}_m \tag{4.5}$$

(w_k is a dimensionless function that depends only on N). We emphasize that both coefficients (preceding w_R and w_h) are quadratic in the renormalization transformations. Substituting (4.2) in (4.5) and recognizing that

$$\sum_{n,m}\to\sum_{n',m'}\approx g^{-2}\sum_{n,m}, \tag{4.6}$$

we obtain $w_H\to w_H'=w_H$, whence follows an equally correct law for the renormalization of the effective diffusion coefficient D_φ for the Zimm model.

We describe now the smoothening procedure. Let

$$\mathbf{R}(x,\rho)\equiv\int g_\rho(x'-x)\,\mathbf{r}(x')\,dx',$$

$$g_\rho(x)=\pi^{-1/2}\rho^{-1}\exp(-x^2/\rho^2). \tag{4.7}$$

The smoothening radius ρ depends on x: $\rho=\rho(x)$; we define the function $\rho(x)$ implicitly as the (only) solution of the equation

$$\int_0^\rho d\rho'\int_0^1 dy\,\frac{Q(x,y)}{|\mathbf{R}(x,\rho')-\mathbf{R}(y,\rho')|^4}=\varepsilon(Na^2)^{-2}, \tag{4.8}$$

where ε is a fixed number assumed below to be small. Finally, we determine the smoothened trajectory:

$$\mathbf{R}(x)\equiv\mathbf{R}(x,\,\rho(x)). \tag{4.9}$$

It is easy to show that the formulated procedure meets the conditions (1) and (2) above, and furthermore ensures, in a certain sense, the maximum possible smoothening of the polymer-chain trajectory.

5. FINAL RESULTS

We proceed now to a calculation of $t[\varphi^M]$. It is easy to show that the value of $s=s(N)$ hardly changes when φ is replaced by φ^M; in particular, all the renormalization relations obtained in Sec. 3 remain in force for this quantity. Thus,

$$s=\mathrm{const}\,N^{1/2},\quad N\gg1. \tag{5.1}$$

We consider now the function $w_R(N)$ that characterizes the effective diffusion coefficient for the Rouse model. By analogy with Eqs. (3.17)–(3.19) we write (we omit the subscript R for brevity)

$$w(N)=u(N)+v(N), \tag{5.2}$$

$$u(N)\approx a^2\left\langle\sum_n\left(\frac{\partial q_\sigma}{\partial x}\right)^2\mathbf{H}_n^2\right\rangle, \tag{5.3}$$

$$v(N)\approx a^2\left\langle\sum_n q_\sigma^2(x)\left[\frac{\partial\mathbf{R}}{\partial x}\mathbf{E}_n\right]^2\right\rangle, \tag{5.4}$$

where

$$x=n/N,\quad\mathbf{H}_n=\mathbf{H}^{(\sigma)}(\mathbf{R}(x)),\quad\mathbf{E}_n=\mathrm{rot}\,\mathbf{H}^{(\sigma)}(\mathbf{R}(x)),$$

and the field $\mathbf{H}^{(\sigma)}(\mathbf{R})$ is given by [cf. (3.16)]

$$\mathbf{H}^{(\sigma)}(\mathbf{R})=\int_0^1 dy\,q_{3-\sigma}(y)\left[\frac{\partial\mathbf{R}(y)}{\partial y}(\mathbf{R}(y)-\mathbf{R})\right]|\mathbf{R}(y)-\mathbf{R}|^{-3}. \tag{5.5}$$

Relations (5.3) and (5.4), in contrast to (3.18) and (3.19), are approximate: they are valid provided that the fields $\mathbf{H}(\mathbf{r})$ and $\nabla\times\mathbf{H}(\mathbf{r})$ change little within the limits of the trajectory-smoothening radius. It is easy to verify that the described smoothening procedure certainly ensures satisfaction of this condition if the parameter ε [see (4.8)] is small enough. In addition, it is easy to show that smoothening does not lead to any noticeably change of the values of $\mathbf{H}_n$ (in other words, calculations using (3.16) and (5.5) yield practically the same results). It follows hence directly that $u(N)$

is not sensitive to smoothening, since the right-hand sides of (3.18) and (5.3) practically coincide. Thus, the previous result (3.30) remains in force:

$$u(N)=\mathrm{const}\,N^{1/2},\quad N\gg 1. \tag{5.6}$$

The quantity $v = v(N)$, on the contrary, is most sensitive to smoothening, since $(\partial\mathbf{R}/\partial x)^2$ (for the smoothened trajectory) is almost everywhere considerably smaller than $(\partial\mathbf{r}/\partial x)^2$ (for the initial trajectory). The law governing the renormalization of v can be obtained with the aid of the reasoning of Sec. 3. As expected, this law turns out to be valid:

$$v=v'+\langle\tilde{v}\rangle_1, \tag{5.7}$$

where $v = v(N)$, $v' = v(N/g)$, and the term $\langle\tilde{v}\rangle_1$ is due to the contacts. If it is assumed that the field $\nabla\times\mathbf{H}$ in the region of the contact is the same as if it were created only by a contacting blob, i.e., neglecting the contribution to $\nabla\times\mathbf{H}$ from the remote sections of the chain, the contribution from each contact should be approximately the same as that made by a chain consisting of g links (i.e., equal to $v(g)$)a. Multiplying by the average number of contacts, we get

$$\langle\tilde{v}\rangle_1=\mathrm{const}\,(N/g)^{1/2}v(g). \tag{5.8}$$

Equation (3.32) was derived in fact assuming a relation of the form (5.8) to be valid. Actually, however, (5.8) is not exact,[3)] since the contribution to $\nabla\times\mathbf{H}$ [more accurately, to $(\nabla\times\mathbf{H})^2$] from the remote sections of the chain is not small. To verify this, we write down the explicit expression for the field $\mathbf{E}(\mathbf{r})\equiv\nabla\times\mathbf{H}(\mathbf{r})$. Using (5.5), we get

$$\mathbf{E}(\mathbf{r})=\int_0^1 dy\,\frac{\partial q_{3-\sigma}(y)}{\partial y}\,(\mathbf{r}-\mathbf{R}(y))\,|\mathbf{r}-\mathbf{R}(y)|^{-3}. \tag{5.9}$$

Simple analysis of Eq. (5.9) shows that the contribution from one blob (of g links) is of the order of

$$\Delta E_g\sim\Delta y/R_g^2=(g/N)/a^2g=1/Na^2,$$

and the contribution from the remote sections of the chain is

$$\Delta E_N\sim 1/R_N^2=1/Na^2,$$

i.e., is of the same order.

Exact calculation using (5.9) shows that the remote sections actually make a logarithmic contribution:

$$\langle\mathbf{E}_{ex}^2\rangle=\mathrm{const}(Na^2)^{-2}\ln(N/g), \tag{5.10}$$

where the subscript "ex" means that the field $\mathbf{E}_{\mathrm{ex}}$ is produced only by those sections of the chain which do not belong to the selected (contacting) blob. It is thus necessary to write in place of (5.8)

$$\langle\tilde{v}\rangle_1=\mathrm{const}(N/g)^{1/2}\{v(g)+v_{ex}\}. \tag{5.11}$$

Here

$$v_{ex}=a^2N^2\left\langle{\sum}'q_\sigma^2(x)\left[\frac{\partial\mathbf{R}}{\partial n}\mathbf{E}_{ex}\right]^2\right\rangle,\qquad x=\frac{n}{N}, \tag{5.12}$$

where the primed sum denotes summation over all the links n belonging to one of the contacting blobs. Recognizing that the field $\mathbf{E}_{\mathrm{ex}}$ and the blob conformation should be practically independent, we can rewrite (5.12) in the form

$$v_{ex}={}^2/_3a^2N^2\langle\mathbf{E}_{ex}^2\rangle\left\langle{\sum}'q_\sigma^2(x)\,(\partial\mathbf{R}/\partial n)^2\right\rangle$$
$$=\mathrm{const}\ln(N/q)\,\Phi(g), \tag{5.13}$$

where

$$\Phi(g)\equiv a^{-2}\left\langle{\sum}'(\partial\mathbf{R}/\partial n)^2\right\rangle \tag{5.14}$$

(it is taken into account in (5.13) that $q_\sigma(x)\sim 1$).

To calculate the function $\Phi(g)$ we use again the scaling method. As a result we arrive at the following recurrence relation for this function:

$$\Phi(N)=\Phi(N/g)+\mathrm{const}(N/g)^{1/2}\Phi(g),\quad g\gg 1. \tag{5.15}$$

The solution of (5.15) is of the form

$$\Phi(N)=\mathrm{const}\,N^{1/2},\quad N\gg 1. \tag{5.16}$$

Substituting (5.16) in (5.13), (5.13) in (5.11), and (5.11) in (5.7) we obtain a recurrence relation for v:

$$v(N)=v(N/g)+\mathrm{const}(N/g)^{1/2}v(g)$$
$$+\mathrm{const}(N/g)^{1/2}g^{1/2}\ln(N/g),\ g\gg 1, \tag{5.17}$$

whose solution is

$$v(N)=\mathrm{const}\,N^{1/2}\ln N,\qquad N\gg 1. \tag{5.18}$$

Using (5.18), (5.6), (5.2), (5.1), (3.13), and (2.16) we obtain ultimately the value of $t[\varphi^M]$ for the Rouse model:

$$t_R[\varphi^M]=\mathrm{const}(a^2/D_0)N^2/\ln N,\quad N\gg 1. \tag{5.19}$$

Thus [cf. (5.19) and (3.34)], the use of a modified trial function has led to a substantial improvement of the estimate of the maximum relaxation time. For the Rouse model, however, the estimate (5.19) lacks substance.

We obtain now $t[\varphi^M]$ for the Zimm model. This calls for calculation of w_h [see (4.5)]. By analogy with (5.5), we write (omitting the subscript h)

$$w(N)=u(N)+v(N), \tag{5.20}$$

where, as before, $u(N)\propto\mathbf{H}^2$ while $v(N)\propto(\nabla\times\mathbf{H})^2$. (For brevity, we leave out the explicit expressions for u and v.) Using the scaling method, we obtain the following recurrence equation for the function $u(N)$:

$$u(N)=u(N/g)+\mathrm{const}\,u(g),\quad g\gg 1, \tag{5.21}$$

the solution of which (with logarithmic accuracy) is:

$$u(N)=\mathrm{const}\ln N,\quad N\gg 1. \tag{5.22}$$

Using the same method as in the analysis of the Rouse method, we can obtain for the $v(N)$ the equation

$$v(N)=v(N/g)+\mathrm{const}(N/g)^{1/2}\{(g/N)^{1/2}v(g)+v_{ex}\}, \tag{5.23}$$

where v_{ex} has the same meaning as before (i.e., v_{ex} is due to the field E_{ex} produced by chain sections that are far from the contact region).[4)] After certain transformations we obtain [cf. (5.13)]

$$v_{ex}=\frac{1}{3}N^{3/2}a^3\langle\mathbf{E}_{ex}^2\rangle\left\langle\sum_{n,m}{}'q_\sigma\left(\frac{n}{N}\right)q_\sigma\left(\frac{m}{N}\right)\frac{1}{r}$$

$$\times\left\{3\frac{\partial\mathbf{R}}{\partial n}\frac{\partial\mathbf{R}}{\partial m}-\frac{1}{r^2}\left(\mathbf{r}\frac{\partial\mathbf{R}}{\partial n}\right)\left(\mathbf{r}\frac{\partial\mathbf{R}}{\partial m}\right)\right\}\right\rangle, \qquad \mathbf{r}=\mathbf{r}_n-\mathbf{r}_m. \tag{5.24}$$

Using (5.10), we transform (5.24) into

$$v_{ex}=\mathrm{const}(g/N)^{1/2}\ln(N/g)\Phi(g), \tag{5.25}$$

where

$$\tilde{\Phi}(g)=(g^{1/2}a)^{-1}\left\langle\sum_{n,m}{}'\frac{1}{r}\left\{3\frac{\partial\mathbf{R}}{\partial n}\frac{\partial\mathbf{R}}{\partial m}-\frac{1}{r^2}\left(\mathbf{r}\frac{\partial\mathbf{R}}{\partial n}\right)\left(\mathbf{r}\frac{\partial\mathbf{R}}{\partial m}\right)\right\}\right\rangle. \tag{5.26}$$

The function $\tilde{\Phi}(g)$ satisfies the following recurrence equation:

$$\tilde{\Phi}(N)=\tilde{\Phi}(N/g)+\mathrm{const}\,\tilde{\Phi}(g), \quad g\gg1, \tag{5.27}$$

whose solution is

$$\tilde{\Phi}(N)=\mathrm{const}\ln N, \quad N\gg1. \tag{5.28}$$

Substituting (5.28) and (5.25) in (5.23) we obtain the equation

$$v(N)=v(N/g)+\mathrm{const}\,v(g)+\mathrm{const}\ln(N/g)\ln g, \quad g\gg1. \tag{5.29}$$

Solving this equation with logarithmic accuracy, we get

$$v(N)=\mathrm{const}(\ln N)^2. \tag{5.30}$$

Using (5.30), (5.22), (5.20), (5.1), and (4.4), we obtain ultimately the value of $t[\varphi^M]$ for the Zimm model:

$$t_h[\varphi^M]=\mathrm{const}(\eta_s a^3/T)N^2(\ln N)^{-2}, \quad N\gg1. \tag{5.31}$$

Comparing (5.31) with (1.8) we conclude that introduction of topological constraints increases significantly the relaxation time of a Zimm chain (at $N\gg1$), by at least a factor $N^{1/2}(\ln N)^{-2}$.

6. CONCLUSION

Thus, it is shown in this paper that the forbiddenness of self-intersection, for a Gaussian chain with hydrodynamic interaction, increases noticeably the dynamic exponent [see (1.2)] from $z = 3/2$ to a certain $z\geqslant2$. It is natural to ask: should the true dynamic exponent (for a chain with topological constraints) be close to the obtained lower bound ($z = 2$) or not? The answer should be apparently in the negative for the following reason. In the analysis, the chain was arbitrarily divided into two equal halves, and only intersection of one half with the other was forbidden. In other words, the result (5.31) remains in force even of each half of the chain is allowed to be self-intersecting. The result for the maximum relaxation time likewise remains unchanged if one considers not two halves of one chain but two independent chains, initially entangled with one another (in which case the relaxation time is the disentanglement time). It is known that the topological state of two (closed) chains, each of which can intersect itself but not another chain, is completely determined by the value of the Gauss invariant. On the other hand, the number of topological states of two (closed) chains, which can neither intersect one another nor be individually nonintersecting, is immeasurably larger[5]: the Gauss invariant is very weak in this case.[7] It is therefore reasonable to assume that the disentanglement time of two (open) chains should be much larger in the second case (when self-intersections are forbidden) than in the first (when self-intersections are possible). It is thus natural to expect the dynamic exponent z to be substantially larger than 2. This accords with the result $z = 3$ obtained in Ref. 5 on the basis of a semiphenomenological model.

[1] More accurately, it is first necessary to regard Σ_Ω as a forbidden layer of thickness δ near the forbidden surface, and take the limit $\delta\to0$ only at the very end.

[2] Note that the coefficient preceding w_R in (3.13) is invariant to renormalization transformations (if the natural transformation law $D_0\to D'_0 = D_0/g$) is assumed for the diffusion coefficient of the link).

[3] The corresponding inaccuracy in Eq. (3.32) pertains to the second nonprincipal term, and therefore does not affect the final result (3.33).

[4] An additional factor $(g/N)^{1/2}$ appears in (5.23) because the coefficients of w_R and w_h in (3.14) and (4.4) contain different powers of N.

[5] The problem of the effective classification of these states remains unsolved to this day.

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