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Reaction rate study of a statistical disentangling model

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Abstract. To illustrate the plausibility and difficulties involved in problems that require a modification of the *winding number* notion, we study the statistical model of a long chain entangling with a straight rod, and calculate the statistical rate for the chain to become disentangled using the reaction rate point of view. For the measure of entanglement the usual distinction between the clockwise and the anti-clockwise winding numbers is no longer applicable because, as far as the mutual snaring is concerned, only the sum of these two numbers is relevant. We perform the calculations for the equilibrium case with a small friction and the static case with a large friction. Our results are consistent with the prediction of the existing phenomenological 'tube' model for polymers.

1. Introduction

The concept of the winding number is widely used in the physical and mathematical problems. For instance, it is related to the Biot-Savart law of electromagnetism, and can be easily calculated as

$$n_1 = \int \mathrm{d}s_1 \int \mathrm{d}s_2 \frac{(\boldsymbol{r}_1 - \boldsymbol{r}_2) \cdot (\boldsymbol{r}_1' \times \boldsymbol{r}_2')}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|^3} \tag{1}$$

where $\boldsymbol{r}_1$, $\boldsymbol{r}_2$ are two arbitrary loops and $\boldsymbol{r}' \equiv \mathrm{d}\boldsymbol{r}/\mathrm{d}s$ with s being the arc-length parameter along the loop. Equation (1) contains both the clockwise and the anticlockwise windings (denoted by n_c and n_a separately), and n_1 is equal to $n_c - n_a$. This expression is independent of the detailed shapes of the loops [1] and is known as the 'Gauss invariant' of the loops. Although this formula strictly applies to closed loops only, it is frequently used for open loops: one may imagine the finite strings to be extended and to close on themselves without additional entanglement.

However there are circumstances when the winding number concept needs to be modified. For example, in the normal states of the high-transition-temperature superconductors charged particles are believed [2] to be strongly coupled to the fluctuating spin background, and the spin backflow accompanying the particle motion introduces an extra phase (ϕ) to the Hamiltonian, which mimicks the Aharonov-Bohm phase from a real magnetic field. After averaging over the rapid quantum fluctuation intrinsic to these systems:

$$\langle \phi(\boldsymbol{r}, t)\phi(0, 0)\rangle = \langle \phi^2 \rangle \delta(\boldsymbol{r})\, \mathrm{e}^{-\omega_{ch} t}$$

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where ω_{ch} is the intrinsic fluctuating frequency and t denotes the time, this phase becomes a negative definite quantity [3]. Since $\phi(r)$ fluctuates independently at different spatial points, in the imaginary-time path integral formalism this negative quantity suppresses the paths that enclose a large area irrespective of their handedness† [4], and therefore the distinction between the clockwise and anticlockwise winding numbers is to some extent not applicable. This is illustrated in figure 1. The total flux in case (a1) being the sum of fluxes of regions 1 and 2, $\phi_1+2\phi_2$, it becomes

$$\langle(\phi_1+2\phi_2)^2\rangle_\phi=\langle\phi_1^2\rangle+4\langle\phi_2^2\rangle$$

after the Gaussian averaging, $\langle\ldots\rangle_\phi$, over $\phi(r)$ at all r. While for case (a2), the result is just $\langle\phi_1^2\rangle$ which cannot be obtained by assigning a positive weight to the anticlockwise winding as the clockwise one. Neither is it correct to put the absolute sign over the total flux, which will give zero for case (b2) while in fact it is equal to $\langle\phi_1^2\rangle+\langle\phi_2^2\rangle$ the same as case (b1).

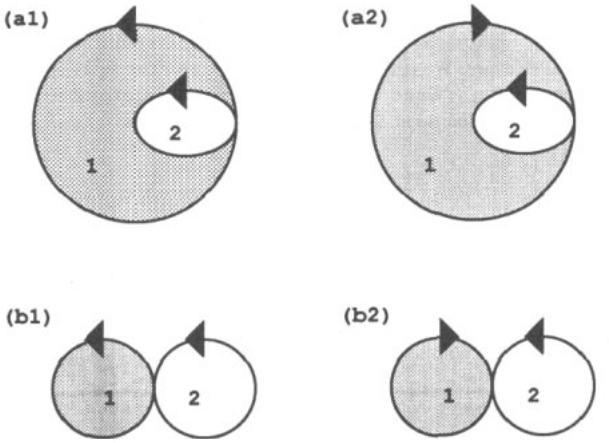

Figure 1. Examples of close loops which illustrate the inadequacy of the winding-number definition (see text). Arrows denote the direction of the path.

Another example is the description of entanglement‡ for polymer chains in dense solutions or melts, which is crucial in giving rise to the interesting viscoelastic behaviour [5]. For these systems the concept of 'tube' (for a review, see [7]) has been fruitfully employed as a phenomenological way of modelling the confinement (due to the excluded volume and entanglement of the chains). The 'tube' simulates the fact that polymer chains are massively entangled with one another and, when the density is high, therefore cannot move freely in the sidewise directions. Microscopically if we try to describe the degree of entanglement, say, between two chains, the usual notion of the winding number needs to be modified because, as far as muture snaring of the chains is concerned, both the clockwise and anticlockwise windings should be given a positive weight. This concept has been proposed [8] by des Cloizeaux and other

† In the lattice case, this corresponds to the 'retraced path restriction' described in [4].

‡ Many people have contributed to this problem, especially Edwards and Doi, and de Gennes. References can be found in [5]. Concerning different aspects of topological entanglements for polymers, a detailed discussion and further references can be found in [6].

authors†. They analyse the mean square linking number, i.e. squaring equation (1) before averaging over all possible configurations of both chains. Providing the chains are very long, these windings can be considered as independent, and thus the former quantity counts the total number of windings with the same positive weight (negative sign for the anticlockwise windings has been erased by the squaring).

In this paper we shall study a simplified scenario for the second example: the entanglement between a long chain and a long straight rod [6]. Firstly the measure of the entanglement is introduced and compared with the usual winding number notion of equation (1). At finite temperatures we treat the thermal agitation of the chain by an ensemble average, and calculate the reaction rate for the chain to become disentangled from the rod. Derivations are shown explicitly for both the equilibrium case with a small friction and the static case with a large friction. Finally we discuss consistency of our results with the prediction of the phenomenological 'tube' model for polymers.

2. Measure of the degree of entanglement

Since both the clockwise and the anticlockwise windings (n_c and n_a) serve equally to describe the snaring of the chain on the rod, we use n_c+n_a (denoted by n_2) as the measure for the entanglement. It will be explained later that detailed calculations of n_2, as in [8], can be circumvented by a simple scaling argument. Note that n_2 is different from the Gauss invariant formula, equation (1), which is equal to their difference $n_c-n_a\equiv n_1$. Since we shall be discussing the rate with which the chain disentangles itself from the rod, the time derivatives of n_1 and n_2 (denoted by $\dot{n}_1$ and $\dot{n}_2$) and their distribution functions need to be considered. As usual we use t to denote the time, and hence $\dot{n}_{1,2}\equiv \mathrm{d}n_{1,2}/\mathrm{d}t$.

Use f_1, f_2, f_3 and f_4 to denote the probabilities for finding n_1, n_2, $\dot{n}_1$ and $\dot{n}_2$. In general, f_4 can be written as:

$$f_4(\dot{n}_2)=\int_{-\infty}^{\infty}\mathrm{d}\dot{n}_c\int_{-\infty}^{\infty}\mathrm{d}\dot{n}_a\,Q(\dot{n}_c,\dot{n}_a)\delta(\dot{n}_2-\dot{n}_c-\dot{n}_a) \tag{2}$$

where $Q(\dot{n}_c,\dot{n}_a)$ is the probability of finding $\dot{n}_c$ and $\dot{n}_a$. Since in equilibrium the thermal agitation has no prejudice toward either increasing or decreasing n_a:

$$Q(\dot{n}_c,-\dot{n}_a)=Q(\dot{n}_c,\dot{n}_a).$$

By changing the variable $\dot{n}_a$ in equation (2) to $-\dot{n}_a$, it gives that $f_4(\dot{n}_2)$ is equal to $f_3(\dot{n}_2)$ which is relatively easier to find‡. In the large friction case, if the deviation from equilibrium is small the above arguments still hold for the lowest order approximation. However, note that f_1 is different from f_2, and the distinction between n_1 and n_2 is still necessary.

As for $f_2(n_2)$,

$$\begin{aligned}f_2(n_2)&=\langle\delta(n_2-n_c-n_a)\rangle_{\text{ensemble average}}\\&=\frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega\,\mathrm{e}^{\mathrm{i}\omega n_2}\langle\mathrm{e}^{-\mathrm{i}\omega(n_c+n_a)}\rangle\end{aligned} \tag{3}$$

† By Pohl, des Cloizeaux and Ball, and Duplantier. References can be found in [8].

‡ To avoid confusion, the reason why f_3 is expressed as a function of $\dot{n}_2$ here, rather than $\dot{n}_1$, is that we are equating f_3 to f_4 for which the variable is $\dot{n}_2$.

where the ensemble averaging is over all possible chain configurations. Expand the exponential inside $\langle \ldots \rangle$ into polynomials,

$$1 - i\omega\langle n_c + n_a\rangle - \frac{\omega^2}{2}\langle (n_c + n_a)^2\rangle + O(\omega^3).$$

It has been proved by des Cloizeaux [8], and is in fact reasonable to expect, that $(n_c + n_a)$ is an extensive quantity, i.e. proportional to N where N is the length of the chain. Similarly, $\langle (n_c + n_a)^2\rangle$ is proportional to N^2, etc. Therefore the $\langle \ldots \rangle$ in equation (3) is a function of ωN. When the chain is fully disentangled from the rod, $n_2 = 0$ and equation (3) can be shown to have the following dependence:

$$f_2(n_2 = 0) \propto \frac{1}{N} \tag{4}$$

by changing the variable ωN to ω'.

For our model, set the r_2 chain in equation (1) to be the rigid rod which lies along the z-axis. It is straightforward to obtain:

$$n_1 = \int_0^N \mathrm{d}s \frac{-x'y + xy'}{x^2 + y^2} \tag{5}$$

$$\dot{n}_1 = \frac{1}{2\pi}\left[\frac{x(N)\dot{y}(N) - \dot{x}(N)y(N)}{x^2(N) + y^2(N)} - \frac{x(0)\dot{y}(0) - \dot{x}(0)y(0)}{x^2(0) + y^2(0)}\right] \tag{6}$$

where $(x(0), y(0))$ and $(x(N), y(N))$ are the positions of the chain ends (the z-coordinate does not affect the winding number). Caution needs to be taken in distinguishing between the arc-length derivative x' and the time derivative $\dot{x}$. Equation (6) being dependent only on the end points of the chain is consistent with the 'Gauss invariant' property of the winding number. That is, $\dot{n}_1$ cannot depend on how much the middle of the chain wriggles—the only change to n_1 must come from the movement of end points. When expressed in the Fourier conjugates $(q, \boldsymbol{q}_T)$ of $(s, \boldsymbol{r}_T)$ where the sub-index T denotes the transverse direction, equations (5) and (6) become

$$n_1 = \frac{i}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{q}_T \, \mathrm{e}^{i\boldsymbol{q}_T \cdot \boldsymbol{R}} \frac{\gamma}{|\boldsymbol{q}_T|^2}[\boldsymbol{D}(-\boldsymbol{q}_T) \times \boldsymbol{q}_T]_{z\text{-component}} \tag{7}$$

$$\dot{n}_1 = \frac{i}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{q}_T \, \mathrm{e}^{i\boldsymbol{q}_T \cdot \boldsymbol{R}} \frac{\gamma}{|\boldsymbol{q}_T|^2} \mathrm{e}^{i\boldsymbol{q}_T \cdot \sum_q \boldsymbol{r}_q \mathrm{e}^{iqs}} \left[\sum_q \boldsymbol{r}_q \times \boldsymbol{q}_T \, \mathrm{e}^{iqs}\right]_{z\text{-component}, s=N}$$
$$- [\text{same term but with } s = 1] \tag{8}$$

where $\boldsymbol{R}$ is the transverse position of centre-of-mass of the free chain which will be set to be at the origin, and

$$\gamma \equiv \pi \int_{-\infty}^{\infty} \frac{x \sin x - \cos x}{x^2} \mathrm{d}x$$

$$\boldsymbol{D}(-\boldsymbol{q}_T) = \int \mathrm{d}s \left[\sum_q iq\boldsymbol{r}_q \, \mathrm{e}^{iqs}\right] \exp\left(i\boldsymbol{q}_T \sum_q \boldsymbol{r}_q \, \mathrm{e}^{iqs}\right). \tag{9}$$

Note that for $\langle \dot{n}_2 \rangle$ at equilibrium the rate formula needs to be multiplied by a Heaviside step function, $\theta(\dot{n}_2)$, because $\dot{n}_2$ is equally likely to be positive and negative. When the friction is large, $\dot{n}_2$ has a preferred direction and we do not need $\theta(\dot{n}_2)$.

3. Reaction rate for disentanglement

3.1. Equilibrium case with a small friction

The potential energy of a long chain is mainly of entropic origin, and correspondingly does not arrive at an Arrhenius formula with an exponential temperature dependence. We proceed by calculating the ensemble average of the rate, $(\mathrm{d}n_2/\mathrm{d}t)\delta(n_2)$, where the delta function focuses our interest on the moment when the chain is disentangled from the rod. The statistical weight is

$$\psi_e(\boldsymbol{r}) \exp\left[-\frac{m\beta}{2}\sum_{j=1}^{N}\left(\frac{\mathrm{d}\boldsymbol{r}_j}{\mathrm{d}t}\right)^2\right] \tag{10}$$

where m is the mass of the chain constituent and $\beta = 1/k_B T$ with T the temperature. The equilibrium entropy weight is defined as:

$$\psi_e(\boldsymbol{r}) \equiv \exp\left[-\frac{3}{2l^2}\sum_{j=1}^{N-1}(\boldsymbol{r}_{j+1}-\boldsymbol{r}_j)^2\right] \tag{11}$$

where l is the unit length of the chain constituent. The small friction limit corresponds to the old argument by which the absolute rate theory was established for chemical reaction rate constants, where one simply counts the number of times per unit time that particles in the tail of a Maxwell velocity distribution make it over the reaction barrier. Friction appears nowhere in this argument (however, we know it must not be too low [9]). In the reaction rate theory, the time average in the crossing rate:

$$\text{rate} = \lim_{t'\to\infty}\frac{1}{2t'}\int_{-t'}^{t'}\delta(t-t_i)\,\mathrm{d}t \tag{12}$$

(where t_i are the instants at which the reaction is achieved) is replaced by an ensemble average,

$$\begin{aligned}\text{rate} &= \langle \dot{n}_2\theta(\dot{n}_2)\delta(n_2)\rangle_{\text{ensemble average}}\\ &= f_2(0)\int_0^{\infty}\dot{n}_2 f_3(\dot{n}_2)\,\mathrm{d}\dot{n}_2\end{aligned} \tag{13}$$

where the θ-function guarantees the counting over forward crossings only. Having shown that $f_4(\dot{n}_2) = f_3(\dot{n}_2)$ and $f_2(0) \propto 1/N$, we proceed to calculate the average $\langle \dot{n}_1\rangle$ with the weight:

$$\exp\left(-\frac{\beta m N}{2}\sum_q |\dot{\boldsymbol{r}}_q|^2 - \sum_q |\boldsymbol{\rho}_q|^2\right) \tag{14}$$

where

$$\boldsymbol{\rho}_q \equiv \sqrt{aN/2\pi}\; q\boldsymbol{r}_q \tag{15}$$

and $a = 3/2l^2$. After performing the $\dot{\boldsymbol{r}}_q$ integration, we get

$$\begin{aligned}\langle \mathrm{e}^{-\mathrm{i}\omega(\dot{n}_c-\dot{n}_a)}\rangle = \int\prod_q \mathrm{d}\boldsymbol{\rho}_q\, \mathrm{e}^{-\Sigma_q|\boldsymbol{\rho}_q|^2}\exp\Bigg\{-\sum_{q'}\frac{\omega^2\gamma^2}{(2\pi)^4 2\beta m N}\\ \times\Bigg[\Bigg[\int_{-\infty}^{\infty}\frac{\mathrm{d}\boldsymbol{q}_T}{|\boldsymbol{q}_T|^2}\Bigg(\exp\Bigg(\mathrm{i}\boldsymbol{q}_T\sum_q\sqrt{\frac{2\pi}{aN}}\,\frac{\boldsymbol{\rho}_q}{q}\Bigg)\boldsymbol{q}_{t,y}\\ -\exp\Bigg(\mathrm{i}\boldsymbol{q}_T\sum_q\sqrt{\frac{2\pi}{aN}}\,\frac{\boldsymbol{\rho}_q}{q}\,\mathrm{e}^{\mathrm{i}q}\Bigg)\boldsymbol{q}_{t,y}\,\mathrm{e}^{\mathrm{i}q'}\Bigg)\Bigg]^2 - [y\to x]^2\Bigg]\Bigg\}.\end{aligned} \tag{16}$$

Since the weight in equation (14) favours small $|\dot{r}_q|$ and small $\dot{n}_1$ (they are proportional from equation (8)), large-ω contributions will be more important when we integrate over ω later. This enables us to use the saddle-point method in evaluating equation (16). Using the well known completeness property:

$$\sum_{q=(2\pi/N)}^{(2\pi/N)N} e^{imq} = N\delta_{m,0} \tag{17}$$

the exponent on the right-hand side of equation (16) can be simplified† to (note that from now on, numerical constants will be omitted in order to concentrate on the N and β dependences):

$$-\sum_q |\boldsymbol{\rho}_q|^2 - N\frac{\omega^2}{\beta m N}\frac{N}{Q^2}$$

where Q is the magnitude of $\boldsymbol{Q} \equiv \Sigma_q \boldsymbol{\rho}_q/q$. The saddle points are obtained by taking the gradient with respect to $\boldsymbol{\rho}_q$:

$$-\boldsymbol{\rho}_{-q,x} + \frac{\omega^2 N}{\beta m}\frac{Q_x}{Q^4 q} = 0. \tag{18}$$

Multiplying both sides of equation (18) by $1/q$ and summing‡ over q enables us to solve for Q:

$$|\boldsymbol{Q}| \approx \frac{|\omega|^{1/2} N^{3/4}}{(\beta m)^{1/4}}. \tag{19}$$

Putting equation (19) back in equation (18) gives:

$$|\boldsymbol{\rho}_q| \approx \frac{|\omega|^{1/2}}{(\beta m)^{1/4} q N^{5/4}} \tag{20}$$

and the parameter dependence of equation (16) can be extracted to be:

$$\langle e^{-i\omega(\dot{n}_c - \dot{n}_s)}\rangle \approx \exp\left(-\frac{|\omega|}{\sqrt{N\beta m}}\right). \tag{21}$$

It may seem puzzling at first glance that, when we go from the left-hand side of equation (21) to the right-hand side, the coefficient of ω in the exponent changes from being pure imaginary to a real number. This is totally due to the ensemble averaging, after the first of which over $\dot{r}_q$ the lowest ω-dependent term is of order ω^2 with a real coefficient (see equation (16)). The overall N and βm dependence of the disentangling rate in equation (13) is then:

$$\begin{aligned} \text{rate} &\approx f_2(0) \int_0^\infty d\dot{n}\, \dot{n} \int_{-\infty}^{\infty} d\omega \exp\left[i\omega\dot{n} - \frac{|\omega|}{\sqrt{N\beta m}}\right] \\ &\propto \frac{1}{N^{1.5}\sqrt{\beta m}} \end{aligned} \tag{22}$$

where the property $f_2(0) \propto 1/N$ from equation (4) has been used.

† Since the q_T is the transverse direction and its magnitude scales like $Q/\sqrt{N}$, the two-dimensional q_T integration in equation (16) exhibits the unit of $|q_T|^2$, i.e., N/Q^2.

‡ Since qs are integer multiples of $2\pi/N$, the summation over $1/q^2$ gives roughly $(N/2\pi)^2$ when N is large.

3.2. Static case with a large friction

In the large friction limit the absolute rate theory breaks down [9] and the Fokker–Planck equation is reduced to the Smoluchowski equation [10]. The statistical weight becomes

$$\left(\psi_0+\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t}\psi_1\right)\cdot\exp\left[-\frac{m}{2k_BT}\sum_{j=1}^{N}\left(\frac{\mathrm{d}\boldsymbol{r}_j}{\mathrm{d}t}\right)^2\right] \tag{23}$$

where

$$\psi_0=\psi_e+\delta\psi \tag{24}$$

$$\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t}\psi_1=-\frac{1}{2\eta}\sum_{j=1}^{N}\frac{\mathrm{d}\boldsymbol{r}_j}{\mathrm{d}t}(\nabla_{r_j}+\beta\nabla_{r_j}U)\psi_0 \tag{25}$$

and η is the friction constant of the chain. The potential energy U for our model consists mainly of the entropy of the chain. Note that the deviation, $\delta\psi$, from equilibrium ψ_e is necessary to avoid a null result because $(\nabla_{r_j}+\beta\nabla_{r_j}U)\psi_e=0$. We choose the probability for the occurrence of a particular $\delta\psi$ on the basis of the usual entropic considerations: the probability for the distribution ψ_o to occur is

exp(entropy) δ(⟨energy⟩) δ(static constraint)

$$\approx\exp\left[-\int\psi_0\ln\psi_0\prod_j\mathrm{d}\boldsymbol{r}_j-\lambda_1\int H\psi_0\prod_j\mathrm{d}\boldsymbol{r}_j+\lambda_2\sum_j\nabla_{r_j}\cdot\boldsymbol{J}(\boldsymbol{r}_j)\right]. \tag{26}$$

The first Lagrange parameter, λ_1, corresponds to a given average energy of the system, while the second parameter, λ_2, restricts to ψ_0s that obey number conservation (in the stationary case of interest here). The static constraint can be obtained from the lowest order of the Smoluchowski equation [10] as:

$$\sum_j\nabla_{r_j}\cdot\boldsymbol{J}(\boldsymbol{r}_j)=\sum_q\frac{\partial}{\partial\boldsymbol{r}_q}\left[\frac{\partial}{\partial\boldsymbol{r}_{-q}}+\frac{aN}{\pi}\boldsymbol{r}(q)q^2\right]\psi_0=0 \tag{27}$$

where $a\equiv\frac{3}{2}l^2$. For small $\delta\psi$, the exponent in equation (26) can be expanded up to the second order of $\delta\psi$, and the weight function is of the Gaussian form.

Since $\dot{n}_1$ is linear in $\mathrm{d}\boldsymbol{r}/\mathrm{d}t$ from equation (6), only the second term in the statistical weight, equation (23), contributes to $\langle\dot{n}_1\rangle$ (because odd functions of $\mathrm{d}\boldsymbol{r}/\mathrm{d}t$ are averaged to zero). Now $\langle\dot{n}_1\rangle$ is of the order of $|\mathrm{d}\boldsymbol{r}/\mathrm{d}t|^2$ which, when multiplied by the $1/\eta$ coefficient in equation (25), gives us the expected $1/m\beta\eta$ coefficient.

Using the definitions of equations (15) and (24), we expand $\delta\psi$ in terms of the Hermite polynomials:

$$\delta\psi\equiv B\sum_{\mathbf{n}}a_{\mathbf{n}}H_{\mathbf{n}}(\rho)\exp\left[-\sum_q|\boldsymbol{\rho}_q|^2\right] \tag{28}$$

where $\mathbf{n}$ denotes all the ns and $\rho^2\equiv\Sigma_q|\boldsymbol{\rho}_q|^2$. The advantage of using the Hermite polynomials is that their normalization relation involves an exponential weight which makes the Gaussian weight of $\delta\psi$ look quadratic:

$$\exp\left[-\frac{1}{2}\int\frac{(\delta\psi)^2}{\psi_e}\prod_q\mathrm{d}\boldsymbol{\rho}_q\right]=\exp\left[-\frac{1}{2}\sum_{\mathbf{n}}a_{\mathbf{n}}^2\varepsilon_{\mathbf{n}}\right] \tag{29}$$

where

$$\varepsilon_n\equiv 2^n n!.$$

The equilibrium entropy weight in equation (11), when normalized, is expressed as:

$$\psi_e = B \exp(-\rho^2)$$

where

$$B \equiv \prod_{q=2\pi/N}^{N2\pi/N} \frac{aNq^2}{2\pi^2}.$$

Similarly the static constraint in equation (27) can be written as:

$$\sum_n a_n C_n(\rho) = 0 \tag{30}$$

where

$$C_n(\rho) \equiv \sum_q \frac{q^2}{2\pi} \frac{\partial}{\partial \rho_q} \left[\frac{\partial}{\partial \rho_{-q}} + 2\rho_q \right] H_n(\rho)\, e^{-\rho^2}.$$

Notice that when the constraint equation is enforced by a δ-function:

$$\delta\left(\sum_n a_n C_n\right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\mu \exp\left(i\mu \sum_n a_n C_n\right) \tag{31}$$

care needs to be taken not to bring in extra spurious dependence of N or β, which can only be checked in the end.

The weight of the ensemble average is:

$$\int \prod_n da_n \int d\mu\, e^{(\ldots)} \frac{\exp[-\frac{1}{4}\beta N m \Sigma_q |\dot{r}_q|][\psi_e + \delta\psi + \Sigma_q \dot{r}_q \cdot L_q \delta\psi]}{\int \exp[-\frac{1}{4}\beta N m \Sigma_q |\dot{r}_q|^2][\psi_e + \delta\psi + \Sigma_q \dot{r}_q \cdot L_q \delta\psi] \Pi_q \, d\rho_q \, d\dot{r}_q} \tag{32}$$

where

$$L_q \equiv -\frac{q}{\eta} \sqrt{\frac{aN}{2\pi}} \left[\frac{\partial}{\partial \mathcal{R} \rho_q} + \frac{\partial}{\partial \mathcal{I} \rho_q} + 2\rho_q \right] \tag{33}$$

and $\mathcal{R}$ and $\mathcal{I}$ denote the real and the imaginary parts. The exponent $(\ldots)$ is equal to the sum of the two exponents in equations (29) and (31) which, when completed in a square form, can be expressed as:

$$\text{exponent} = -\frac{1}{2} \sum_n \varepsilon_n \left[a_n - \frac{i\mu C_n(\rho)}{\varepsilon_n} \right]^2 - \frac{1}{2} \sum_n \frac{\mu^2 C_n(\rho)^2}{\varepsilon_n}. \tag{34}$$

Since the a_n-integration in equation (33) ranges from $-\infty$ to ∞, the argument inside the bracket of equation (34) can be shifted and redefined as a_n. The third term in the denominator of equation (32) does not contribute because it is odd in v_q, and the first term equals one from the normalization condition. Then 1/denominator can be Taylor-expanded as:

$$1 - \int \delta\psi \prod_q d\rho_q + O((\delta\psi)^2). \tag{35}$$

For the non-equilibrium case, the disentangling rate is defined as:

$$\text{rate} = \langle \dot{n}_2 \delta(n_2) \rangle_{\text{ensemble average}}$$

where, in contrast to equation (13), a step-function is not needed. Since the deviation $\delta\psi$ is small, we expect $f_2(n_2)$ to be close to the equilibrium distribution (denoted by $f_{2,e}$), and the above equation can be written as:

$$\begin{aligned}\text{rate} &= f_{2,e}(0)\int_{-\infty}^{\infty}\dot{n}_2 f_3(\dot{n}_2)\,\mathrm{d}\dot{n}_2\\ &= f_{2,e}(0)\int_{-\infty}^{\infty}\dot{n}_1 f_3(\dot{n}_1)\,\mathrm{d}\dot{n}_1\end{aligned}\tag{36}$$

where $f_{2,e}(0)\propto 1/N$ from equation (4), and

$$\begin{aligned}f_3(\dot{n}_1) &\equiv \langle\delta(\dot{n}_1-\dot{n}_c+\dot{n}_a)\rangle\\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\mu\,\mathrm{e}^{\mathrm{i}\mu\dot{n}_1}\langle\mathrm{e}^{-\mathrm{i}\mu(\dot{n}_c-\dot{n}_a)}\rangle.\end{aligned}\tag{37}$$

Since $\dot{n}_1$ is proportional to v_q from equation (6), only the third term in the numerator of equation (32) (also linear in v_q in order not to be averaged to zero) is important for the ensemble averaging in equation (37). But because this term is also linear in $\delta\psi$, the first term in equation (35) does not contribute after the averaging over $a_{\mathbf{n}}$. Up to now, equation (32) has been simplified to:

$$\begin{aligned}&\int\prod_{\mathbf{n}}\mathrm{d}a_{\mathbf{n}}\int\mathrm{d}\mu\,\exp\left[-\frac{1}{2}\sum_{\mathbf{n}}\varepsilon_{\mathbf{n}}a_{\mathbf{n}}^2-\frac{1}{2}\sum_{\mathbf{n}}\frac{\mu^2C_{\mathbf{n}}^2(\rho)}{\varepsilon_{\mathbf{n}}}-\frac{\beta Nm}{2}\sum_q|\dot{r}_q|^2\right]\\ &\quad\times\sum_q\dot{r}_q\cdot L_qB\sum_{\mathbf{n}}\left[a_{\mathbf{n}}+\frac{\mathrm{i}\mu C_{\mathbf{n}}(\rho)}{\varepsilon_{\mathbf{n}}}\right]H_{\mathbf{n}}(\rho)\,\mathrm{e}^{-\rho^2}\\ &\quad\times\sum_{\mathbf{n}}\int\left[a_{\mathbf{n}}+\frac{\mathrm{i}\mu C_{\mathbf{n}}(\rho')}{\varepsilon_{\mathbf{n}}}\right]H_{\mathbf{n}}(\rho')\,\mathrm{e}^{-(\rho')^2}\prod_q\mathrm{d}\boldsymbol{\rho}'_q.\end{aligned}\tag{38}$$

Note that the ρ' variable in the last integral is just a dummy variable in distinction from the original ρ. After performing the $a_{\mathbf{n}}$ integration, we find that both the linear and quadratic terms do not contribute, which means that the shift of $a_{\mathbf{n}}$ due to the introduction of the static constraint is crucial. Without the static constraint, the averaging rate is zero (the reason is that the last integral in equation (38) without the $C_{\mathbf{n}}(\rho)$ is non-zero only when $\mathbf{n}$ are all zero, but in this case $L_qH_0\,\mathrm{e}^{-\rho^2}$ gives zero). Equation (38) now becomes

$$\begin{aligned}&B\int\mathrm{d}\mu\,\exp\left[-\frac{1}{2}\sum_{\mathbf{n}}\frac{\mu^2C_{\mathbf{n}}^2(\rho)}{\varepsilon_{\mathbf{n}}}-\frac{\beta Nm}{2}\sum_q|\dot{r}_q|^2\right]\sum_q\dot{r}_q\cdot L_q\\ &\quad\times\sum_{\mathbf{n}}\left(\frac{\mu}{\varepsilon_{\mathbf{n}}}\right)^2C_{\mathbf{n}}(\rho)H_{\mathbf{n}}(\rho)\,\mathrm{e}^{-\rho^2}\zeta_{\mathbf{n}}\end{aligned}\tag{39}$$

where $\zeta_{\mathbf{n}}$ is defined as:

$$\zeta_{\mathbf{n}}\equiv\int C_{\mathbf{n}}(\rho')H_{\mathbf{n}}(\rho')\,\mathrm{e}^{-(\rho')^2}\prod_q\mathrm{d}\boldsymbol{\rho}'_q.$$

It can be simplified further after the μ integration:

$$B\sum_{\mathbf{n}}\frac{\zeta_{\mathbf{n}}}{\varepsilon_{\mathbf{n}}^2}\left[\sum_q\dot{r}_q\cdot L_qC_{\mathbf{n}}(\rho)H_{\mathbf{n}}(\rho)\,\mathrm{e}^{-\rho^2}\right]\left[\sum_{\mathbf{m}}\frac{C_{\mathbf{m}}^2(\rho)}{\varepsilon_{\mathbf{m}}}\right]^{-1.5}\cdot\exp\left[-\frac{\beta Nm}{2}\sum_q|\dot{r}_q|^2\right].\tag{40}$$

The expression for $\dot{n}_1$ is in equation (8), and because of equation (17) the $s=1$ term does not contribute after the $\dot{r}_q$ integration. The two-dimensional integration over q_T gives

$$\int\int_{-\infty}^{\infty} \mathrm{d}q_T \frac{q_T}{|q_T|^2} \exp\left[\mathrm{i}q_T \cdot Q\sqrt{\frac{2\pi}{aN}}\right] = -\mathrm{i}\sqrt{2\pi aN}\,\frac{Q}{|Q|^2} \tag{41}$$

where the definition of

$$Q \equiv \sum_q \frac{\rho_q}{q} \mathrm{e}^{\mathrm{i}qN} = \sum_q \frac{\rho_q}{q}$$

is the same as before. Similarly equation (37), after integrating over $\dot{r}_q$, becomes

$$\begin{aligned}\langle \mathrm{e}^{-\mathrm{i}\mu(\dot{n}_c-\dot{n}_a)}\rangle = {} & \frac{1}{2\pi}\sum_n \frac{\zeta_n}{\varepsilon_n^2}\int_{-\infty}^{\infty}\prod_q \mathrm{d}\rho_q \sum_q [L_q C_n(\rho) H_n(\rho)\,\mathrm{e}^{-\rho^2}]_{z\text{-component}} \\ & \times \frac{\gamma\mu}{(2\pi)^2\beta mN}\left[-\mathrm{i}\sqrt{2\pi aN}\,\frac{Q_y}{|Q|^2}\right] \\ & \times \exp\left[-\frac{\gamma^2\mu^2}{(2\pi)^4 2\beta mN}\,\frac{2\pi aN}{|Q|^2}\right]\left[\sum_m \frac{C_m^2(\rho)}{\varepsilon_m}\right]^{-1.5}.\end{aligned} \tag{42}$$

The exponent on the right-hand side can be expressed roughly as

$$\text{exponent} \approx -\sum_q |\rho_q|^2 + \ln Q_y - 2\ln Q - \frac{\mu^2}{\beta mQ^2}. \tag{43}$$

When μ is large, the saddle-point solutions satisfy: $Q_x = 0$, $Q_y \approx N$, $\rho_{q,x} = 0$, $\rho_{q,y} \approx 1/N_q$, and $\mu \approx \sqrt{\beta m}N$. We can check that:

$$C_n(\rho) \approx \sum_q q^2 \rho_q \approx \frac{2\pi}{N^2}\sum_{q=1}^{N-1} q$$

is independent of N when N is large. This is consistent with the requirement that the expression of equation (30) for the static constraint should not introduce any further N dependence. We can further estimate that

$$\sum_q L_q C_n(\rho) H_n(\rho)\,\mathrm{e}^{-\rho^2} \approx \frac{\sqrt{N}}{\eta}\sum_q q^3 \rho_q \approx \frac{\sqrt{N}}{\eta}. \tag{44}$$

From the above results, we deduce the parameter dependence of equation (42) as:

$$\langle \mathrm{e}^{-\mathrm{i}\mu(\dot{n}_c-\dot{n}_a)}\rangle \approx \frac{\mu}{\eta\beta mN}$$

where the coefficient of μ changes from being pure imaginary before the ensemble averaging to a real number similar to equation (21). Equation (37) can be shown to scale like:

$$f_3(\dot{n}_1) \approx \eta\beta mN$$

and

$$\langle \dot{n}_1 \rangle \approx \frac{1}{\eta\beta mN}. \tag{45}$$

Finally, the parameter dependence for the disentangling rate in equation (36) can be extracted as:

$$\text{rate} \approx f_2(n_2 = 0)\langle \dot{n}_1 \rangle \approx \frac{1}{\eta\beta m N^2}. \tag{46}$$

Compared with the rate in equation (22) for the equilibrium case with a small friction constant, equation (46) depends more sensitively on the chain length and is inversely proportional to the friction constant.

4. Discussion

In many cases, e.g., the randomly fluctuating fictitious field mentioned in the introduction, the concept of winding number needs further modifications and analytic treatments often become intractable if not impossible. The model discussed here is thus useful in that it can be solved analytically, at least in the limiting cases. This study was motivated by the entanglement of polymers in dense solutions or melts. Although there has been a large amount of literature on this topic, most of it is based on the phenomenological 'tube' model [5, 7]. In contrast, our studies start from a more microscopic basis. If we identify the inverse of the disentangling rate in equation (46) as a characteristic timescale for the system, it happens to have the same N (the length of the chain or the polymerization) dependence as the viscoelastic time interval (τ) prediction by the 'tube' model [5]. In the 'tube' model τ is identified as the time for the chain to 'reptate' out of its original 'tube', which equals [5]:

$$\text{diffusion time} = \frac{(\text{length})^2}{\text{diffusion constant}} = \frac{(Nl)^2}{k_B T/\eta} \tag{47}$$

where $k_B T/\eta$ comes from Einstein's relation†. As far as the prediction of τ is concerned the phenomenological model is far simpler‡ [15]. However, our model provides a more microscopic basis and illustrates the plausibility of an analytic approach to problems which require similar modifications to the winding number concept.

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† Since η is defined in equation (25) as the friction constant of the chain, it is an extensive quantity proportional to N. Therefore the overall N-dependence in equations (46) and (47) goes like N^3.

‡ Therefore we will not try to modify our model to account for the also well known 0.4–0.5 discrepancy for the N dependence of τ with the experiments. There has been a sustained effort in the literature based on the 'tube' model, see for instance [11].

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