

Adsorption Effects and NMR Properties: Continuous Chain Approach

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The NMR properties of nuclei linked to long linear polymer molecules are sensitive to the influence of hard walls. In this context, the residual energy of tensorial spin-spin interactions is calculated using a path integral approach. Several thermodynamic quantities of the polymer system (free energy, equation of state,...) are also expressed, taking chain stiffness effects and the presence of two repulsive walls into consideration.

KEY WORDS: Nuclear magnetic resonance; polymers; stiffness; path integrals; adsorption.

1. INTRODUCTION

The statistical mechanics of the adsorption of long, flexible polymer chains at surfaces has been extensively studied in recent years.^(1,2) The behavior of a macromolecule restricted to a bounded domain is of great technological and fundamental interest in order to understand the layer properties of adsorbed polymers in the vicinity of solids, and colloidal stabilization. We shall concentrate our attention on a space region confined between two repulsive walls of infinite size. The topological constraints resulting from the impenetrability of the walls affect the orientation of the polymer segments, as it occurs in a melt due to the presence of entanglements or in a covalent gel.⁽³⁾ However, the corresponding asymmetry of motions of monomeric units induces a residual energy of tensorial interactions of nuclear spins attached to the chain skeleton, and, as is well known, the relaxation of the transverse nuclear magnetization is governed by the average of this residual energy over the whole sample.

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The aim of this work is to compute the global energy of spin-spin interactions for a continuous chain according to the description previously proposed by Edwards⁽⁴⁾ and Freed.⁽⁵⁾ Following these authors, the statistical properties of stiff chains is modeled through a path integral formulation assuming that the configuration of a macromolecule is identical to the trajectory of a fictitious "particle" in a three-dimensional space. The distribution probabilities are expressed in terms of Wiener measures.

Since the presence of repulsive walls breaks the rotational symmetry of the physical space, the nonisotropic behavior of monomeric units is described by the statistical properties of the chain tangent vectors similar to the velocity of the corresponding "particle." Furthermore, the residual energy of spin-spin interactions can be expressed in a tensorial form of the velocity components. This supports the use of the Wiener-type functional integral method in order to predict the NMR response.

2. CONTINUOUS CHAIN MODEL

A continuous model of polymer chains will be used throughout this work. We start from a Gaussian macromolecule and then add the interaction terms describing stiffness effects or external fields of constraints. The sum over all configurations is carried out by applying the path integral method.

2.1. Gaussian Chain

Given the maximum contour length L of a polymer, Gaussian chains are characterized by the following identity:

$$\langle \mathbf{R}^2 \rangle = Ll$$

\mathbf{R} is the end-to-end vector of the chain and l depends upon its monomeric structure and the temperature because of hindered internal rotations. Starting from a discrete model picturing a polymer as a freely jointed chain, we divide it into n equivalent Gaussian bonds of equal contour lengths Δs_j (Fig. 1), restricted to

$$\sum_{j=1}^n \Delta s_j = L$$

Using general properties of random walks and Brownian motion, the

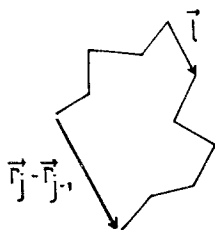


Fig. 1. Freely jointed chain model; the skeletal bonds \mathbf{l} are freely connected, every sub-molecule has a fixed end-separation vector $\mathbf{r}_j - \mathbf{r}_{j-1}$.

probability distribution function associated with an individual bond can be written as

$$P(\mathbf{r}_j - \mathbf{r}_{j-1}, \Delta s_j) = \left(\frac{3}{2\pi l \Delta s_j} \right)^{3/2} \exp \left[- \frac{3}{2l \Delta s_j} (\mathbf{r}_j - \mathbf{r}_{j-1})^2 \right] \quad (1)$$

provided that each bond contains enough monomer units to obey a Gaussian statistics. Taking all the bonds into account, the continuous description is obtained when the limits $n \rightarrow \infty$ and $\Delta s_j \rightarrow 0$ are reached. Then the distribution function of the end-separation vector \mathbf{R} can be written in a functional form:

$$G(\mathbf{R}) = \int_{\mathbf{r}(0)=0}^{\mathbf{r}(L)=\mathbf{R}} \mathcal{D}[\mathbf{r}(s)] \exp \left[-3/2l \int_0^L \left(\frac{d\mathbf{r}}{ds} \right)^2 ds \right] \quad (2)$$

where $G(\mathbf{R})$ obeys the simple diffusion equation (2):

$$\left(\frac{\partial}{\partial L} - \frac{l}{6} \nabla_{\mathbf{R}}^2 \right) G(\mathbf{R}) = \delta(L) \delta(\mathbf{R}) \quad (3)$$

2.2. Stiffness Effect

According to models proposed by Freed⁽⁶⁾ and Saito *et al.*,⁽⁷⁾ the stiffness effect is introduced from a mechanical point of view, associating a potential energy function with the bending of the chain. The energy per unit length is written as

$$v = \frac{\varepsilon/2}{\mathcal{D}_c^2} \quad (4)$$

where \mathcal{R}_c is the radius of curvature of the curve $\mathbf{r}(s)$, and ε is a rigidity parameter which depends upon the chemical structure of the monomeric units,

$$\mathcal{R}_c^{-1} = \left| \frac{d\mathbf{u}}{ds} \right| = \left| \frac{d^2\mathbf{r}}{ds^2} \right| \quad (5)$$

According to Eq. (4), an amount of energy is required to bend a chain and the straight chain is energetically the most favored. The summation over all segments leads to the following form for (5):

$$\frac{\varepsilon}{2} \int_0^L \left(\frac{d^2\mathbf{r}}{ds^2} \right)^2 ds \quad (6)$$

The associated probability distribution function of the end-separation vector of a macromolecule is

$$G(\mathbf{R}) = \int_{\mathbf{r}(0)=\mathbf{0}}^{\mathbf{r}(L)=\mathbf{R}} \mathcal{D}[\mathbf{r}(s)] \exp(-\beta H_0) \quad (7)$$

with

$$\beta H_0 = \frac{\beta\varepsilon}{2} \int_0^L \left(\frac{d^2\mathbf{r}}{ds^2} \right)^2 ds + \frac{3}{2l} \int_0^L \left(\frac{d\mathbf{r}}{ds} \right)^2 ds$$

2.3. External Field of Constraints

When a constraint is applied on the chain, for example, by entanglements in a melt or cross-links in the gel, it results in a potential energy which acts on each monomer. In the continuous description, this energy is drawn by a potential per unit length $V[\mathbf{r}(s)]$. The corresponding Wiener integral reads

$$\exp \left\{ -\beta \int_0^L V[\mathbf{r}(s)] ds \right\} \quad (8)$$

In order to describe the chain in terms of the local velocity $\mathbf{u}(s) = d\mathbf{r}/ds$ instead of $\mathbf{r}(s)$, a partial integration is performed from (8),

$$\begin{aligned} \int_0^L V[\mathbf{r}(s)] ds &= [sV(s)]_0^L - \int_0^L s \frac{dV}{ds} ds \\ &= \text{const} + \int_0^L s \mathbf{f}(s) \cdot \frac{d\mathbf{r}}{ds} ds \end{aligned} \quad (9)$$

where $\mathbf{f}(s) = -\nabla_{\mathbf{r}(s)}V[\mathbf{r}(s)]$ is the force per unit length which is applied on the monomers. The first term of the right-hand part of Eq. (9) is included in the normalization constant and

$$\exp \left\{ -\beta \int_0^L V[\mathbf{r}(s)] ds \right\}$$

can be rewritten as

$$\exp \left\{ \int_0^L \mathbf{j}(s) \cdot \frac{d\mathbf{r}}{ds} ds \right\} \tag{10}$$

with $\mathbf{j}(s) = -\beta s \mathbf{f}(s)$.

The probability distribution function for all paths is now expressed as

$$G[\mathbf{R}, \mathbf{j}] = \int_{\mathbf{r}(s)=0}^{\mathbf{r}(L)=\mathbf{R}} \mathcal{D}[\mathbf{r}(s)] \exp(-\beta H) \tag{11}$$

with

$$\beta H = \frac{\beta \epsilon}{2} \int_0^L \left(\frac{d^2 \mathbf{r}}{ds^2} \right)^2 ds + \frac{3}{2l} \int_0^L \left(\frac{d\mathbf{r}}{ds} \right)^2 ds - \int_0^L \mathbf{j}(s) \cdot \frac{d\mathbf{r}}{ds} ds$$

2.4. Tangent Vector Description

We note that $G[\mathbf{R}, \mathbf{j}]$ depends only upon the derivatives $d\mathbf{r}/ds$. Then it is convenient to reexpress Eq. (11) as a function of the tangent vector $\mathbf{u}(s) = d\mathbf{r}/ds$.⁽⁵⁾

Providing that the boundary conditions for chain end points are specified by

$$\mathbf{U}_0 = \left. \frac{d\mathbf{r}}{ds} \right|_0 \quad \text{and} \quad \mathbf{U}_L = \left. \frac{d\mathbf{r}}{ds} \right|_L$$

we obtain instead of Eq. (11) the distribution function in the form

$$G_0[\mathbf{U}_0, \mathbf{U}_L, j] = \int_{\mathbf{u}(0)=\mathbf{u}_0}^{\mathbf{u}(L)=\mathbf{u}_L} \mathcal{D}[\mathbf{u}(s)] \exp \left[-\beta \int_0^L F_0(s) ds \right] \tag{12}$$

with

$$\beta F_0(s) = \frac{\beta \epsilon}{2} \left(\frac{d\mathbf{u}}{ds} \right)^2 + \frac{3}{2l} \mathbf{u}(s)^2 - \mathbf{j}(s) \cdot \mathbf{u}(s)$$

In fact, the correct path integral measure should contain the constraint $\prod_s \delta(\mathbf{u}^2(s) - 1)$, which leads to a more complicated expression. In this paper I would like to follow the approaches of Doi and Edwards⁽⁸⁾ and Freed,⁽⁶⁾ where the above constraint is ignored. A further discussion about this simplification can be found in Freed.⁽⁶⁾ For more rigorous treatments see also Kholodenko.⁽⁹⁾

$G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]$ satisfies the differential equation:

$$\left(\frac{\partial}{\partial L} - \frac{1}{2\beta\epsilon} \nabla_{\mathbf{U}}^2 + \frac{3}{2l} \mathbf{U}^2 - \mathbf{j} \cdot \mathbf{U} \right) G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}] = \delta(L) \delta(\mathbf{U}_0 - \mathbf{U}_L) \quad (13)$$

This equation is related to an equation of motion for the density matrix of the harmonic oscillator, and has an analytical solution⁽¹⁰⁾

$$G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}] = \left(\frac{b}{\pi \operatorname{sh}\{L/K\}} \right)^{3/2} \exp\{\phi[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]\} \quad (14)$$

with

$$K = \left(\frac{\beta\epsilon l}{3} \right)^{1/2}, \quad b = \left(\frac{3\beta\epsilon}{4l} \right)^{1/2}$$

and

$$\phi[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}] = \chi(L, K, b) - \xi(L, K, b)$$

Here the expressions for χ and ξ are given by

$$\chi(L, K, b) = \frac{1}{8b} \int_0^L \int_0^L ds ds' e^{-|s-s'|/K} \mathbf{j}(s) \cdot \mathbf{j}(s')$$

and

$$\begin{aligned} \xi(L, K, b) = \frac{b}{\operatorname{sh}\{L/K\}} & \left[(\mathbf{U}_0^2 + \mathbf{U}_L^2) \operatorname{ch}\left\{\frac{L}{K}\right\} - 2\mathbf{U}_0 \cdot \mathbf{U}_L \right. \\ & + 2\mathbf{A} \cdot (\mathbf{U}_0 e^{L/K} - \mathbf{U}_L) + 2\mathbf{B} \cdot (\mathbf{U}_L e^{L/K} - \mathbf{U}_0) \\ & \left. + (\mathbf{A}^2 + \mathbf{B}^2) e^{L/K} - 2\mathbf{A} \cdot \mathbf{B} \right] \end{aligned}$$

with

$$\mathbf{A} = \frac{1}{4b} \int_0^L e^{-s/K} \mathbf{j}(s) ds$$

and

$$\mathbf{B} = \frac{1}{4b} \int_0^L e^{-(L-s)/K} \mathbf{j}(s) ds$$

3. RESIDUAL ENERGY OF SPIN-SPIN INTERACTIONS

In NMR, the task consists of relating chain statistical properties to the relaxation resulting from proton spin interactions. A macromolecule is pictured as a succession of skeletal bonds \mathbf{l} , freely connected (Fig. 1). Given a relative orientation of a spin pair \mathbf{l} and a distance between the protons a , the angular part of the dipolar interaction is proportional to the spherical harmonic $Y_2^0(\theta_1^0)$, where θ_1^0 measures the angle between the constant magnetic field \mathbf{B}_0 applied along the z_0 axis and \mathbf{l} . Since dipolar coupling decreases as a^{-3} , it is assumed that each proton only interacts with its nearest neighbor. The proton pairs are supposed to be linked on the chain, the distance a remaining constant.

The Hamiltonian corresponding to a proton pair in the field \mathbf{B}_0 is written as

$$\hbar\mathcal{H} = \hbar\mathcal{H}_z + \hbar\mathcal{H}_D \quad (15)$$

$\hbar\mathcal{H}_z$ is the Zeeman energy and $\hbar\mathcal{H}_D$ is the dipole-dipole coupling within a pair. Also, we have

$$\hbar\mathcal{H}_D = (\mathbf{I}^1 \cdot \mathbf{I}^2 - 3I_z^1 I_z^2) A_{12} \quad (16)$$

with

$$A_{12} = \gamma^2 \hbar (3 \cos^2 \theta_1^0 - 1) / 2a^3$$

where γ is the gyromagnetic ratio of a proton and $\mathbf{I}_1, \mathbf{I}_2$ the two nuclear spins.

The expression of the relaxation function of the transverse magnetization $M_x(t)$ in the rotating frame is known to be⁽¹¹⁾

$$M_x(t) = \text{Tr}\{\mathcal{M}_x(t) \mathcal{M}_x\} / \text{Tr}\{\mathcal{M}_x^2\} \quad (17)$$

where the spin operator \mathcal{M}_x represents a proton pair and

$$\mathcal{M}_x(t) = e^{i\mathcal{H}_D t} \mathcal{M}_x e^{-i\mathcal{H}_D t}$$

The spin-system response can be conveniently described with⁽¹²⁾

$$M_x^0(t) = \cos[\langle \varepsilon_0(\mathbf{l}) \rangle_{\text{orien}} t] \quad (18)$$

where

$$\varepsilon_0(\mathbf{l}) = 3\gamma^2\hbar(3\cos^2\theta_1^0 - 1)/4a^3$$

The expression $(3\cos^2\theta_1^0 - 1)$ has to be averaged over all bond orientations compatible with a fixed end-separation vector $\mathbf{r}_j - \mathbf{r}_{j-1}$ (Fig. 1). This constraint induces an orientational order and $\langle \varepsilon_0(\mathbf{l}) \rangle_{\text{orien}}$ is different from zero. The result is expressed as⁽¹²⁾

$$\langle 3\cos^2\theta_1^0 - 1 \rangle_{\text{orien}} = (3\cos^2\theta_{(\mathbf{r}_j - \mathbf{r}_{j-1})}^0 - 1) \mathcal{L}^* \left(3 \frac{|\mathbf{r}_j - \mathbf{r}_{j-1}|}{\Delta s_j} \right)$$

where

$$\mathcal{L}^*(x) = 1 + \frac{3}{x^2} - \frac{3}{x} \text{cth } x \quad (19)$$

This expression becomes, in the continuous limit

$$\{3\cos^2[\theta^0(\mathbf{u}(s))] - 1\} \mathcal{L}^*(3|\mathbf{u}(s)|) \quad (20)$$

and we have

$$\mathcal{L}^*(3|\mathbf{u}(s)|) = \frac{3}{5}\mathbf{u}^2(s) - \frac{18}{35}[\mathbf{u}^2(s)]^2 + \dots \quad (21)$$

$[\mathbf{u}^2(s)]^2$ is associated with $\delta^4/\delta\mathbf{j}^4(s)$ [see Eq. (28)], and the corresponding term for $D(s)$ behaves as \mathbf{j}^4 . If $|\mathbf{j}|$ is not too high, it is possible to neglect $[\mathbf{u}^2(s)]^2$ compared with $\mathbf{u}^2(s)$ in the average values.

The $\mathcal{L}^*(x)$ expansion in power series of x is then restricted to its first term, and the residual dipolar coupling $D(s)$ is now expressed as

$$D(s) = \frac{3}{5}[2u_{z_0}^2(s) - u_{x_0}^2(s) - u_{y_0}^2(s)] \quad (22)$$

An xyz frame, different from the $x_0y_0z_0$ frame, will be introduced in Section 5 to express the potential energy $V[\mathbf{r}(s)]$ in a simpler manner. $Y_2^0(\theta_1^0)$ can be expressed in the new frame xyz using known transformation formulas. $D(s)$ now includes an orientational average:

$$D(s) = \frac{3}{5} \frac{3\cos^2\eta - 1}{2} [2\overline{u_z^2(s)} - \overline{u_x^2(s)} - \overline{u_y^2(s)}] \quad (23)$$

where η measures the angle between \mathbf{z} and \mathbf{z}_0 .

The next sections are devoted to computing $D(s)$ in the presence of two repulsive walls.

4. REPULSIVE WALLS

In order to depict the essential features of the mineral-filled polymers, we replace the intricate situation where the chains are adsorbed on various silica fillers with different surface structures (Fig. 2) by a simpler one (Fig. 3) that we now describe. We suppose that the chains are independent and a single polymer is placed between two infinite repulsive walls. It gives a convenient picture for the mineral fillers, whose typical size is about 10^{-7} m. The walls are parallel and the z axis is chosen to be perpendicular to both. The corresponding interaction is represented by a potential vanishing in the region $0 < z < a$ while it takes infinite values for $z = 0$ or $z = a$, given by⁽¹³⁾

$$V[z(s)] = \delta_s[-\delta[z(s)] + \delta[z(s) - a]]$$

The strength of the polymer–surface interaction is δ_s . To obtain a reflecting barrier, the chain is restricted to be in the space domain $0 \leq z(s) \leq a$. Then, the end-to-end vector distributions automatically satisfy the boundary conditions. We consider the role of (15) on the orientation distribution $G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]$. The polymer is linked to the walls by a set of contact points s_i, s_j such that $z(s_i) = 0$ and $z(s_j) = a$.

The indices i (resp. j) correspond to the wall A (resp. B) and are distributed along the curve $\mathbf{r}(s)$. The chain ends are supposed not to be linked, since the corresponding statistical weights are simpler. This assumption will become more explicit in the next section.

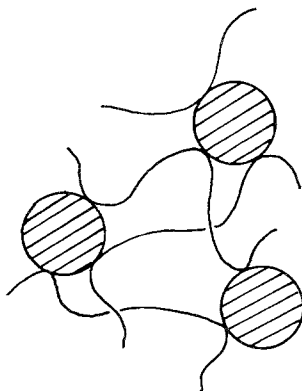


Fig. 2. The real situation corresponds to a many-chain system where the macromolecules are adsorbed on various filler surfaces. The discs with hatched lines represent the mineral fillers.

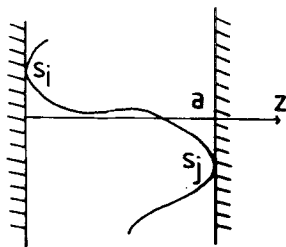


Fig. 3. The model involves two infinite repulsive walls A and B , which are parallel and separated by a distance a . The chain is restricted to be in the domain $0 < z < a$.

5. TWO-WALL ADSORPTION: THERMODYNAMIC PROPERTIES

5.1. Probability Distribution Function

The physical quantities of the system are now calculated from the statistical distribution of the tangent vectors $G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]$. Now we shall concentrate our attention on the situation where the chains have free end orientations. Despite its specificity, the choice made for $Z_0[\mathbf{j}]$ (see below) leads to physical predictions identical to those obtained from the well-known freely jointed chain model.⁽¹⁴⁾ By performing an integration over \mathbf{U}_0 and \mathbf{U}_L compatible with this model, a new distribution $Z_0[\mathbf{j}]$ is derived from $G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]$ in the following way:

$$Z_0[\mathbf{j}] = \int d\mathbf{U}_L \int d\mathbf{U}_0 G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}] = Z_0[\mathbf{j} = \mathbf{0}] \exp(W_0[\mathbf{j}]) \quad (24)$$

An expression for $W_0[\mathbf{j}]$ has been already proposed⁽¹⁰⁾

$$W_0[\mathbf{j}] = \frac{1}{2} \int_0^L \int_0^L j_p(s_1) j_l(s_2) \Delta^{pl}(s_1, s_2) ds_1 ds_2 \quad (25)$$

where $\Delta^{pl}(s_1, s_2) = \delta^{pl} A(s_1, s_2)$, δ^{pl} is the Kronecker symbol, and

$$A(s_1, s_2) = \frac{\text{ch}\{|s_1 - s_2| - L/2\} 1/K\}}{4b \text{sh}\{L/2K\}} \quad (26)$$

If the chain ends are linked to the walls, the situation where no specific choice about \mathbf{U}_0 and \mathbf{U}_L is required is not physically acceptable because of the repulsive character of the walls. We suppose that the physical predictions of the model are not modified in a dramatic way if only a small

fraction of macromolecules have ends that lie in the neighborhood of the walls. Accordingly, we shall only use $Z_0[\mathbf{j}]$ instead of $G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]$ in what follows.

5.2. Averages Values

The above distribution function includes a source $\mathbf{j}(s)$ defined at any point of the chain. The average value of any given functional $f[\mathbf{u}(s)]$ of $\mathbf{u}(s)$ is defined by

$$\langle f[\mathbf{u}(s)] \rangle = \frac{\int_{\mathbf{U}_0}^{\mathbf{U}_L} \mathcal{D}[\mathbf{u}(s)] f[\mathbf{u}(s)] \exp[-\beta \int_0^L F_0(s) ds]}{\int_{\mathbf{U}_0}^{\mathbf{U}_L} \mathcal{D}[\mathbf{u}(s)] \exp[-\beta \int_0^L F_0(s) ds]} \quad (27)$$

This can also be rewritten as

$$\langle f[\mathbf{u}(s)] \rangle = [G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]]^{-1} f \left[\frac{\delta}{\delta \mathbf{j}(s)} \right] G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}] \quad (28)$$

Using $Z_0[\mathbf{j}]$ instead of $G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]$, we get

$$\begin{aligned} \langle f[\mathbf{u}(s)] \rangle &= Z_0^{-1}[\mathbf{j}] f \left[\frac{\delta}{\delta \mathbf{j}(s)} \right] Z_0[\mathbf{j}] \\ &= \exp(-W_0[\mathbf{j}]) f \left[\frac{\delta}{\delta \mathbf{j}(s)} \right] \exp(W_0[\mathbf{j}]) \end{aligned} \quad (29)$$

5.3. Equation of State

In case computation of $\langle \mathbf{u}(s) \rangle$ is of interest, Eq. (29) involves only a first-order functional

$$\langle \mathbf{u}(s) \rangle = \frac{\delta W_0[\mathbf{j}]}{\delta \mathbf{j}(s)} \quad (30)$$

Following the notations of Section 2.3 (see Fig. 3), the source $j_z(s)$ can be expressed as

$$\begin{aligned} j_z(s) &= \beta s \frac{d}{dz(s)} V[z(s)] \\ &= -\beta s \delta_s \frac{d}{dz(s)} [\delta[z(s)] - \delta[z(s) - a]] \end{aligned} \quad (31)$$

Now,

$$\begin{aligned} \langle u_z(s) \rangle &= \int_0^L j_z(s') \Delta(s, s') ds' \\ &= \frac{\beta \delta_s l}{6 \operatorname{sh}\{L/2K\}} \left[\sum_i \frac{f(s_i, s)}{[\dot{z}(s_i)]^2} - \sum_j \frac{f(s_j, s)}{[\dot{z}(s_j)]^2} \right] \end{aligned} \quad (32)$$

where we use the relation

$$\delta[z(s)] = \frac{\sum_i \delta(s - s_i)}{|\dot{z}(s_i)|} \quad \text{for } z(s_i) = 0$$

and

$$f(s_i, s) = f_1(s_i, s) + f_2(s_i, s) \quad (33)$$

where

$$f_1(s_i, s) = \operatorname{ch} \left\{ \frac{1}{K} \left(|s_i - s| - \frac{L}{2} \right) \right\} \quad (34)$$

and

$$f_2(s_i, s) = \frac{s_i}{K} \operatorname{sgn}(s_i - s) \operatorname{sh} \left\{ \frac{1}{K} \left(|s_i - s| - \frac{L}{2} \right) \right\} \quad (35)$$

Moreover, $\langle u_x(s) \rangle$ and $\langle u_y(s) \rangle$ vanish because both $j_x(s)$ and $j_y(s)$ are equal to zero. The state equation, in the end-to-end coordinates, is easily evaluated by integrating $\langle \mathbf{u}(s) \rangle$ over all s values:

$$\langle x \rangle = \int_0^L \langle u_x(s) \rangle ds = 0 \quad (36)$$

$$\langle y \rangle = \int_0^L \langle u_y(s) \rangle ds = 0 \quad (37)$$

$$\begin{aligned} \langle z \rangle &= \int_0^L \langle u_z(s) \rangle ds \\ &= \frac{l}{3} (\beta \delta_s K) \left\{ \sum_i \frac{1}{|\dot{z}(s_i)|^2} - \sum_j \frac{1}{|\dot{z}(s_j)|^2} \right\} \end{aligned} \quad (38)$$

Formula (38) shows that the polymer has to be contracted by the presence of the two walls, since $\langle z \rangle$ vanishes when the chain has no contact points

with walls. Remembering that $V[z(s)]$ is equal to zero when $0 < z(s) < a$, the physical behavior in this space domain must be isotropic. As expected, $\langle z \rangle$ increases with the stiffness K according to Eq. (38).

5.4. Entropy

To calculate the entropy S , it is necessary to know the partition function

$$Z_0[\mathbf{j}] = \exp(W_0[\mathbf{j}]) \quad (39)$$

Replacing $j_z(s)$ by

$$\beta s \delta_s \frac{d}{dz(s)} [z(s)] \quad (40)$$

it is possible to give an exact expression for W_0 :

$$W_0 = \frac{(\beta \delta_s l)(\beta \delta_s K)}{12 \operatorname{sh}\{L/2K\}} \left\{ \sum_{i,i'} \frac{h(s_i, s'_i)}{|\dot{z}(s_i)|^2 |\dot{z}(s'_i)|^2} + \sum_{j,j'} \frac{h(s_j, s'_j)}{|\dot{z}(s_j)|^2 |\dot{z}(s'_j)|^2} - 2 \sum'_{i,j} \frac{h(s_i, s_j)}{|\dot{z}(s_i)|^2 |\dot{z}(s_j)|^2} \right\} \quad (41)$$

with

$$h(s_i, s_j) = \left(1 - \frac{s_i s_j}{K^2} \right) \operatorname{ch} \left\{ \frac{1}{K} \left(|s_i - s_j| - \frac{L}{2} \right) \right\} + \frac{|s_i - s_j|}{K} \operatorname{sh} \left\{ \frac{1}{K} \left(|s_i - s_j| - \frac{L}{2} \right) \right\} \quad (42)$$

The calculation is based on the fact that the chain ends are not linked to the wall.

We can easily show that the entropy S can simply be related to W_0 through

$$S = -kW_0 \quad (43)$$

According to the previous results, W_0 depends upon the ratio K/L . By increasing K/L , or δ_s , the number of configurations decreases and the chain entropy is reduced. The discussion of the results is easier in the limit $K \gg 1$, since

$$\lim_{K \rightarrow \infty} h(s_i, s_j) = 1 \quad (44)$$

and consequently, W_0 can be written in this limit as

$$W_0 = \frac{(\beta\delta_s l)(\beta\delta_s L)}{6} \left(\frac{K}{L}\right)^2 (E_A + E_B - 2E_{AB}) \quad (45)$$

where

$$E_A = \sum_{i,i'} \frac{1}{|\dot{z}(s_i)|^2 |\dot{z}(s'_i)|^2} \quad (46)$$

$$E_B = \sum_{j,j'} \frac{1}{|\dot{z}(s_j)|^2 |\dot{z}(s'_j)|^2} \quad (47)$$

$$E_{AB} = \sum_{i,j} \frac{1}{|\dot{z}(s_i)|^2 |\dot{z}(s_j)|^2} \quad (48)$$

The last term in (45) includes two individual energies E_A and E_B relative to each separated wall. An interaction energy E_{AB} arising from the wall connection due to the polymer has to be subtracted from these. A flexibility effect can be described in the limit $K/L \gg 1$ starting from (45). When we deal with two disconnected chains (Fig. 4), each linked to a wall, W_0 becomes

$$W_0 = \frac{(\beta\delta_s l)(\beta\delta_s L)}{6} \left(\frac{K}{L}\right)^2 (E_A + E_B) \quad (49)$$

Now, the fact that the two chains are linked together sharply raises the entropy because of the presence of E_{AB} (Fig. 5).

This behavior can be understood by looking at the simpler situation where the chain only connects two points in front of each other (Fig. 6). When the chain is cut, the allowed configurations of each part are principally those contained in the planes, as a consequence of the stiffness.

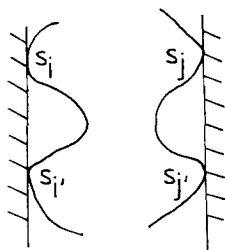


Fig. 4. The two disconnected chains are each linked on a wall.

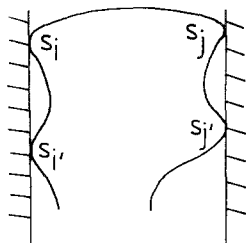


Fig. 5. The $A-B$ wall connection is realized by a single macromolecule.

To evaluate their number, it is sufficient to count all the possible rod orientations in a plane.

But when both pieces are joined together, the number of allowed configurations is increased, since we also have to take into account the orientations of the chain portion included between the planes, the bulk, in addition to those lying in the surfaces. Subsequently, the entropy is increased.

5.5. Dependence of the Free Energy upon the Distance between Walls

In fact, in the whole polymer system, either the chains are linked to different mineral fillers or they form loops on each surface. Since the contact points are randomly distributed, physical quantities have to be averaged over all s_i, s_j values. By way of illustration, we suppose that the

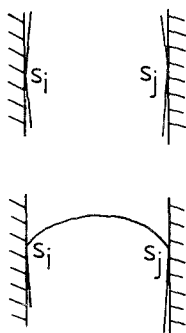


Fig. 6. Very stiff chain illustration; each polymer part behaves as a rod. Those with only one contact point tend to collapse on the walls, while those connecting $A-B$ walls are very bent.

corresponding probability distribution $P(s_i, s_j)$ is rectangular, and we consider chains with only one contact point on each wall:

$$P(s_i, s_j) = \frac{1}{L(L-a)} \quad \text{if } 0 \leq s_i \leq L \text{ and } L \geq s_j - s_i \geq a \quad (50)$$

$$P(s_i, s_j) = 0 \quad \text{otherwise}$$

with s_i on the A wall, s_j on the B wall, and $s_j > s_i$.

Although this crude assumption appears unrealistic to model an experimental situation, the resulting free energy qualitatively reflects the global behavior of a polymer solution with mineral fillers. An equilibrium distance between the walls can be found when F reaches its single minimum (Fig. 7); this explains the absence of collapse of such a polymer solution. Some stiffness effects can also be discussed (see the end of the section).

Taking the previous hypothesis into account and

$$|\dot{z}(s_i)| = 1$$

the free energy is now

$$\beta F = -\frac{(\beta \delta_s l)(\beta \delta_s L)}{6 \operatorname{sh}\{L/2K\}} h(s_i, s_j) \quad (51)$$

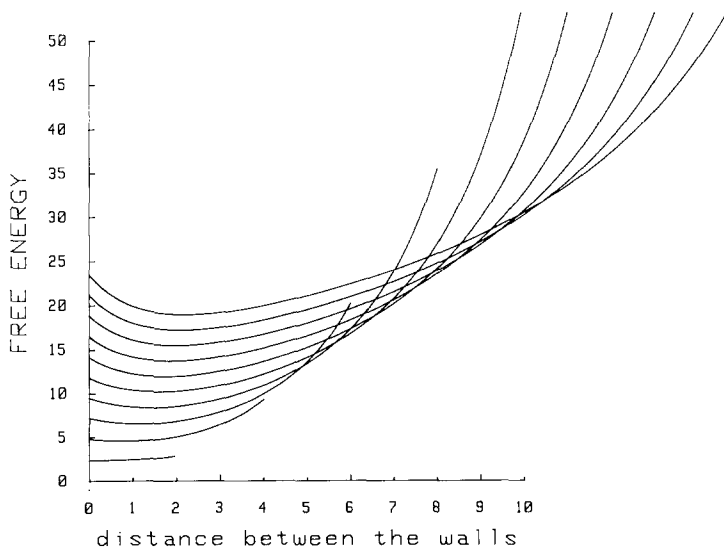


Fig. 7. Theoretical free energy behavior according to formula (54), when the dimensionless parameter a/K varies. Each plot corresponds to a chain length and exhibits a minimum which is the equilibrium distance between walls.

where

$$h(s_i, s_j) = \left(1 - \frac{s_i s_j}{K^2}\right) \operatorname{ch} \left\{ \frac{1}{K} \left(|s_i - s_j| - \frac{L}{2} \right) \right\} + \frac{|s_i - s_j|}{K} \operatorname{sh} \left\{ \frac{1}{K} \left(|s_i - s_j| - \frac{L}{2} \right) \right\} \quad (52)$$

Thus, the average free energy can be calculated:

$$\beta \bar{F} = \int_0^L \int_0^L ds_i ds_j P(s_i, s_j) \beta F \quad (53)$$

$$\beta \bar{F} = \frac{(\beta \delta_s l)(\beta \delta_s L)}{6(a' - L')} \left[\left(\frac{a' L'}{2} + \frac{L'}{3} \right)^2 \frac{\operatorname{sh}(a' - L'/2)}{\operatorname{sh}\{L'/2\}} - \left(a' + \frac{L'}{2} \right) \frac{\operatorname{ch}(a' - L'/2)}{\operatorname{sh}\{L'/2\}} - \frac{5}{6} L'^2 + \frac{3}{2} L' \operatorname{cth} \left\{ \frac{L'}{2} \right\} \right] \quad (54)$$

with

$$a' = a/K \quad \text{and} \quad L' = L/K$$

Free energy plots of $6\beta \bar{F}/(\beta \delta_s l)(\beta \delta_s L)$, taking a' as a variable for different L' values, always exhibit a minimum (Fig. 7). This minimum corresponds to the equilibrium distance between the walls; it satisfies the equation

$$\frac{\partial \bar{F}}{\partial a'} = 0$$

and therefore,

$$\left(-a'^2 + \frac{a' L'}{2} - \frac{L'^2}{3} \right) \frac{\operatorname{sh}(a' - L'/2)}{\operatorname{sh}\{L'/2\}} + \left(\frac{a'^2 L'}{2} - \frac{a' L'^2}{6} - \frac{L'^3}{3} \right) \frac{\operatorname{ch}(a' - L'/2)}{\operatorname{sh}\{L'/2\}} + \frac{5}{6} L'^2 = 0 \quad (55)$$

Figure 8 shows how this equilibrium length varies as a function of L , showing that K is homogeneous to a length which measures stiffness range.

When $K > L$, stiffness effects are present within all chains, and the polymer exhibits rodlike behavior, being entirely unfolded between the plates. Accordingly, in the vicinity of the origin, the $a(L)$ dependence is nearly linear. Moreover, when $K \ll L$, the stiffness is only sensitive within small chain parts, bent configurations are allowed, and the increase of $a(L)$ slows down.

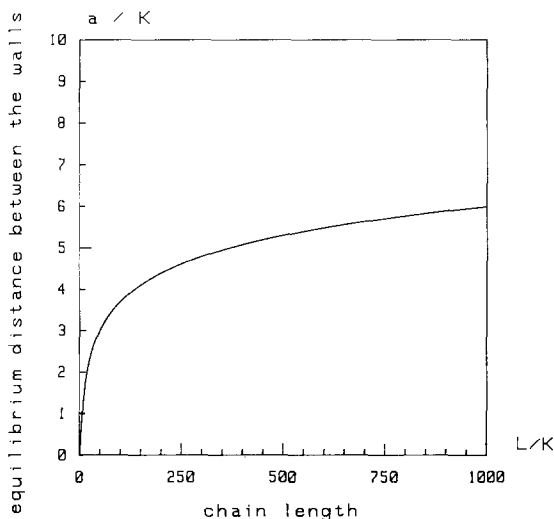


Fig. 8. Numerical illustration of the wall equilibrium distance deduced from (55). The increase of a/K as a function of L/K is a typical flexibility effect.

6. NMR PROPERTIES

We now turn to the computation of the average value for dipolar coupling $D(s)$ in the case where a single macromolecule is confined inside two infinite repulsive walls.

Formula (28), involving squares of $\mathbf{u}(s)$ components, can be reexpressed using second-order derivatives of $G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]$:

$$D(s) = M_{pl} \left[\frac{\delta^2 \text{Ln } G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]}{\delta j_p(s) \delta j_l(s)} - \frac{\delta \text{Ln } G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]}{\delta j_p(s)} \frac{\delta \text{Ln } G_0[\mathbf{U}_0, \mathbf{U}_L, \mathbf{j}]}{\delta j_l(s)} \right] \quad (56)$$

with

$$M_{pl} = \frac{3}{5} \begin{pmatrix} -1 & & \\ & -1 & \\ & & 2 \end{pmatrix}$$

After integration over \mathbf{U}_0 and \mathbf{U}_L , (56) becomes

$$D(s) = M_{pl} \left[\frac{\delta^2 W_0[\mathbf{j}]}{\delta j_p(s) \delta j_l(s)} + \frac{\delta W_0[\mathbf{j}]}{\delta j_p(s)} \frac{\delta W_0[\mathbf{j}]}{\delta j_l(s)} \right] \quad (57)$$

Using definition (25), we obtain

$$\frac{\delta^2 W_0}{\delta j_p(s) \delta j_l(s)} = \delta^{pl} \Delta(s, s) \quad (58)$$

which is independent of \mathbf{j} . Since $\text{Tr } M = 0$, the corresponding term in (47) vanishes. The contributions to $D(s)$ arise only from the equation of state:

$$\langle u_p(s) \rangle = \frac{\delta W_0[\mathbf{j}]}{\delta j^p(s)} \quad (59)$$

so that the expression in Eq. (57) acquires a simpler form:

$$D(s) = \frac{3}{5} (3 \cos^2 \eta - 1) [\langle u_z(s) \rangle]^2 \quad (60)$$

For the sake of simplicity, let us first deal with a single repulsive wall, by taking $z = 0$. The chain is contained in the half-space $z \geq 0$. An expression for $D(s)$ is obtained directly from (60) and (32):

$$\begin{aligned} D(s) = & \frac{3}{5} (3 \cos^2 \eta - 1) \left(\frac{\beta \delta_s l}{6 \text{sh}\{L/2K\}} \right)^2 \sum_{i,i'} \frac{1}{|\dot{z}(s_i)|^2 |\dot{z}(s_{i'})|^2} \\ & \times \{ f_1(s_i, s) f_1(s_{i'}, s) + f_1(s_i, s) f_2(s_{i'}, s) \\ & + f_1(s_{i'}, s) f_2(s_i, s) + f_2(s_i, s) f_2(s_{i'}, s) \} \end{aligned} \quad (61)$$

where f_1 and f_2 are defined by (34) and (35).

In most cases NMR measurements give access to the residual dipolar coupling D for the whole polymer:

$$D = \frac{1}{L} \int_0^L D(s) ds \quad (62)$$

The integration over contour lengths leads to

$$D = \frac{3}{5} (3 \cos^2 \eta - 1) \left(\frac{\beta \delta_s l}{6 \text{sh}\{L/2K\}} \right)^2 \sum_{i,i'} \frac{g(s_i, s_{i'})}{|\dot{z}(s_i)|^2 |\dot{z}(s_{i'})|^2} \quad (63)$$

and

$$\begin{aligned} g(s_i, s_{i'}) = & \left(1 - \frac{s_i s_{i'}}{K^2} \right) \text{ch} \left\{ \frac{|s_i - s_{i'}|}{K} \right\} \\ & + \frac{K}{L} \text{sh} \left\{ \frac{L}{K} \right\} \left(1 - \frac{s_i s_{i'}}{K^2} \right) \text{ch} \left\{ \frac{|s_i - s_{i'}|}{K} \right\} \\ & - \frac{K}{L} \text{ch} \left\{ \frac{L}{K} \right\} \left(1 - \frac{s_i s_{i'}}{K^2} \right) \frac{|s_i - s_{i'}|}{K} \text{sh} \left\{ \frac{|s_i - s_{i'}|}{K} \right\} \end{aligned} \quad (64)$$

The case of two repulsive walls can be immediately deduced from the expression above, by summations over indices i, i' (resp. j, j') for the A wall (resp. B), and mixed summations over i, j (Fig. 5):

$$D = \frac{3}{5} (3 \cos^2 \eta - 1) \left(\frac{\beta \delta_s l}{6 \operatorname{sh}\{L/2K\}} \right)^2 \left\{ \sum_{i,i'} \frac{g(s_i, s_{i'})}{|\dot{z}(s_i)|^2 |\dot{z}(s_{i'})|^2} + \sum_{j,j'} \frac{g(s_j, s_{j'})}{|\dot{z}(s_j)|^2 |\dot{z}(s_{j'})|^2} - 2 \sum_{i,j} \frac{g(s_i, s_j)}{|\dot{z}(s_i)|^2 |\dot{z}(s_j)|^2} \right\} \quad (65)$$

This formula does not show any symmetry property because the contact points are uniformly distributed. Fitting the relaxation spectra with (65) remains rather difficult since it depends upon a large number of parameters, $\beta \delta_s l$, s_i/K , s_j/K , L/K . For comparison with experiments a further calculation, including the choice of the derivatives $\dot{z}(s_i)$ and a realistic probability measure over all contact points $P(s_i, s_j)$, is needed. The situation becomes simpler in the case of very stiff chains, since then the quantities s_i/K , s_j/K , L/K vanish in the limit of $K \rightarrow \infty$. Then we have

$$\lim_{K \rightarrow \infty} g(s_i, s_j) = 2 \quad (66)$$

and

$$D = \frac{2}{15} (3 \cos^2 \eta - 1) (\beta \delta_s l)^2 \left(\frac{K}{L} \right)^2 (E_A + E_B - 2E_{AB}) \quad (67)$$

The prefactor contains expected terms, because the anisotropy increases with the ratio stiffness over the chain length K/L and with the polymer surface interaction parameter $\beta \delta_s l$. The A - B wall connection, due to the polymer, reduces the anisotropy, as already shown. Although this result is quite trivial, it could, in principle, predict the NMR response for a spin system of a polymer sample at low temperatures where $K \rightarrow \infty$.

7. CONCLUSION

The first purpose of this work was to establish a continuous chain model, using a path integral formulation, which can apply to polymer adsorption at surfaces. The stochastic measures introduced to describe the behavior of a stiff macromolecule were of Wiener type. In this description, the constraints along the chain can be conveniently represented by a local potential acting on the monomeric units. If the corresponding Hamiltonian in Eq. (11) remains isotropic, no orientational order is induced upon the polymer segments and the average end-to-end chain vector vanishes. But

the presence of two repulsive walls breaks the rotational symmetry of the physical space, except in the direction to parallel plates. This constraint leads to a probability distribution which is equivalent to a Ginzburg-Landau functional with a local magnetic field. As expected, the average value of the end-to-end z coordinate does not vanish and it is an increasing function of both the stiffness and the number of contact points on the walls [Eq. (38)]. The Wiener-type formulation allows us to calculate the equilibrium distance between the walls through the minimization of the free energy. It is a way of understanding the distribution of the mineral fillers within the polymer system.

The second aim of this work was to connect our statistical approach with NMR experiments. Introducing $\mathbf{u}(s)$ as the tangent vector along the continuous chain, we take $\mathbf{u}(s)$ as order parameter. As shown in this paper, the dipolar interaction between the spins can be expressed using $\mathbf{u}(s)$. The deviations from isotropy, resulting from the confinement effects within a space domain bounded by the walls, generate a residual dipolar energy. This fact is already mentioned in a previous paper,⁽³⁾ where the topological constraints were applied to chain ends. Considering the reflections on the walls, the orientational order increases the dipolar energy and decreases the entropy. For very stiff chains the previous quantities are proportional to each other [Eqs. (45), (67)].

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