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On a path integral having application in polymer physics

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Abstract. Using a path integral approach an explicit expression is obtained for the two-particle probability of a polymer chain for which both the elastic energy of stretching and the elastic energy of bending are taken into account. The end-to-end distribution function is extracted from this result. We point out that because of the elastic energy of bending the probability is non-Markoffian and, thus, in this case the two-particle probability is not identical in form to the end-to-end distribution. Moreover, when calculating averages over the length of the polymer it is necessary to use the two-particle probability rather than the end-to-end distribution. As an example we calculate the particle scattering factor for a dilute solution of polymers.

1. Introduction

The chain model has been used for simulating the configurational behaviour of polymers. In particular, the continuous chain model has the advantage that one can employ the methods of functional integration as has been shown in a series of papers by Edwards (see, e.g., Edwards 1965, 1969, 1974). Early work on the theory of polymer distribution functions includes that of Daniels (1952) and Hermans and Ullman (1952). A discussion of models employed for simulating polymers together with the associated probabilities is given by Freed (1971) and by Yamakawa and Fujii (1973, 1974).

In the present work we deal with the configurational probabilities of molecular chains in a state of thermodynamic equilibrium. For a chain of molecular units $0, 1, 2, \dots, N$ the probability of finding a particular configuration of the molecules in the vicinity of the points $\mathbf{x}_0, \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N$ is given by

$$P(\mathbf{x}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \prod_{j=0}^N d\mathbf{x}_j = \frac{\exp(-\beta U)}{\int \exp(-\beta U) \prod_{j=0}^N d\mathbf{x}_j} \prod_{j=0}^N d\mathbf{x}_j, \quad (1.1)$$

where $U = U(\mathbf{x}_0, \mathbf{x}_1, \dots, \mathbf{x}_N)$ is the intermolecular potential energy of the chain and $\beta = (kT)^{-1}$. Probability (1.1) contains more thermodynamic information than is usually needed for calculations. Thus, for example, a two-point reduced distribution

$$P_{jk}(\mathbf{x}_j, \mathbf{x}_k) d\mathbf{x}_j d\mathbf{x}_k = d\mathbf{x}_j d\mathbf{x}_k \int P(\mathbf{x}_0, \mathbf{x}_1, \dots, \mathbf{x}_N) \prod_{\substack{i=0 \\ i \neq j, k}}^N d\mathbf{x}_i \quad (1.2)$$

suffices in many cases of interest. The frequently used end-to-end distribution (e.g., see Flory 1969) is obtained for $j = 0$ and $k = N$.

In this paper we obtain the two-particle distribution for a continuous polymer chain model for which both the elastic energy of stretching and the elastic energy of bending are taken into account. In the discrete counterpart of the model the stretching corresponds to nearest-neighbour linear interactions and the bending is associated with first- and second-nearest-neighbour linear interactions. In our approach we show how the picture of a continuous chain employed by Edwards (1965) arises from statistical mechanical principles when the number of particles in the chain increases indefinitely. In this case the label of a point in the chain is the contour length s of the polymer segment from one of its ends to the point in question. In the continuous model the probability (1.2) goes over to $P_{ss'}(\mathbf{x}, \mathbf{x}') d\mathbf{x} d\mathbf{x}'$.

For the case we wish to consider, the potential energy takes the form: (discrete case)

$$U[\mathbf{x}_j] = \sum_{j=0}^{N-1} \frac{\alpha (\mathbf{x}_{j+1} - \mathbf{x}_j)^2}{2 \Delta s_j} + \sum_{j=1}^{N-1} \frac{\gamma (\mathbf{x}_{j+1} - 2\mathbf{x}_j + \mathbf{x}_{j-1})^2}{2 (\Delta s_j)^3}; \quad (1.3a)$$

(continuous case)

$$U[\mathbf{x}(s)] = \frac{1}{2} \int_0^L \left[\alpha \left(\frac{d\mathbf{x}}{ds} \right)^2 + \gamma \left(\frac{d^2\mathbf{x}}{ds^2} \right)^2 \right] ds. \quad (1.3b)$$

The first term in (1.3a) and (1.3b) represents the elastic energy of stretching and the second the elastic energy of bending (torsion). The coefficient $\alpha = 3/(l\beta)$, where l is the mean bond length (see Edwards and Freed 1970).

When $\gamma = 0$ the two-point probability evaluation is particularly simple and is given by

$$P_{ss'}(\mathbf{x}, \mathbf{x}') d\mathbf{x} d\mathbf{x}' = V^{-1} G(\mathbf{x}s | \mathbf{x}'s') d\mathbf{x} d\mathbf{x}', \quad (1.4a)$$

where

$$G(\mathbf{x}s | \mathbf{x}'s') = \left(\frac{\alpha\beta}{2\pi|s-s'|} \right)^{3/2} \exp\left(-\frac{\alpha\beta}{2|s-s'|} (\mathbf{x} - \mathbf{x}')^2 \right). \quad (1.4b)$$

With appropriate interpretation of $|s-s'|$, G is the conditional probability distribution for a free Brownian particle. The track of a Brownian particle simulates a linear polymer (Kuhn 1934). The probability G is Markoffian, i.e.

$$G(\mathbf{x}s | \mathbf{x}'s') = \int G(\mathbf{x}s | \mathbf{x}''s'') G(\mathbf{x}''s'' | \mathbf{x}'s') d\mathbf{x}''. \quad (1.5)$$

Property (1.5) enables one to consider the polymer segments from s to s' independently of the exterior segments of the polymer chain. The interesting feature when one includes the energy of bending is that the Markofficity of the chain is destroyed and, therefore, the end-to-end probability of a segment of the polymer can no longer be considered independent of the polymer as a whole.

The case of potential energy (1.3b) (bending included) was considered by Saito *et al* (1967) who approached the problem by solving an approximate differential equation in polar coordinates. Also Edwards and Freed (1970) used a differential equation for the probability using phase space variables. In the present work we carry out a functional integral evaluation of the probability and produce an explicit expression. We apply our result to the problem of light scattering from weak solutions of polymers.

2. Path integral evaluation

To enable ourselves to proceed with the path integral evaluation of a two-particle (two-point) distribution of a continuous chain of particles we work as follows: we consider initially the discrete case and then proceed to the limit of continuity. Let s, s' be the positions of two particles in the chain and let $j_s, j_{s'}$ be the corresponding indices labelling the particles at the positions s, s' . Then the two-particle distribution takes the form:

$$P_{ss'}^{(N)}(\mathbf{x}, \mathbf{x}') \, d\mathbf{x} \, d\mathbf{x}' = \frac{1}{Z^{(N)}} \left(\int \exp(-\beta U) \delta(\mathbf{x} - \mathbf{x}_{j_s}) \delta(\mathbf{x}' - \mathbf{x}_{j_{s'}}) \prod_{j=0}^N d\mathbf{x}_j \right) \, d\mathbf{x} \, d\mathbf{x}' \quad (2.1a)$$

where $Z^{(N)}$ is the configurational partition function for the system, given by:

$$Z^{(N)} = \int \exp(-\beta U) \prod_{j=0}^N d\mathbf{x}_j. \quad (2.1b)$$

Now, if we pass to the limit of the continuous chain, both $Z^{(N)}$ and the multiple integral $P_{ss'}^{(N)}$ go to zero. Of course, their ratio goes to something between 0 and 1. We can extract the limit by multiplying both the integral (numerator) and $Z^{(N)}$ (denominator) through by the factor $[\prod_{j=0}^{N-1} \alpha\beta/2\pi(\Delta s_j)^3]^{3/2}$ thus making out of the numerator and denominator proper path integrals.

We have for the two-particle distribution:

$$P_{ss'}^{(N)}(\mathbf{x}, \mathbf{x}') = \frac{1}{Z_1^{(N)}} \int \exp(-\beta U) \delta(\mathbf{x} - \mathbf{x}_{j_s}) \delta(\mathbf{x}' - \mathbf{x}_{j_{s'}}) \left(\prod_{j=0}^{N-1} \frac{1}{\Delta s_j} \right)^3 \mathcal{D}[\mathbf{x}_j] \, d\mathbf{x}_0 \, d\mathbf{x}_N, \quad (2.2a)$$

where

$$Z_1^{(N)} = \int \exp(-\beta U) \left(\prod_{j=0}^{N-1} \frac{1}{\Delta s_j} \right)^3 \mathcal{D}[\mathbf{x}_j] \, d\mathbf{x}_0 \, d\mathbf{x}_N, \quad (2.2b)$$

and where $\mathcal{D}[\mathbf{x}_j]$ is the path differential:

$$\mathcal{D}[\mathbf{x}_j] = \left(\frac{\alpha\beta}{2\pi\Delta s_0} \right)^{3/2} \prod_{j=1}^{N-1} \left(\frac{\alpha\beta}{2\pi\Delta s_j} \right)^{3/2} d\mathbf{x}_j. \quad (2.2c)$$

The appearance of the factor $\prod_{j=0}^{N-1} (\Delta s_j)^{-3}$ in (2.2a, b) in addition to the normalizing factor of the usual path differential is due to the three-particle interaction in the potential energy, essentially against which the averaging is done. In contrast, in the Feynman path integral the averaging relates to the kinetic energy, whereas here we have what would correspond to something proportional to the square of the acceleration.

We proceed to the evaluation of our path integral by making the transformation from the variables $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N$ to $\mathbf{v}_0, \mathbf{v}_1, \dots, \mathbf{v}_{N-1}$ through

$$\mathbf{v}_j = \frac{\mathbf{x}_{j+1} - \mathbf{x}_j}{\Delta s_j}. \quad (2.3)$$

The Jacobian of the transformation is

$$\left| \frac{\partial \mathbf{x}_l}{\partial \mathbf{v}_k} \right| = \left(\prod_{j=0}^{N-1} \Delta s_j \right)^3.$$

Upon introducing the transformation (2.3) into (2.2a, b) we are led in the limit of continuity to the following expression for our two-point distribution:

$$P_{ss'}(\mathbf{x}, \mathbf{x}') = Z_1^{-1} \int d\mathbf{x}_0 d\mathbf{v}_0 \int_{\substack{\mathbf{v}(0)=\mathbf{v}_0 \\ \mathbf{v}(L)=\mathbf{0}}} \exp\left(-\frac{\beta}{2} \int_0^L (\gamma \dot{\mathbf{v}}^2(s) + \alpha \mathbf{v}^2(s)) ds\right) \times \delta\left(\mathbf{x} - \mathbf{x}_0 - \int_0^s \mathbf{v}(s'') ds''\right) \delta\left(\mathbf{x}' - \mathbf{x}_0 - \int_0^{s'} \mathbf{v}(s'') ds''\right) \mathcal{D}[\mathbf{v}] \tag{2.4a}$$

where Z_1 is now the limiting value of (2.2b) when $N \rightarrow \infty$, i.e.

$$Z_1 = \int d\mathbf{x}_0 d\mathbf{v}_0 \int_{\substack{\mathbf{v}(0)=\mathbf{v}_0 \\ \mathbf{v}(L)=\mathbf{0}}} \exp\left(-\frac{\beta}{2} \int_0^L (\gamma \dot{\mathbf{v}}^2(s) + \alpha \mathbf{v}^2(s)) ds\right) \mathcal{D}[\mathbf{v}]. \tag{2.4b}$$

The path integrals appearing in (2.4a, b) are now of known forms. The one in (2.4b) is that for an harmonic oscillator, while the one in (2.4a) by a Fourier decomposition of the δ functions involved becomes that for a forced harmonic oscillator. These path integrals, when s stands for time, are path integrals in velocity space. For transformations of such path integrals see Papadopoulos (1967, 1968). We have:

$$P_{ss'}(\mathbf{x}, \mathbf{x}') = Z_1^{-1} (2\pi)^{-6} \int d\mathbf{q} d\mathbf{q}' d\mathbf{x}_0 d\mathbf{v}_0 \exp[i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}_0) + i\mathbf{q}' \cdot (\mathbf{x}' - \mathbf{x}_0)] \times \int \exp\left(-\beta \int_0^L \left[\frac{1}{2}\gamma \dot{\mathbf{v}}^2(s'') + \frac{1}{2}\alpha \mathbf{v}^2(s'') + i\beta^{-1}(\mathbf{q}\theta(s-s'') + \mathbf{q}'\theta(s'-s''))\right] \times \mathbf{v}(s'') ds''\right) \mathcal{D}[\mathbf{v}] \tag{2.5}$$

where $\theta(s)$ is the Heaviside step function.

Using, appropriately, the expression for the propagator for a forced harmonic oscillator (see Feynman and Hibbs 1965, Papadopoulos 1969) and the expression for the propagator of a simple harmonic oscillator (2.5) becomes:

$$P_{ss'}(\mathbf{x}, \mathbf{x}') = (\int d\mathbf{x}_0 d\mathbf{v}_0 \exp(-\beta S_0))^{-1} (2\pi)^{-6} \int d\mathbf{q} d\mathbf{q}' d\mathbf{x}_0 d\mathbf{v}_0 \exp(-\beta S_1). \tag{2.6}$$

In this expression

$$S_0 = \frac{1}{2}\gamma\Omega v_0^2 \coth(\Omega L), \tag{2.7a}$$

and

$$S_1 = \frac{1}{2}\gamma\Omega v_0^2 \coth(\Omega L) + i(\beta\Omega)^{-1} \mathbf{v}_0 \cdot (\mathbf{q}A(s) + \mathbf{q}'A(s')) + (\gamma\Omega^3\beta^2)^{-1} [\mathbf{q}^2B(s) + \mathbf{q}'^2B(s') + \mathbf{q} \cdot \mathbf{q}'(C(s, s')\theta(s'-s) + C(s', s)\theta(s-s'))], \tag{2.7b}$$

where

$$A(s) = [1 - \cosh(\Omega s)] \coth(\Omega L) + \sinh(\Omega s), \tag{2.7c}$$

$$B(s) = \frac{1}{2}\Omega s - \frac{1}{2}[1 - \cosh(\Omega s)]^2 \coth(\Omega L) - [1 - \cosh(\Omega s)] \sinh(\Omega s), \tag{2.7d}$$

$$C(s, s') = \Omega s - [1 - \cosh(\Omega s)][1 - \cosh(\Omega s')] \coth(\Omega L) - \sinh(\Omega s) - [1 - \cosh(\Omega s)] \sinh(\Omega s') \tag{2.7e}$$

and

$$\Omega = (\alpha/\gamma)^{1/2}. \tag{2.7f}$$

In proceeding with this result it is convenient to assume, say, $s < s'$ but clearly from the symmetry of the problem our final answer cannot depend on an interchange of s and s' . Thus performing the remaining integrals which are straightforward one finds

$$P_{ss'}(\mathbf{x}, \mathbf{x}') = \frac{1}{V} \left(\frac{\gamma \Omega^3 \beta}{2\pi D(s, s', L)} \right)^{3/2} \exp\left(-\frac{\gamma \Omega^3 \beta}{2D(s, s', L)} (\mathbf{x} - \mathbf{x}')^2 \right) \quad (2.8a)$$

where

$$D(s, s', L) = \Omega |s - s'| - \{1 + \cosh[\Omega(s + s')] - \cosh[\Omega(s - s')]\} \tanh(\Omega L) \\ + \sinh[\Omega(s + s')] - \sinh(\Omega |s - s'|) - \sinh[\Omega(s + s')] \cosh(\Omega |s - s'|). \quad (2.8b)$$

The expression (2.8b) can be written in a somewhat more compact form but, rather we chose to demonstrate that s and s' can be made to appear only as a sum and difference in $D(s, s', L)$. We also emphasize that this two-point probability depends on the entire length L of the chain. Here the dependence on s, s' and on L is a manifestation of the non-Markofficity of the chain when the elastic energy of bending is included in the interatomic potential. This is in contrast to the situation for which only the stretching elastic energy is taken into account in the interatomic potential. In this latter case (cf equation (1.4b)) the two-point probability depends only on the difference of the arc lengths $|s - s'|$. In fact, in this instance the two-point probability corresponding to an integral segment of the chain has the same form as the end-to-end probability.

We can find the end-to-end probability corresponding to equations (2.8a, b) by letting $s \rightarrow 0, s' \rightarrow L$ and noting that $D(0, L, L) = \Omega L - \tanh(\Omega L)$. Then

$$P_{0L}(\mathbf{x}_0, \mathbf{x}_L) = \frac{1}{V} \left(\frac{\gamma \Omega^3 \beta}{2\pi[\Omega L - \tanh(\Omega L)]} \right)^{3/2} \exp\left(-\frac{\gamma \Omega^3 \beta (\mathbf{x}_L - \mathbf{x}_0)^2}{2[\Omega L - \tanh(\Omega L)]} \right). \quad (2.9)$$

From this result one can obtain, for example, the end-to-end moments

$$\langle \mathbf{x}^2 \rangle = 3[\Omega L - \tanh(\Omega L)] / (\gamma \Omega^3 \beta), \quad (2.9a)$$

and

$$\langle (\mathbf{x}^2)^2 \rangle = 15[\Omega L - \tanh(\Omega L)]^2 / (\gamma \Omega^3 \beta)^2. \quad (2.9b)$$

(2.9) agrees with the corresponding result of Freed (1971). However, the new result here is the joint probability distribution $P_{ss'}(\mathbf{x}, \mathbf{x}')$ for any two points of the chain. It is precisely this distribution that has to be employed for light scattering calculations. This is done in the next section. In contrast Saito *et al* (1967) and Freed (1971) essentially make use of the end-to-end distribution for trimmed away chains, a thing not applicable in the present case.

3. Particle scattering factor

With the aid of the two-point probability one can find the particle scattering factor $P(\mu)$ which gives the angular distribution of the intensity of electromagnetic radiation scattered from a solution of polymers. If \mathbf{k}_0 and \mathbf{k} are the propagation vectors for the

incident and scattered beams, one has for a dilute solution of polymers, that

$$P(\mu) = L^{-2} \int_0^L ds \int_0^L ds' \int P_{ss'}(\mathbf{x}, \mathbf{x}') \exp[i\boldsymbol{\mu} \cdot (\mathbf{x} - \mathbf{x}')] d\mathbf{x} d\mathbf{x}'. \quad (3.1)$$

where $\mu = |\mathbf{k} - \mathbf{k}_0|$ (see Flory 1969). In the case where only the elastic energy of stretching is taken into account one uses equation (1.4) in (3.1) and finds

$$P(\mu) = 2 \left\{ \left(\frac{2\alpha\beta}{\mu^2 L} \right)^2 \left[\exp\left(-\frac{\mu^2 L}{2\alpha\beta} \right) - 1 \right] + \frac{2\alpha\beta}{\mu^2 L} \right\}. \quad (3.2)$$

Likewise, when both stretching and bending elastic energies are taken into account, one uses equation (2.8a) in (3.1) and finds

$$P(\mu) = L^{-2} \int_0^L ds \int_0^L ds' \exp[-\mu^2 D(s, s', L) / (2\gamma\Omega^3\beta)], \quad (3.3)$$

where $D(s, s', L)$ is given by (2.8b). This expression can be evaluated numerically in terms of the quantities $\alpha\beta L$ and $\eta = (\gamma/L)/(\alpha L)$. The results are shown in figure 1 for several values of η . It is evident from this figure that the bending can make a considerable contribution to the scattering.

As a final remark, by taking $\gamma \rightarrow 0$, the ratio $D/(\gamma\Omega^3)$ goes to $|s - s'|$ and in this limit the double integral in (3.3) can be evaluated, leading again to the Debye form (3.2) for $P(\mu)$.

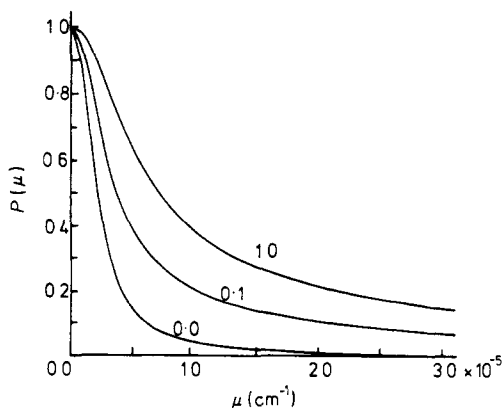


Figure 1. The particle scattering factor $P(\mu)$ against μ for different values of η . The curves correspond to the same asymptotic end-to-end distance $L\Omega/(\gamma\Omega^3\beta) = L/(\alpha\beta)$. The energy per bond associated with these modes is about 10^{-2} eV and typical bond lengths are 1–2 Å. Thus, taking $\beta^{-1} \sim 10^{-2}$ eV at room temperature and letting $L = 1 \mu\text{m}$ we used $\alpha\beta L = 10^4$ to obtain these plots. The case $\eta = 0.0$ corresponds to stretching only.

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