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Fig. 1

Figure 1: Fig. 1

Abstract

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PHYSICS

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ON THE CONFIGURATIONAL STATISTICS OF HIGH-MOLECULAR CHAINS

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The methods existing in the configurational statistics of high-molecular chains are usually based on the so-called approximation of independent rotations or free gyroscopes (^{1}). The first attempt to consider the model of "hindered rotations" was made in (^{2}). In (^{2}) and other works, approximate calculations were given for the configurational integral for potentials depending only on the differences of spatial angles between planes passing through pairs of neighboring links. In the present work a method is given for the exact calculation of the configurational integral for the latter model, and a planar polymer chain of the type analyzed in (^{3}) is also considered.

1. Planar high-molecular chain. Let us consider a high-molecular chain consisting of N links of equal length l (Fig. 1). The angles $\omega_{i,i+1}$ between neighboring links change as a result of thermal motion and under the action of an external force. We introduce the potential $\Phi(x)$ of the forces acting between the centers of neighboring links. The distance between the center of the i-th and the center of the $(i+1)$-st links will be denoted by $|x_{i+1} - x_i| = \Delta x_{i+1,i}$.

Fig. 1

As is known, the statistical integral of such a system is

$$z_N = \left\{ \frac{mkT}{2\pi\hbar^2} \right\}^{N/2} \frac{Q_N}{N!}, \tag{1}$$

where m is the reduced mass and

$$Q_N = \int_0^L \cdots \int_0^L \exp\left(-\frac{U_N}{kT}\right) dx_1 \cdots dx_N, \qquad L = \sum_{(1\le i\le N)} \Delta x_{i,i-1}. \tag{2}$$

We introduce

$$x_k = \sum_{(1\le i\le k)} \Delta x_{i,i-1}.$$

Then

$$0 \le x_1 \le x_2 \le \cdots \le x_N \le L.$$

The potential energy of the system is written in the form

$$U_N = \sum_{(1\le i\le N-1)} \Phi(x_{i+1} - x_i) + U_L + U_0, \tag{3}$$

where U_L is the energy of interaction with the wall, realized in the form of links of the same nature, and U_0 is the potential of the external force. We take the potential $\Phi(x)$ in the form

$$\Phi(x) = \begin{cases} \infty, & (x < a), \\ \overline{\Phi}(l)\,\theta(x), & (a \le x \le l), \\ \infty, & (x > l), \end{cases} \tag{4}$$

where a is the true radius of the particle. The relation between x and ω is established by

$$x_{i,i+1} = l \sin(\omega_{i,i+1}/2).$$

Now, using the results of [4], we write the asymptotic estimate for Q_N as $N, L \to \infty$ and N/L, remaining constant:

$$Q_N(L) = N!\{\varphi(s_0)\}^{N+1} \exp\left\{\frac{U_0}{kT} + s_0 L\right\}, \tag{5}$$

where $s_0 = ap/kT$ (p is the pressure) and

$$\varphi(s_0) = \int_0^\infty \exp\left(-\frac{px + \Phi(x)}{kT}\right) dx = \int_a^l \exp\left(-\frac{px + \overline{\Phi}\theta(x)}{kT}\right) dx. \tag{6}$$

Let us note that for the mean value of the angle ω we have the expression

$$\overline{\omega} = 2\arcsin(L/Nl). \tag{7}$$

The connection with thermodynamics is effected through the fundamental relations. The free energy is

$$F = -kT\ln Z_N = -kT\left\{\frac{N}{2}\ln\left(\frac{mkT}{2\pi\hbar^2}\right) + (N+1)\ln\varphi(s_0)\right\} - (pL + U_0).$$

The thermodynamic potential is

$$G(p,T) = -NkT\left[\ln\varphi(s_0) + \frac{1}{2}\ln\left(\frac{mkT}{2\pi\hbar^2}\right)\right] - U_0.$$

The chemical potential is

$$\mu = \frac{\partial G}{\partial N} = -kT\left[\ln a(s_0) + \frac{1}{2}\ln\left(\frac{mkT}{2\pi\hbar^2}\right)\right].$$

The equation of state is

$$p = kT\frac{\partial Q_N}{Q_N\partial L}, \qquad L = -\left(\frac{\partial G}{\partial p}\right)_T$$

or

$$\bar{l} + kT\frac{d}{dp}\ln\theta(s_0) = 0.$$

As an example, consider a system with potential (1)

$$\theta(\omega) = 1 - \cos 2\omega$$

or

$$\theta\left(\frac{x}{l}\right) = 2\left[1 - 4\frac{x^2}{l^2}\left(1 - \frac{x^2}{l^2}\right)\right].$$

Then the calculation of the thermodynamic functions of the system reduces to an elementary quadrature:

$$\varphi = \exp\left(-\frac{2\overline{\Phi}}{kT}\right)\int_0^l \exp\left\{\frac{1}{kT}\left[-px + \frac{8x^2}{l^2}\left(1 - \frac{x^2}{l^2}\right)\right]\right\}dx. \tag{6a}$$

Fig. 2

Figure 2: Fig. 2

§ 2. Spatial high-molecular chain

Consider a spatial chain (Fig. 2). The valence angles between neighboring links ω and the lengths of the links $K_1K_2 = K_2K_3 = K_3K_4 = \ldots = l$ are constant, while only the angles φ between neighboring planes passing through pairs of adjacent links vary. Introduce the potentials $\Phi(x)$ of the forces acting between A and A'—the geometric centers of neighboring triangles constructed on neighboring pairs of links. Then

$$AK_3 \perp K_1K_4 \perp AK_2.$$

Fig. 2

Let $AO = A'O = \xi$ and let the angle $A\hat{O}A' = \psi$. Obviously, $x = 2\xi \sin\psi/2$ and $\cos\psi/2 = \cos\vartheta \cos\varphi/2$, where $\vartheta = K_4\hat{O}N = K_1\hat{O}M$.

A simple geometrical consideration makes it possible to relate x to (l, ω, φ):

$$x = 2l\cos\omega \frac{\sqrt{1 - \sin^2\omega\cos^2\varphi/2}}{\sin^2\omega + \cos\omega\sqrt{1 + 4\sin^4\omega/2}}. \tag{8}$$

In view of (8),

$$x_{\text{min}} = \frac{2l\cos^2\omega}{\sin^2\omega + \cos\omega\sqrt{1 + 4\sin^4\omega/2}}, \qquad x_{\text{max}} = \frac{2l\cos\omega}{\sin^2\omega + \cos\omega\sqrt{1 + 4\sin^4\omega/2}}.$$

The potential $\Phi(x)$ should be taken in the form

$$\Phi(x) = \begin{cases} \infty, & (x < x_{\text{min}}), \\ \overline{\Phi}(l)\,\theta(x), & (x_{\text{min}} \le x \le x_{\text{max}}), \\ \infty, & (x > x_{\text{max}}). \end{cases}$$

Obviously, (1), (2), (3), (5), and the expressions for the thermodynamic functions, as well as the equation of state, remain unchanged, while (6) is replaced by

$$\varphi(s_\omega) = \int_{x_{\text{min}}}^{x_{\text{max}}} \exp\left\{-\frac{px + \overline{\Phi}\theta(x)}{kT}\right\} dx.$$

If, as an example, we take $\theta_1(\varphi) = 1 - \cos 2\varphi$, then, by virtue of (8),

$$\theta(x) = 1 - 8\left[\frac{2}{\sin^2\omega} + \frac{x^2}{\rho\sin^2 2\omega}\right]\left[1 - \frac{2}{\sin^2\omega} + \frac{x^2}{\rho\sin^2 2\omega}\right],$$

where

$$\sqrt{\rho} = l/(\sin^2\omega + \cos\omega\sqrt{1 + 4\sin^4\omega/2}).$$

Thus, $\varphi(p, kT)$ is again expressed through a quadrature of type (6a), differing from the latter only in the limits of integration and in the coefficients of the powers of x in the exponential under the integral sign. Finally, substitution of φ into (5) gives the statistical integral.

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