

Localization of polymer chains in random media

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A theory is derived for localized states of polymer chains.

The localization of polymers was first detected in numerical simulations¹ in which the chains were simulated by a random walk of l steps of length a on a 3D lattice from which a fraction ν/a^3 of the sites had been removed. It was shown that the Gaussian size of the chain, $R = al^{1/2}$, reaches an asymptotic value $R_{\max} \approx a^4/\nu$ as l increases. In the present letter we derive a theory for the localization of chains in the case of Ref. 1 and also in the case in which the actual interaction between the units of the chains is taken into account.

We show that localization occurs in randomly distributed regions with dimensions $R < R_{\max} \approx a^4/\nu$. The concentration of such regions with a size less than R is found from the asymptotic formula

$$c(R) \approx R^{-3} S(R) e^{-S(R)}, \quad S(R) = 2.57 a^4 / \nu R \gg 1. \quad (1)$$

According to (1), the condition $R \approx R_{\max}$ corresponds approximately to the threshold for an overlap of these regions. The behavior of the unpinned chains is very different from that of the chains with a single fixed end.¹ The chains with a fixed end are localized in the nearest region of size $\sim R_{\max}$. The free chains find sparsely distributed [see (1)] but deeper energy minima with $R \ll R_{\max}$.

The free energy of a polymer with a density $\rho(\mathbf{x})$ in a weakly fluctuating localized state is determined by the Lifshitz expression²

$$\frac{F_0}{T} = \int d\mathbf{x} \left\{ \frac{a^2}{6} [\nabla \rho^{1/2}(\mathbf{x})]^2 + V(\mathbf{x}) \rho(\mathbf{x}) \right\}, \quad \int d\mathbf{x} \rho(\mathbf{x}) = l, \quad (2)$$

where T is the temperature, and $V(\mathbf{x})$ is a random Gaussian potential with

$$\overline{V(\mathbf{x})V(\mathbf{x}')} = \nu \delta(\mathbf{x} - \mathbf{x}'). \quad (3)$$

Introducing the Lagrange multiplier μ to deal with the second condition in (2), we find the equilibrium density distribution $\rho(\mathbf{x}) = \text{const} \psi^2(\mathbf{x})$ from the condition for a minimum of F_0 . Here $\psi(\mathbf{x})$ is the eigenfunction of the equation corresponding to the eigenvalue $\epsilon = \mu$:

$$\left[\epsilon - \frac{a^2}{6} \nabla^2 + V(\mathbf{x}) \right] \psi(\mathbf{x}) = 0. \quad (4)$$

The most probable function $\psi(\mathbf{x})$ is well known from the theory of Anderson localization.³

$$\psi(x) = (\epsilon/v)^{1/2} \chi(\epsilon^{1/2} x/a), \quad \chi(0) \sim 1, \quad \chi(t \rightarrow \infty) \rightarrow 0. \quad (5)$$

It describes a localization over a length scale $R = a\epsilon^{-1/2} < R_{\max}$ with distribution function (1) for the dimensions of these regions. Substituting the solution found for $\rho(x)$ into (2), we find the free energy of the chain, $F(R)/T = -a^2 l/R^2$. The condition $|F| \gg T$ for the existence of this solution can be written in the form $l \gg l_{\min} = (R/n)^3$.

When the interaction of the units, w , is taken into account, the free energy of the polymer is

$$F = F_0 + F_{\text{int}}, \quad F_{\text{int}} = \frac{wT}{2} \int dx \rho^2(x). \quad (6)$$

Using the method of Ref. 4, we expand the unknown solution $\varphi(x) = \rho^{1/2}(x) = c_0 \psi(x) + \dots$ in the eigenfunctions of Eq. (4). Restricting the discussion to the lowest eigenvalue [see (5)] in the localized region $R \ll R_{\max}$, and substituting the solution found into the second equation in (2) in order to determine μ , we find

$$\epsilon_0^2 = (\epsilon - \mu)v/4\epsilon w, \quad \mu = \epsilon - 3.1wl\alpha^{-3}\epsilon^{3/2}. \quad (7)$$

Substituting solution $\rho(x)$ and (7) into (6), we can calculate the free energy of the polymer which is localized at a length scale R :

$$F(R)/T = -a^2 l/R^2 + 1.56wl^2/R^3. \quad (8)$$

The conditions for the existence of this solution, $F < 0$ and $|F| \gg T$, can be written in the form

$$a^3 w^{-1} R = l_{\max} > l > l_{\min} = (R/\alpha)^2. \quad (9)$$

The inequality $R \ll a^4/u$, which follows from (9), and the inequality $R < R_{\max} \approx a^4/v$ [see (1)] determine the maximum localization radius R . Estimates of the Flory type^{5,6} yield only an upper bound on R at $v > w$, not the distribution [see (1)] of the energy wells, which also prevails at $v < w$.

We now consider the behavior of long chains, with $l \gg l_{\max}$ [see (9)]. In the case of a slight disorder, $v < w$, the potential wells of size $R < a^4/w$ are exponentially rare [see (1)]. Since the energy disadvantage for a chain outside the wells is much greater than the energy advantage [see (8)] inside the wells, the tensile force of a chain pulls it out of the potential wells. In the case of a pronounced disorder, $v \gg w$, such chains consist of l/g globular blobs of size $R = R_{\max}$. The average number of units in these blobs, g_1 , is found by minimizing the free energy of the chain,

$$\frac{F_1}{T} = \frac{l}{g} \left[-\frac{a^2 g_1}{R^2} + 1.56 \frac{w g_1^2}{R^3} + \frac{L^2}{a^2 g_2} + \frac{a^2 g_2}{D^2} \right], \quad (10)$$

with respect to g_1 and with respect to the number $g_2 = g - g_1$, which is the number of fragments of the chain between nearest wells. The average distance between them is $L = c^{-1/3}(R_{\max})$ [see (1)]. A fragment of this sort is in an effective tube of diameter

$D \approx R_{\max}$, which is produced by random potential (2). Since the interaction of the units within a tube is unimportant under the condition $w \ll v$, the free energy of this fragment is the (additive) sum of the energies of the extension of the chain along the tube, $\sim L^2$, and the energy of the compression of the chain in the perpendicular direction (see Chapter 1 in Ref. 7). A minimization of (10) leads to

$$g_1 \approx \kappa^{1/2} a^6 / w^{1/2} v^{3/2}, \quad g_2 \approx LD/a^2 \ll g_1, \quad (11)$$

where the dimensionless parameter $\kappa = L/D$ is greater than one. The quantity g_1 is less than l_{\max} under the condition $v > \kappa w$ because of the partial pulling of the chain out of the potential wells, which we mentioned above.

The condition $F_l < 0$ holds only if there is a sufficiently pronounced disorder: $v > \kappa w$. Under this condition, only short chains, with $l < g_1$, localize in one potential well. For chains with $l \gg g_1$, it is advantageous from the energy standpoint to become distributed among several wells.

The system described above might be realized by (for example) placing deuterated chains in a polymer network. The inhomogeneity characteristics of such a network were calculated in Ref. 8. When a localization of the chains occurs, one should observe a minimum in the intensity of neutron scattering at wave vectors $q \sim R^{-1}$. It is not difficult to generalize the theory presented above to the case of a space of dimensionality $d = 2$, which would describe polymers adsorbed on a rough surface.

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