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1 Self-Consistent Field Theory of Polymers

Self-Consistent Field Theory (SCFT), represents a powerful theoretical method for calculating the phase separation structures and interfacial structures of dense polymer systems. This method uses the mean field approximation in order to reduce the many-chain problem to a single-chain problem in an external field, where the chain conformation of the tagged chain is calculated using the path integral method.

1.1 Mean-Field Approximation and Self-Consistent Field

The essence of the mean field approximation is the decoupling and preaveraging of some of the variables in the many-body correlations. In a concentrated polymer system such as a semi-dilute polymer solution or a polymer melt, chains overlap each other. In such a concentrated system, the excluded volume interaction is canceled through screening effect. Due to this effect, the correlations between different chains are suppressed and the chain conformations become almost independent of each other. We want to calculate conformational probability distribution for a single chain placed in a net of the tagged chains. It is suitable to consider this problem using a mean field approximation where the correlations between the tagged chain and the other chains are neglected. So the problem is simplified to the problem of treating an ideal chain in an average external potential field $V(r)$ generated by the surrounding chains Fig[1]. Such an external potential field is called the mean field or self-consistent field. It accounts for the interactions between a segment of the tagged chain and the surrounding segments, including the other segments of the tagged chain. As such an interaction depends on the species of the tagged segment, so does the mean field $V(r)$. If one considers a system composed of several segment species A, B,...the mean field acting on the tagged segment of K-type at position $r$ is given by

$$V_K(r) = k_BT \sum_{K'} \chi_{KK'} \phi_{K'}(r) + \gamma(r),$$  \hspace{1cm} (1)

where $\chi_{KK'}$ is the interaction parameter between a pair from a K-type segment and K'-type segment, $\phi_K(r)$ is the number density of the K-type segment at position $r$ and $\gamma(r)$ is the constraint force due to external conditions such as the incompressibility condition. The goal is to calculate the equilibrium segment distribution function $\{\phi_K(r)\}$ taking the chain conformations into account. Such a segment density can be calculated from the equilibrium probability distribution of the tagged chain, which is assumed to be an ideal chain, in the mean field $V_K(r)$. Due to the consistency of the whole theoretical framework, the calculated segment density should be equal to the segment density appearing on the right-hand side of (1). After such a self-consistent condition, the mean field $\{V_K(r)\}$ is
An interacting many-chain system is approximated by a single ideal chain in averaged potential field $V(r)$, called the self-consistent field (SFC), and this theoretical framework is called the self-consistent field theory. Within this SCF theory, the equilibrium segment densities, the probability distributions of the chain conformation, and the self-consistent fields are determined simultaneously.

### 1.2 Path Integral Formalism for Polymers

In the self-consistent field theory, it is essential to calculate the equilibrium conformation of the tagged chain in the self-consistent field. Let us consider the part of a chain composed of $K$-type segments with indices $(k, k+1, ..., l-1, l)$, Fig 2. Hereafter we call it a subchain. The total number of segments participating in this subchain is $|l-k|$. This subchain is assumed to be in equilibrium in the external self-consistent field $V_K(r)$, which depends on the position $r$ and the segment species $K$. Then the statistical weight of this subchain having a certain conformation is given by the Boltzmann factor of the Hamiltonian by

$$\exp(-\beta H) = \exp[-\frac{3}{2b^2} \sum_{i=k}^{l-1} |r_{i+1} - r_i|^2 - \beta \sum_{i=k}^{l} V_K(r_i)], \quad (2)$$

If the positions of both ends of the subchain, $i = k$ and $i = l$, are fixed at $r$ and $r'$, the statistical weight of such a subchain is obtained by summing the Boltzmann factor for all possible conformations under the condition that both ends are fixed. Therefore, the total statistical weight of a subchain whose ends are fixed at $r$ and $r'$ is expressed in path integral form by

$$Q_K(k, r; l, r') \equiv \nu \frac{\nu}{Z_0(|l-k|)} \times \sum' \exp[-\frac{3}{2b^2} \sum_{i=k}^{l-1} |r_{i+1} - r_i|^2 - \beta \sum_{i=k}^{l} V_K(r_i)], \quad (3)$$

where $\nu$ is the system volume which accounts for the translational degree of freedom of the center of mass of the chain and $Z_0(|l-k|)$ is the partition function of an ideal subchain composed of $|l-k|$ segments and the sum $\sum'$ indicates summation over all possible conformations satisfying $r_k = r$ and $r_l = r'$. With this definition of path integral we can easily check the relation

$$Q_K(s, r; s', r') = \int d\mathbf{r}''Q_K(s, r; s'', r'')Q_K(s'', r''; s', r'), \quad (4)$$

which expresses the statistical independence of the conformations of subchains that have no common segments (except for the end segment). It is known as the Chapman-Kolmogorov relation.
Figure 3: In order to derive a recurrence relation for the path integral, the last segment is treated separately from the other segments of the subchain. Due to the statistical independence between different subchains, the orientation of the bond that connects the separated segment and the others is statistically independent of the other bond.

1.3 Recurrence Formula for the Path Integral

If we split subchain \( i = k, \ldots, l \) into two parts \( i = k, \ldots, l - 1 \) and \( i = l - 1, l \), as it is shown in Fig 3, we can obtain the following diffusion-type partial differential equation:

\[
\frac{\partial}{\partial s} Q_K(s', r'; s, r) = \frac{\nu^2}{6} \nabla^2 Q_K(s', r'; s, r) - \beta V_K(r) Q_K(s', r'; s, r),
\]

where \( \nu \equiv \frac{\nu}{Z_0(1)} \) is the increment in the index \( i \) per segment. Here, \( \mathbf{ab} \) denotes the dyadic product of two vectors \( \mathbf{a} = (a_i) \) and \( \mathbf{b} = (b_i) \) defined as \( \mathbf{ab} = (a_i b_j) \), and the notation \( \mathbf{A} : \mathbf{B} \) is a scalar product of two second rank tensors \( \mathbf{A} \) and \( \mathbf{B} \) defined by \( \mathbf{A} : \mathbf{B} \equiv \text{trace} (\mathbf{A} \cdot \mathbf{B}) = \sum_{ij} A_{ij} B_{ji} \). For further integration performing we have to use formulas:

\[
\int dr'' \left( \frac{3}{2(\Delta t)b^2} \right)^{3/2} \exp \left( -\frac{3}{2(\Delta t)b^2} |r'' - r'|^2 \right) (r'' - r') = 0,
\]

\[
\int dr'' \left( \frac{3}{2(\Delta t)b^2} \right)^{3/2} \exp \left[ -\frac{3}{2(\Delta t)b^2} |r'' - r'|^2 \right] (r'' - r') (r'' - r') = \frac{b^2}{3} (\Delta t) \mathbf{1}.
\]

The next step is replacing the discrete index \( i \) by continuous variable \( s \), then, taking the limit \( \Delta s \to 0 \), we finally obtain the following diffusion-type partial differential equation:

\[
\frac{\partial}{\partial s} Q_K(s', r'; s, r) = \frac{\nu^2}{6} \nabla^2 Q_K(s', r'; s, r) - \beta V_K(r) Q_K(s', r'; s, r),
\]

where the term containing \( V_K \nabla^2 Q_K \) was dropped because it is of higher order in \( \Delta s \), which vanishes in the limit \( \Delta s \to 0 \). The equation (9) is the basic equation for calculating the path integral. One can indentity the path integral \( Q_K \) with the wave function, so the equation (9) can be regarded as the Schrodinger equation of quantum mechanics, which provides us to import various techniques from quantum mechanics to polymer physics.

1.4 Self-Consistency Condition

In order to solve the partial differential equation (9) we have to know external potential \( V_K(r) \), then we are able to obtain the path integral \( Q_K(0, r_1; s, r) \). Using this path integral, the density distribution of the K-type segment is calculated in the following way: the statistical weight of a chain whose \( s \)th segment is located at the position \( r \) is
Figure 4: Calculating the segment density distribution using path integrals. Density distribution of the \( s \)-th segment at \( r \) is obtained by integrating the product of the path integrals for the two subchains over all possible positions of the two end segments \( r_0 \) and \( r_{N_K} \) under the condition that the position of the \( s \)-th segment is fixed at \( r \).

Calculated by integrating the product of the statistical weights of the two subchains meeting at the \( s \)-th segment over all possible positions of the two end segments \( r_0 \) and \( r_{N_K} \), Fig 4. Then the density distribution of the \( s \)-th segment is given by properly normalizing this statistical weight. Integrating this distribution of the \( s \)-th segment over the segment index \( s \), we obtain the following formula for the total segment density of the \( K \)-type chain:

\[
\phi_K(r) = M_K \frac{\int_{r_0}^{r_{N_K}} ds \int dr_0 \int dr_{N_K} Q_K(0, r_0; s, r)Q_K(s, r; N_K, r_{N_K})}{\int dr_0 \int dr_{N_K} Q_K(0, r_0; s, r)},
\]

(10)

where \( M_K \) is the total number of \( K \)-type chains in the system and a single chain is composed of \( N_K + 1 \) segments. The denominator is the normalizing constant, where the normalization condition for \( \phi_K(r) \) is given by

\[
\int \phi_K(r) dr = (N_K + 1)M_K.
\]

(11)

The self-consistency condition is realized by a numerical iteration procedure. The self-consistent field theory is useful for calculating mesoscopic structures in inhomogeneous systems, including phase separation structures in polymer blends or block copolymer melts.

1.5 Classical Approximation for Self-Consistent Field Theory

In generally, it is difficult to obtain an analytical solution for the set of self-consistent equations (1), (9) and (10), so numerical calculations come at the scene. However, there are a few exceptions where the set of self-consistent equations can be solved analytically. One such example is, so called, classical limit. As this analytical derivation is important in obtaining an intuitive understanding of the self-consistent field calculation, here it will be briefly described. We pointed out that the path integral \( Q(0, r_0; s, r) \) for a polymer chain can be identified with the wave function of a quantum particle when we identify the segment index \( s \) with the variable \( t \). The distribution of each segment is then identified with the probability distribution of a quantum particle at each instant of time. In the classical limit of such a quantum system (\( \hbar \to 0 \)), the solution of the path integral equation (9) is well approximated by the classical path of Newton’s equation of motion, where the fluctuations around the classical path of the particle are negligible. This corresponds to a strongly stretched chain whose conformation fluctuates only weakly around the straight conformation, Fig 5. One of the appropriate targets of this classical approximation is the polymer brush—polymer chains grafted onto a solid surface. For simplicity, we only consider polymer chains which are fixed on the surface by chemical bonds that can neither be detached nor migrate on the surface. An important parameter that determines the physical properties of a polymer brush is the grafting density \( \sigma_a \), which is defined by \( \sigma_a = M/S \), where \( M \) is the number of chains grafted to the surface and \( S \) is total area of the surface. If the average distance between neighboring grafting points is much smaller than a gyration radius \( R_G \) of the chain, the chains overlap one another. Translated to mathematical language, it means:

\[
\sigma_a^{-1/2} \ll R_G.
\]

(12)

In this case, the chains are strongly stretched in the direction perpendicular to the solid surface due to the repulsive excluded volume interaction between the segments. In this limit, we will consider the behavior of the path integral...
One can see analogy between conformations of polymer chains and path of ”quantum particles”, where the segment index \( s \) is identified with the time. Due to this correspondence, the first and the second terms in the argument of the exponential function in (3) are identified with the kinetic energy and the potential energy of the ”quantum particle”, respectively. The quantum uncertainty effect causes the path of the ”quantum particle” to fluctuate around its classical trajectory. This fluctuation corresponds to the thermal fluctuation of the polymer chain conformation. In the limit (12), the chain conformation becomes almost straight due to the strong excluded volume interaction. As the result, the fluctuation in the trajectory of the ”quantum particle” becomes less important. Then the trajectory of the ”quantum particle” converges to a certain unique path, which corresponds to the classical path. Such a classical path \( \{ \mathbf{r}_i \} \) is defined as the one that maximizes the argument of the exponential function on the right-hand side of (3). This extremal condition leads to the following equation for arbitrary segment index \( i \):

\[
\frac{\partial}{\partial z_i} \left[ -\frac{1}{2b^2} \sum_j |z_j - z_{j+1}|^2 - \beta \sum_k V(z_k) \right] = 0,
\]

where \( z \)-axis is taken in the direction perpendicular to the solid surface, \( z_i \) is the \( z \) component of \( \mathbf{r}_i \), and we assume that the system is uniform in the direction parallel to the solid surface. Because of the one-dimensional nature of the problem, the coefficient of the spring force is no longer \( 3/(2b^2) \) but \( 1/(2b^2) \). Performing the partial differentiation with respect to \( z_i \) and taking the continuum limit with respect to \( i \), we obtain

\[
\frac{k_B T}{b^2} \frac{d^2}{ds^2} z(s) = V'(z(s)).
\]

If we identify the segment index \( s \) as the time, (14) corresponds to Newton’s equation of motion for a classical particle with mass \( k_B T/b^2 \) moving in a potential \( -V(z) \).

References