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Effective propagators for quenched disorder in linear polymers

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A chain conformation space path integral theory is implemented to study the statistics of inhomogeneous polymers randomly constructed from two different kinds of monomers. A replica approach analogous to that used in spin glass systems is adopted to average over the quenched randomness. A perturbative analysis requires mixed propagators coupling identical replicas of an arbitrary sequence of monomers. Making use of these effective propagators we estimate the effect of the quenched disorder on intra-chain interactions and calculate the asymptotic behavior of the system in the limit of very large chains. This thermodynamic limit is analyzed comparing the effective Gibbs measure determined by the effective Hamiltonian with the Gibbs measure for a homogeneous polymer system where the intra-chain interactions correspond to the averaged interactions of the original system.

1. Introduction

The process of averaging over the quenched disorder is a problem under active research, particularly in the context of spin glasses [1]. The existence of a built-in quenched disorder determines the breakdown of the ergodicity of the system. A similar situation takes place in dynamic critical phenomena when the onset of a center manifold produces a contraction of the phase space [2].

Linear polymers randomly constructed from two kinds of monomers, X and Y, with short-range intra-chain interactions constitute an example of quenched disorder. Each X-Y sequence is equivalent to a realization of the random variable $s(x)$, where x is a contour variable indicating the position in the chain, $x = 0,1,\ldots,N$; i.e., $s(x) = +1$ if the x-th monomer is X and $s(x) = -1$ otherwise. For a fixed position in the chain, $s(x)$ can take the values ±1 with equal probability.

The averaged free energy of the system is proportional to the average of the quantity $\ln Q$ over the ensemble of realizations of $s(x)$ with $Q = Q(s(x))$ being the partition function. One of the aims of this paper is to calculate this average by means of the so-called replica trick [1]. In doing so, we shall make use of the analogy between disordered polymers and spin glasses [3]. Before giving an outline of the procedure some observations are in order.

For L a positive integer, let $Q(L)$ denote the partition function for L identical replicas of an arbitrary X-Y sequence. Then, $Q(L)$ can be written as follows:

$$Q(L) = \prod_{\beta=1}^{L} Q_\beta \tag{1}$$

with Q_β determined by a Hamiltonian H_β involving exclusively the replica indexed by the specific value of β. On the other hand, we have

$$\langle Q(L)\rangle = \prod_{\alpha=1}^{L} Q_{\mathrm{eff},\alpha} \tag{2}$$

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where $\langle\ \rangle$ represents the average over the ensemble of realizations of $s(x)$ and the effective Hamiltonian $H_{\mathrm{eff},\alpha}$ couples identical replicas labelled by the different subindices. The partition function $Q_{\mathrm{eff},\alpha}$ corresponds to a virtually homogeneous polymer and does not contain any disorder. It will be evaluated making use of a perturbative method. More specifically, we shall find to first order (a valid approximation near the θ point):

$$Q_{\mathrm{eff}} = Q^{(0)} + Q^{(1)}_{\mathrm{eff},2} + Q^{(1)}_{\mathrm{eff},3} \tag{3}$$

with

$$Q = Q^{(0)} + Q^{(1)}_2 + Q^{(1)}_3 + \dots \tag{4}$$

The term $Q^{(0)}$ corresponds to a free propagator with a Hamiltonian consisting only of the elastic energy contribution. The first-order terms $Q^{(1)}_2$ and $Q^{(1)}_3$ correspond to the two- and three-body short-range interactions, respectively. The terms $Q^{(1)}_{\mathrm{eff},2}$ and $Q^{(1)}_{\mathrm{eff},3}$ are the effective first-order contributions and involve the coupling of identical replicas of the system. The mixed propagators associated with such terms will be evaluated explicitly. Once $\langle Q(L)\rangle$ has been defined for integer L, it can be analytically extended for L taking real positive values [1].

From the relation:

$$\exp(L \ln Q) = Q^L = Q(L) \approx 1 + L \ln Q \quad (L \text{ small real number}) \tag{5}$$

we derive the following equation:

$$\langle \ln Q\rangle = \lim_{L\to 0} \frac{1}{L}(\langle Q(L)\rangle - 1) \tag{6}$$

This relation is obviously useful in order to compute free energies and to study the distribution of conformational averages over the ensemble of realizations of $s(x)$.

2. Explicit evaluation of the effective propagators

The bare coupling variable $v(x,x')$ corresponding to the short-range two-body interactions X-X, X-Y and Y-Y must take three possible values. In order to define this variable we shall consider a continuous counterpart of the stochastic process $s(x)$:

$$\langle s(x)s(x')\rangle = \delta(x - x'),\ \langle s(x)\rangle = 0,\quad x \in [0,N] \tag{7}$$

Thus, $v(x,x')$ is defined as follows:

$$v(x,x') = v + A(s(x) + s(x')) + B(s(x)s(x')) \tag{8}$$

where A and B are bare constants and v denotes the bare Flory two-body interaction constant. We are interested in a regime corresponding to a neighborhood of the theta point, i.e., $v \approx 0$. The propagator method holds in this regime.

We shall discretize the domain of the contour variable by introducing an arbitrary partition of the interval $[0,N]$. This discretization, designated as P_{M}, is given by:

$$P_{\mathrm{M}} = \{r_0, r_1, r_2, \dots, r_{M-1}, r_M\} \text{ with } r_j = r(jN/M) \tag{9}$$

The partition function for the system is given by:

$$Q = \lim_{M\to\infty} \int \prod_{j=0}^{M} \mathrm{d}r_j \delta(r_0)\delta(r_M - R)\exp\{-H_M\} \tag{10}$$

where:

$$H_M = \frac{1}{2}\sum_{i=0}^{M}\left[\frac{r_{i+1} - r_i}{N/M}\right]^2 + H'_M = H^{\mathrm{e}}_M + H'_M \tag{11}$$

$$H'_M = \frac{1}{2}\left[\sum_{i,j=0}^{M} v(iN/M, jN/M)\delta_{r_i r_j} + \frac{C}{3}\sum_{k=0}^{M}\delta_{r_i r_j}\delta_{r_i r_k}\right] - f(r_M) \tag{12}$$

The Kronecker symbol is defined as follows:

$$\delta_{r_i r_j} = \begin{cases} +1 & \text{for } r_i = r_j \\ 0 & \text{otherwise} \end{cases} \tag{13}$$

The constant C represents the bare three-body short-range interaction Flory parameter. We shall implement a field theoretical formalism. This requires including a virtual field $f(R)$ controlling the endpoint position of the random coil and taking the limit $f = 0$ in the derivatives of the partition function and its logarithm with respect to f. Making use of the path-integral formalism, the Hamiltonian for the random coil reads:

$$H = \frac{1}{2}\left[\int_0^N \mathrm{d}x \frac{\partial^2 r}{\partial x^2} + \int_0^N \mathrm{d}x \int_0^N \mathrm{d}x' v(x,x') \times \delta(r(x) - r(x'))\right.$$

$$+\frac{C}{3}\int_0^N \mathrm{d}x\int_0^N \mathrm{d}x'\int_0^N \mathrm{d}x''\delta(r(x)-r(x')) \times\delta(r(x')-r(x''))\Big]$$

$$+\int \mathrm{d}Rf(R)\delta(r(N)-R) \tag{14}$$

$$H(r(x)) = \lim_{M\to\infty} H_M \tag{15}$$

Assuming that there exists a measure $m(r(x))$ in conformational space, the partition function Q can be represented as follows:

$$Q=\int_{r(0)=0,r(N)=R} \mathrm{d}m(r(x)) \exp(-H(r(x))) \tag{16}$$

It can be readily verified that

$$\frac{\delta \ln Q}{\delta f(R)}\bigg|_{f=0} = \overline{\delta(r(N)-R)} \tag{17}$$

That is, the functional derivative represents the Green function $G(R)$. The bar above a quantity indicates thermal or statistical average, i.e., the average for all the conformations for a given X-Y sequence. Note that $G(R)$ depends on the specific realization of $s(x)$. The first-order contributions to Q are given by [4].

$$Q_2^{(1)} = -\int_0^R \mathrm{d}r\int_0^N \mathrm{d}x'\int_0^{x'} \mathrm{d}xG_0(r,x)G_0(0,x'-x) \times G_0(R-r,N-x')v(x,x') \tag{18}$$

$$Q_3^{(1)} = -C\int_0^R \mathrm{d}r\int_0^N \mathrm{d}x''\int_0^{x''} \mathrm{d}x'\int_0^{x'} \mathrm{d}xG_0(r,x) \times G_0(0,x'-x)G_0(0,x''-x') \times G_0(R-r,N-x'') \tag{19}$$

Where $G_0(r,x)$ is the free propagator corresponding to a Hamiltonian

$$H^{\mathrm{e}} = \lim_{M\to\infty} H_M^{\mathrm{e}} \tag{20}$$

On the other hand, we have

$$\langle Q(L)\rangle = \lim_{M\to\infty}\int \prod_{\alpha=1}^{L}\prod_{i=0}^{M} \mathrm{d}r_{\alpha i}\delta(r_{\alpha 0})\delta(r_{\alpha M}-R_\alpha) \times\exp(-H_M(L)) \tag{21}$$

where

$$H_M(L) = \sum_{\alpha=1}^{L} H_M^{\mathrm{e}}(\alpha) + \sum_{\alpha=1}^{L}\sum_{i,j=0}^{M}\Bigg[\frac{v}{2}\delta_{r_{\alpha i}r_{\alpha j}} - \tfrac{1}{2}A^2\sum_{\beta\neq\alpha}\sum_{k=0}^{M}\Bigg[\delta_{r_{\alpha i}r_{\alpha j}}\delta_{r_{\beta i}r_{\beta k}} - \frac{C-3A^2}{3A^2}\delta_{r_{\alpha i}r_{\alpha j}}\delta_{r_{\alpha i}r_{\alpha k}}\Bigg] - f(r_{\alpha M})\Bigg] \tag{22}$$

This gives:

$$\int_0^N \mathrm{d}x'\int_0^N \mathrm{d}x\left[\frac{v}{2}+F(x')\right]\delta(r(x)-r(x'))$$

$$= \text{two-body effective interaction term} \tag{23}$$

$$F(x') = \frac{A^2}{2}\sum_{\beta=1}^{L}\int_0^N \mathrm{d}x''\delta(r_\beta(x')-r_\beta(x'')) \tag{24}$$

Therefore, the effective first-order contributions are:

$$Q_{\mathrm{eff},2}^{(1)}(\alpha) = -\int_0^R \mathrm{d}r\int_0^N \mathrm{d}x''\int_0^{x''} \mathrm{d}x'\int_0^{x'} \mathrm{d}x \times\Bigg\{\Bigg[v+3A^2\sum_{\beta\neq\alpha} G_{\beta 0}(r,x') \times G_{\beta 0}(0,x''-x')G_{\beta 0}(R-r,N-x'')\Bigg] \times[G_{\alpha o}(r,x)G_{\alpha 0}(0,x'-x) \times G_{\alpha 0}(R-r,N-x')]\Bigg\} \tag{25}$$

$$Q_{\mathrm{eff},3}^{(1)}(\alpha) = -(C-3A^2)\int_0^R \mathrm{d}r\int_0^N \mathrm{d}x''\int_0^{x''} \mathrm{d}x' \times\int_0^{x'} \mathrm{d}xG_{\alpha 0}(r,x)G_{\alpha 0}(0,x'-x) \times G_{\alpha 0}(0,x''-x')G_{\alpha 0}(R-r,N-x'') \tag{26}$$

Now we can determine the effective interaction constants:

$$v_{\mathrm{eff}} = v + 2A^2\lim_{M\to\infty}\sum_{j=0}^{M}\frac{\partial \ln\left\{\prod_{\alpha=1}^{L} Q_j(\alpha)\right\}}{\partial f(R_\alpha = R = 0)} \tag{27}$$

$$v_{\mathrm{eff}} = v + K(N) \tag{28}$$

and

$$C_{\text{eff}} = C - 3A^2 \tag{29}$$

The effective Hamiltonian is defined as the limit as M goes to infinity of $H_{\text{eff}M}$ which is given by:

$$H_{\text{eff}M} = H^{c}_{M} + \sum_{i,j=0}^{M}\left[\frac{v_{\text{eff}}}{2}\delta_{r_i r_j} + \frac{C_{\text{eff}}}{6}\sum_{k=0}^{M}\delta_{r_i r_j}\delta_{r_j r_k}\right] - f(r_M) \tag{30}$$

Making use of these results, we can evaluate the distribution of thermal averages over the ensemble of X-Y sequences and calculate the effect of the quenched disorder in the thermodynamic limit, i.e., when N tends to infinity.

3. Gibbs measure associated with the effective Hamiltonian

We shall now concentrate on the calculation of the variance of the thermal average $\overline{R^2}$. This quantity is given by

$$\overline{R^2} = -\left.\frac{\partial^2 g(p)}{\partial p^2}\right|_{p=0} \tag{31}$$

where $g(p)$ is the Fourier transform of the Green function in momentum space.

The variance is given by

$$V(\overline{R^2}) = \left\langle\left(\overline{R^2} - \langle[\overline{R^2}]\rangle\right)^2\right\rangle = V \tag{32}$$

$$V = \int\int R_\alpha^2 R_\beta^2 \left.\frac{\partial^2\langle \ln Q\rangle}{\partial f(R_\alpha)\,\partial f(R_\beta)}\right|_{f=0} \mathrm{d}R_\alpha\,\mathrm{d}R_\beta \tag{33}$$

In order to calculate eq. 33, we shall make use of the replica trick, as given by eq. 6. Considering only the first-order contributions given by eqs. 25 and 26, a straightforward calculation gives:

$$V = \frac{1}{128}N^2A^2(\pi^4 + 4\pi^3) \tag{34}$$

In order to evaluate the effect of the quenched randomness in the thermodynamic limit, we first observe that H_{eff} contains no disorder and, therefore, it can be compared with H_{hom}, the Hamiltonian for a homogeneous polymer. Let $H_{\text{hom}} = H_{\text{hom}}(v,C)$ be defined as the Hamiltonian for a homogeneous polymer with two and three bare interaction constants equal to the average values for the ensemble of disordered polymers and the same elastic term. Then, the distance between the two Hamiltonians is given by the Kakutani distance which is given by [5,6]

$$d = d(H_{\text{eff}}, H_{\text{hom}}) = 1 - \frac{\overline{Q}}{[Q_{\text{eff}}Q_{\text{hom}}]^{1/2}} \tag{35}$$

This is a well-defined distance as can be readily verified by the reader. $\overline{Q}$ is the partition function for the average Hamiltonian $\overline{H} = 1/2[H_{\text{eff}} + H_{\text{hom}}]$ and Q_{eff} and Q_{hom} those associated with H_{eff} and H_{hom}, respectively. The natural problem which arises is: What is the behavior of d near the thermodynamic limit? This question can indeed be answered, at least to a first approximation. The first-order contributions to Q_{hom} are given by:

$$Q^{(1)}_{\text{hom},2} = -\int_0^R \mathrm{d}r\int_0^N \mathrm{d}x'\int_0^{x'} \mathrm{d}x\, v G_0(r,x) \times G_0(0,x'-x)G_0(R-r,N-x') \tag{35}$$

$$Q^{(1)}_{\text{hom},3} = Q^{(1)}_3 \tag{36}$$

The computation of the first-order contribution for $\overline{Q}$ is entirely analogous to that for Q_{eff}. Finally, we obtain:

$$d = 1 - \left[\tfrac{1}{2} + (\exp(K(N)) + \exp(-K(N)))^{-1}\right]^{1/2} \tag{37}$$

Therefore, the two Gibbs measures are never concentrated on disjoint sets. The Kakutani distance d represents the effect of the quenched randomness and it tends asymptotically and from below to the limit value $d_0 = 1 - 2^{-1/2}$ as we approach the thermodynamic limit.

References

1 K. Binder and A.P. Young, Rev. Mod. Phys. 58 (1986) 801.
2 A. Fernández and H. Rabitz, Phys. Rev. A 35 (1987) 764.
3 P.W. Anderson, Proc. Natl. Acad. Sci. U.S.A. 80 (1983) 3386.
4 A.L. Kholodenko and K.F. Freed, J. Chem. Phys. 78 (1983) 7390.
5 E.J. Brody, Phys. Rev. Lett. 58 (1987) 179.
6 D.X. Xia, Measure and integration theory on infinite dimensional spaces (Academic Press, New York, 1971).