'Hard' Issues in Softmatter Physics
—A brief survey of polymer field theory

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This article serves as a survey of polymer field theory, from the background to its formalism. Concept of Gaussian chains, Brownian motion picture and n-point transition probability are clarified which serve as the foundation of a polymer field. Then the polymer fields and path integral formalism are introduced, making reference to similar aspects of quantum mechanics. Based on the formalism, mean field theory and Gaussian fluctuation are discussed in detailed and renormalization group theory is also mentioned. The mean field is interpreted as the ground state of a polymer field with Gaussian fluctuations as elementary excitations and correlations energies found in strong fluctuation systems through Hartree approximation are identified as scattering interactions between the quasi-particle 'polymerons'.

I. INTRODUCTION

Conventionally, 'soft' and 'hard' are distinguished through Young's modulus $Y = \epsilon/L^3$. For hard matters, the characteristic energy and length scale are around 6 eV and 1 Å, then $Y \sim 10^{12}$ Pa; for soft matters, characteristic energy is of order $k_B T$ while sizes range from nanometers to microns, therefore $Y \sim (10^{-2} \sim 10^{-4})$ Pa. Soft matters are not only soft but also range widely in Young's modulus which gives rise to intricate phase behaviors.

Soft matters mainly consist of polymers and colloids. At the beginning, they were studied from a chemistry point of view but later physicists discovered universality in this issue since macroscopic properties of polymers are irrelevant to detailed molecular components, consistent with central limit theorem. The coarse grained polymers are randomly oriented floppy chains, and can even be characterized as paths of particles doing Brownian motion. Brownian motion, or random walk, is known to be self-similar under scaling and self-similar chains are said to be Gaussian chains. If we smooth out the discrete atoms then the Gaussian chain becomes a continuous Gaussian thread that are self-similar under infinite scaling.

Quantum field theory and statistical mechanics are equivalent to each other up to a Wick rotation and both of them concern systems with infinite degrees of freedom, the fields. However, the primitive forms of QFT and statistical mechanics both originate in lattice drawing and it is akin to the treatment of polymer chains— discrete chains to continuous thread. The connection become transparent when we identify the length parameter with 'time' of a Brownian particle. From this point, it is proper to introduce the polymer field.

II. THE POLYMER FIELD

A. Random walk to Gaussian chains

First consider the 1D case. Let N be the number of step $(N \gg 1)$ and b the step size, or Kuhn length, then 1D random walk probability distribution, or the probability of finding the walker at position x is

$$P_1(x) = \left(\frac{1}{2\pi N b^2}\right)^{1/2} \exp\left(-\frac{x^2}{2Nb^2}\right) \quad (1)$$

which is a Gaussian distribution with variance Nb^2.

For a d-dimensional random walk, the distribution becomes

$$P_d(\mathbf{r}) = \left(\frac{d}{2\pi N b^2}\right)^{d/2} \exp\left(-\frac{d\mathbf{r}^2}{2Nb^2}\right) \quad (2)$$

For any two points $\mathbf{r}_1$ and $\mathbf{r}_2$ on a 3D Gaussian chain, the transition probability from $\mathbf{r}_1$ to $\mathbf{r}_2$ within n steps $(N \geq n \gg 1)$ is

$$G(\mathbf{r}_1, \mathbf{r}_2; n) = \left(\frac{3}{2\pi n b^2}\right)^{3/2} \exp\left(-\frac{3(\mathbf{r}_1 - \mathbf{r}_2)^2}{2nb^2}\right) \quad (3)$$

Note that $G(\mathbf{r}_1, \mathbf{r}_2; 0) = \delta(\mathbf{r}_1 - \mathbf{r}_2)$, it resembles the diffusion equation solution at $t = 0$. Actually, Gaussian transition probability is the Green function of diffusion equation if n is identified with time t, as shown in the following equation

$$\left[\partial_n - \frac{b^2}{6}\nabla^2\right] G(\mathbf{r}, \mathbf{r}'; n) = \delta(n)\delta(\mathbf{r} - \mathbf{r}') \quad (4)$$

B. Propagator to partition function

To entail the whole information of a Gaussian chain, we should consider all the incremental transitions, namely

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the sequence $\{\mathbf{r}_n\} = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{n-1}, \mathbf{r}_n\}$. The configuration of a chain stored in $\{\mathbf{r}_n\}$ is a *polymer field*. The n-point transition probability reads

$$G(\Delta\mathbf{r}_n; N) = \prod_{n=1}^{N} G(\Delta\mathbf{r}_n; 1) \tag{5}$$

$$= \prod_{n=1}^{N} \left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left(-\frac{3(\Delta\mathbf{r}_n)^2}{2b^2}\right) \tag{6}$$

$$= \left(\frac{3}{2\pi b^2}\right)^{\frac{3N}{2}} \exp\left(-\sum_{n=1}^{N}\frac{3(\mathbf{r}_n - \mathbf{r}_{n-1})^2}{2b^2}\right) \tag{7}$$

where $\Delta\mathbf{r}_n := \mathbf{r}_n - \mathbf{r}_{n-1}$. Now that $N \gg 1$, it is appropriate to replace difference by derivative and sum by integral. Then $G(\Delta\mathbf{r}_n, N)$ becomes

$$G(\{\Delta\mathbf{r}_n\}; N) = \left(\frac{3}{2\pi b^2}\right)^{\frac{3N}{2}} \exp\left(-\frac{3}{2b^2}\int_1^N dn \left(\frac{\partial\mathbf{r}}{\partial n}\right)^2\right) \tag{8}$$

For each polymer field $\{\mathbf{r}\}$, or a state in the system's state space, we have a transition probability $G(\{\mathbf{r}\}, N)$, then the sum of all those probabilities gives the partition function (functional),

$$Z = \sum_{\text{all paths}} G(\{\mathbf{r}(n)\}, N) \tag{9}$$

$$= \int \mathcal{D}[\mathbf{r}]\, G(\{\mathbf{r}(n)\}, N) \tag{10}$$

$$:= \int \mathcal{D}[\mathbf{r}]\, e^{-\beta\mathcal{H}} \tag{11}$$

where energy $\mathcal{H}$ must be

$$\mathcal{H} = \frac{3k_BT}{2b^2}\int_1^N dn \left(\frac{\partial\mathbf{r}}{\partial n}\right)^2 \tag{12}$$

If now we identify n with time (up to a constant), we have the partition function for a Brownian particle.

Applying Hubbard-Stratonovich transformation, namely transforming field $\{\mathbf{r}\}$ to density functional $\{\phi\}$, the partition function is then

$$Z = \int \mathcal{D}[\{\phi\}] e^{-\beta\mathcal{H}[\{\phi\}]} \tag{13}$$

$$:= \int \mathcal{D}[\{\phi\}] e^{-\mathcal{S}[\{\phi\}]} \tag{14}$$

Although the expression is nice and neat, it is hard to evaluate (the dirtiness is actually kicked to the calculation).

The Brownian particle density ϕ satisfies diffusion equation

$$\partial_t\phi(\mathbf{r}, t) = D\nabla^2\phi(\mathbf{r}, t) \tag{15}$$

It is also known in quantum mechanics that Schrödinger equation can be derived from the propagator in path integral formulation. The corresponding imaginary time Schrödinger equation is actually the diffusion equation. Then we can solve the phony Schrödinger equation

$$\mathcal{H}\psi_j(\mathbf{r}) = \epsilon_j\psi_j(\mathbf{r}) \tag{16}$$

and obtain the energy spectrum. The partition function is just the sum of Boltzmann factors

$$Z = \text{Tr}\, e^{-\beta\mathcal{H}} = \sum_j e^{-\epsilon_j/k_BT} \tag{17}$$

If there are more than one chain (labeled by indices $\{i\}$) and exist interactions $V(\{\mathbf{r}\})$, then the total energy is

$$\mathcal{H} = \sum_i \frac{3k_BT}{2b^2}(\partial_n\mathbf{r}_i)^2 + V(\{\mathbf{r}_i\}) \tag{18}$$

it is also the energy of a gas of interacting Brownian particles.

III. PERTURBATION AND NON-PERTURBATION THEORY

A. Mean-field theory

Let $\phi = \langle\phi\rangle + \eta$ with $\eta \ll \langle\phi\rangle$ and $\langle\phi\rangle$ is the mean field. Expand the action in terms of η

$$\mathcal{S}[\phi] = S[\langle\phi\rangle] + S^{(1)}[\langle\phi\rangle]\eta + \mathcal{O}(\eta^2) \tag{19}$$

Setting $S^{(1)}[\phi] = 0$, $\langle\phi\rangle$ can be obtained.

The partition function reads

$$Z = e^{-S}\int \mathcal{D}[\eta]\, e^{-S^{(1)}\eta + \mathcal{O}(\eta^2)} \tag{20}$$

The factor $e^{-S[\langle\phi\rangle]}$ is the mean field partition function. The free energy is $F = -k_BT\ln Z = S/\beta = H[\langle\phi\rangle]$ where $H[\langle\phi\rangle]$ is the zeroth order Hamiltonian.

The advantage of mean field theory is that it converts a many-body problem to a solvable one-particle problem, in other word, it erases correlations and all the particles feel an common effective field. The idea can further be utilized in numerical methods and it becomes the self-consistent field theory.

B. Gaussian fluctuations

Mean field theory requires the first order term of action should vanish. Whether it is stable or unstable depends on sign of second order term. Now we keep up to the second order, the partition function reads

$$Z \approx e^{-S[\langle\phi\rangle]}\int \mathcal{D}[\eta] \exp\left(-\frac{S^{(2)}[\langle\phi\rangle]}{2!}\eta^2\right) \tag{21}$$

Notice it is a Gaussian path integral. The free energy is then

$$F = H[\langle\phi\rangle] - \frac{1}{2}\ln\prod_{\mathbf{k}} G(\mathbf{k}) \qquad (22)$$

where $G(\mathbf{k})$ are independent propagators labeled by $\mathbf{k}$.

C. Renormalization

The mean field and Gaussian field theory proved extremely effective in numerous applications, however, they are well-defined only when fluctuations are small. In the case of strong fluctuations the two methods break down.

Renormalization group theory should then be employed. Again, it looks nice but nasty to evaluate. Hartree (1984) proposed an approximation scheme called *self-consistent one-loop approximation*, which manipulates a Gaussian ansatz with variational method and finds extra correlation energies. Moreover, based on the idea of tadpole renormalization, Efimov and Nogovitism (1996) developed another approach to compute functional integrals arising in classical many-particle systems.

IV. CONCLUSION AND DISCUSSION

There are two giant leaps in the conception of polymers: the first is from chemistry point of view to simple polymer chains; the second is from chains to polymer fields (functional field). The first leap enables us to quantify some basic properties of polymer chains with statistics. The second leap introduces QFT to explore much deeper properties of polymer fields.

The mean field theory provides us the ground state of the polymer field while Gaussian field gives rises to elementary excitations—'polymerons', the quasi-particles of polymer fields. When fluctuations are strong, the 'polymerons' scatter each others and hence, broaden the loop and add correlation energies to the system.

QFT, is by no means the theory of quantum systems, it is just like asserting that calculus is exclusively designed for Newtonian mechanics. Whenever there are fluctuations in a field, QFT can always find its way in.

However, QFT is equivalent to equilibrium statistical mechanics but soft matters are slow in the relaxation toward equilibrium. This may render QFT treatments mentioned above problematic. Future researches should be carried out for polymer fields on the dynamics of relaxation and consequences of being in non-equilibrium states.

[1] Teraoka, Iwao: *Polymer Solutions: An Introduction to Physical Properties*, John Wiley & Sons, Inc., 2002

[2] B. Miao, Lecture note: *Methods of polymer physics*, 2011
[3] Wikipedia, *Polymer field theory*