

Advanced Statistical Physics – CORRECTION OF THE EXAM

Monday 3 january 2022

1 Subdiffusion of a monomer embedded in a long polymer**A. Preliminary : Ornstein-Uhlenbeck process**

1/ The SDE $y'(t) = -\lambda y(t) + \sqrt{2D} \eta(t)$ is linear, hence easy to solve. The solution is

$$y(t) = y_0 e^{-\lambda t} + \sqrt{2D} \int_0^t dt' \eta(t') e^{-\lambda(t-t')} \quad (1)$$

2/ We deduce $\langle y(t) \rangle = y_0 e^{-\lambda t}$ (for y_0 non random) and, using $\langle \eta(t)\eta(t') \rangle = \delta(t-t')$,

$$\text{Var}(y(t)) = \frac{D}{\lambda} (1 - e^{-2\lambda t}) \quad (2)$$

3/ $\eta(t)$ is Gaussian, hence $y(t)$ being its convolution is also Gaussian : the knowledge of its two first moments is sufficient to characterize the full distribution,

$$P_t(y|y_0) = \frac{1}{\sqrt{2\pi \text{Var}(y(t))}} e^{-\frac{(y - \langle y(t) \rangle)^2}{2\text{Var}(y(t))}} = \sqrt{\frac{\lambda}{2\pi D (1 - e^{-2\lambda t})}} \exp \left\{ -\frac{\lambda (y - y_0 e^{-\lambda t})^2}{2D (1 - e^{-2\lambda t})} \right\} \quad (3)$$

Check : for $\lambda \rightarrow 0$ we recover the propagator of the free diffusion.

B. Motion of a polymer.— We consider N monomers with nearest neighbour interactions : $V(\{y_x\}) = \sum_x \frac{\lambda}{2} (y_{x+1} - y_x)^2$.

1/ Equation of motion of monomer x is

$$\frac{\partial y_x(t)}{\partial t} = -\frac{\partial V}{\partial y_x} + \sqrt{2D} \eta_x(t) = -\lambda (2y_x - y_{x+1} - y_{x-1}) + \sqrt{2D} \eta_x(t) \quad (4)$$

The continuum limit of this model is $\partial_t y(x, t) = \partial_x^2 y(x, t) + \sqrt{2D} \eta(x, t)$ (Edwards-Wilkinson model).

2/ We analyze the correlator in Fourier space :

$$\langle \tilde{\eta}_k(t) \tilde{\eta}_{k'}(t') \rangle = \sum_{x, x'} e^{-ikx - ik'x'} \langle \eta_x(t) \eta_{x'}(t') \rangle = \delta(t-t') \sum_x e^{-i(k+k')x} = N \delta_{k, -k'} \delta(t-t') \quad (5)$$

We Fourier-transform the equations of motion

$$\frac{d}{dt} \tilde{y}_k(t) = -\underbrace{\lambda (2 - e^{ikx} - e^{-ikx})}_{=4\lambda \sin^2(k/2) = \Lambda_k} \tilde{y}_k(t) + \sqrt{2D} \tilde{\eta}_k(t) \quad (6)$$

We have obtained uncoupled SDEs of the form of the Ornstein-Uhlenbeck equation.

3/ Solution is

$$\tilde{y}_k(t) = \tilde{y}_k^0 e^{-\Lambda_k t} + \sqrt{2D} \int_0^t dt' \tilde{\eta}_k(t') e^{-\Lambda_k(t-t')} \quad (7)$$

where $\tilde{y}_k^0 = \tilde{y}_k(0)$ is the TF of the initial configuration of the line.

4/ We are interested in the fluctuations of the position of a given monomer :

$$\langle y_x(t)^2 \rangle = \frac{1}{N^2} \sum_{k,k'} e^{-i(k+k')x} \langle \tilde{y}_k(t) \tilde{y}_{k'}(t) \rangle \quad (8)$$

hence we must pay attention to the fact that we need to characterize the correlations between different Fourier modes. We consider

$$\text{Cov}(\tilde{y}_k(t), \tilde{y}_{k'}(t)) = 2D \int_0^t dt_1 \int_0^t dt_2 \overbrace{\langle \tilde{\eta}_k(t_1) \tilde{\eta}_{k'}(t_2) \rangle}^{=N \delta_{k+k',0} \delta(t_1-t_2)} e^{-\Lambda_k(t-t_1) - \Lambda_{k'}(t-t_2)} \quad (9)$$

$$= 2D N \delta_{k+k',0} \int_0^t dt_1 e^{-2\Lambda_k(t-t_1)} = N \delta_{k+k',0} D \frac{1 - e^{-2\Lambda_k t}}{\Lambda_k} \quad (10)$$

where we have used $\Lambda_k = \Lambda_{-k}$. Summation over modes give

$$\text{Var}(y_x(t)) = \frac{1}{N^2} \sum_{k,k'} e^{-i(k+k')x} \text{Cov}(\tilde{y}_k(t), \tilde{y}_{k'}(t)) = \frac{D}{N} \sum_k \frac{1 - e^{-2\Lambda_k t}}{\Lambda_k} \quad (11)$$

Taking the limit $N \rightarrow \infty$, we can replace the sum by an integral over the Brillouin zone

$$\text{Var}(y_x(t)) = D \int_0^\pi \frac{dk}{\pi} \frac{1 - e^{-2\Lambda_k t}}{\Lambda_k} \quad (12)$$

(where we have used the symmetry $\Lambda_k = \Lambda_{-k}$).

5/ $\Lambda_k = 4\lambda \sin^2(k/2) \in [0, 4\lambda]$ is bounded. For short times $\lambda t \ll 1$, we have also $\Lambda_k t \ll 1$ thus we can expand the exponential in the integral

$$\text{Var}(y_x(t)) \simeq D \int_0^\pi \frac{dk}{\pi} 2t = 2Dt \quad (13)$$

we have recovered the behaviour characterizing *normal diffusion*. For short times, the monomers are free and do not feel the interaction with their neighbours.

6/ We study the long time limit, $\lambda t \gg 1$. We remark that $\int_0^\pi \frac{dk}{\pi} \frac{1}{\Lambda_k} \sim \int_0^\pi dk k^{-2} = \infty$, thus the integral goes to infinity as $t \rightarrow \infty$; the presence of the exponential in the integral cut off the divergence. We can estimate the behaviour of the integral by writing $1 - e^{-2\Lambda_k t} \simeq 1$ for $\Lambda_k t \gtrsim 1$ while the behaviour $1 - e^{-2\Lambda_k t} \simeq 2\Lambda_k t$ for $\Lambda_k t \lesssim 1$ simply gives a finite contribution. $\Lambda_k t \sim 1$ corresponds to $k \sim k_c(t) \simeq 1/\sqrt{\lambda t}$, thus

$$\text{Var}(y_x(t)) \simeq D \int_{k_c(t)}^\pi \frac{dk}{\pi} \frac{1}{\Lambda_k} \simeq D \int_{k_c(t)}^\pi \frac{dk}{\pi} \frac{1}{\lambda k^2} \simeq \frac{D}{\pi \lambda} k_c^{-1} = \frac{D}{\pi} \sqrt{\frac{t}{\lambda}} \quad (14)$$

For short times ($\lambda t \ll 1$) and long times ($\lambda t \gg 1$), we have the power law behaviour $\text{Var}(y_x(t)) \sim t^{2\theta}$, corresponding to the scaling $y_x(t) \sim t^\theta$. For short times, we have seen that the exponent is $\theta = 1/2$ corresponding to the normal diffusion $\sim \sqrt{t}$. For long times, we have instead obtained the exponent $\theta = 1/4$ characterizing *subdiffusion*. This is due to the fact that the interactions between the monomers slow down their diffusion.

Remark : this behaviour has been discussed in the short note : S. Alexander & P. Pincus, "Diffusion of labeled particles on one-dimensional chains", Phys. Rev. B **18**, p. 2011 (1978).

2 Scaling of the correlation length

The scaling hypothesis is

$$\xi(t, h) = \ell \xi(\ell^{y_t} t, \ell^{y_h} h) \tag{15}$$

where ℓ is the scaling factor and y_t and y_h are the thermal and magnetic exponents.

- 1/ At zero field we have $\xi(t, 0) = \ell \xi(\ell^{y_t} t, 0)$. We choose $\ell = |t|^{-1/y_t}$, thus $\xi(t, 0) = |t|^{-1/y_t} \xi(\pm 1, 0)$, hence $\nu = 1/y_t$.
- 2/ Similarly, for $t = 0$ we choose $\ell = |h|^{-1/y_h}$, hence $\xi(0, h) = |h|^{-1/y_h} \xi(0, \pm 1)$.
- 3/ For the 2D Ising model, we have $\alpha = 0$ and $\beta = 1/8$, thus $y_t = 1$ and $y_h = 15/8$. We deduce $\xi(t, 0) \sim 1/|t|$ for $t \rightarrow 0$ and $\xi(0, h) \sim |h|^{-8/15}$ for $h \rightarrow 0$.

3 Liquid crystal

A. Order parameter.— The axis of the molecule i is the unit vector $\vec{u}^{(i)}$.

1/ $\theta_i \in [0, \pi]$ is the angle between $\vec{u}^{(i)}$ and \vec{n} . Reversing $\vec{u}^{(i)}$ corresponds to $\theta_i \rightarrow \pi - \theta_i$, hence the distribution of the angle satisfies $p(\theta) = p(\pi - \theta)$.

The isotropic distribution is $\frac{1}{4\pi} d\Omega = \frac{1}{4\pi} d\theta d\varphi \sin \theta$, corresponding to $p(\theta) = \frac{1}{2} \sin \theta$.

In the nematic phase, $p(\theta)$ presents two sharp symmetric peaks close to $\theta = 0$ and $\theta = \pi$.

2/ For $\vec{n} = \vec{e}_z$ we have $\langle \vec{u}^{(i)} \rangle = \vec{e}_z \langle \cos \theta_i \rangle = \vec{e}_z \int_0^\pi d\theta p(\theta) \cos \theta = 0$, whatever is $p(\theta) = p(\pi - \theta)$. Hence, the orientational order cannot be characterized by a vectorial order parameter.

3/ For the molecule i , we introduce the tensor $Q_{\alpha\beta}^{(i)} = u_\alpha^{(i)} u_\beta^{(i)} - \frac{1}{3} \delta_{\alpha\beta}$, which is a symmetric tensor with zero trace. We denote $Q = \langle Q^{(i)} \rangle$ the averaged tensor. For simplicity we set $\vec{n} = \vec{e}_z$.

The off-diagonal elements are zero : $Q_{xy} = \langle \cos \varphi \sin \varphi \sin^2 \theta \rangle = \frac{1}{2} \langle \sin 2\varphi \rangle \langle \sin^2 \theta \rangle = 0$ using the rotational symmetry around \vec{n} . Similarly $Q_{xz} = Q_{yz} = 0$.

The first diagonal element is $Q_{xx} = \langle \cos^2 \varphi \sin^2 \theta \rangle - \frac{1}{3} = \frac{1}{2} \langle \sin^2 \theta \rangle - \frac{1}{3} = \frac{1}{6} - \frac{1}{2} \langle \cos^2 \theta \rangle = -S/3$ with $S = \langle P_2(\cos \theta) \rangle$ where $P_2(x) = (3x^2 - 1)/2$ is the Legendre polynomial. By symmetry $Q_{xx} = Q_{yy}$. Finally $Q_{zz} = \langle \cos^2 \theta \rangle - \frac{1}{3} = 2S/3$. Hence

$$Q = S \begin{pmatrix} -1/3 & 0 & 0 \\ 0 & -1/3 & 0 \\ 0 & 0 & 2/3 \end{pmatrix} \quad (16)$$

In general we can write $Q = S(\vec{n} \otimes \vec{n} - \mathbf{1}_3)$, where the tensor product $\vec{n} \otimes \vec{n}$ is the projector on the unit vector.

• In the **isotropic phase**

$$S = \int_0^\pi d\theta p(\theta) P_2(\cos \theta) = \frac{1}{2} \int_{-1}^{+1} dx P_2(x) = \frac{1}{4} \int_{-1}^{+1} dx (2x^2 - 1) = \frac{1}{2} [x^3 - x]_{-1}^{+1} = 0 \quad (17)$$

• On the contrary, in the **nematic phase**, molecules are aligned and $p(\theta)$ is concentrated symmetrically close to $\theta = 0$ and $\theta = \pi$, hence

$$S = \langle P_2(\cos \theta) \rangle \simeq \frac{1}{2} P_2(+1) + \frac{1}{2} P_2(-1) = +1 \quad (18)$$

4/ The elementary interaction in the Maier-Saupe model is

$$E_{ij} = -\varepsilon \text{Tr} \left\{ Q^{(i)} Q^{(j)} \right\} = -\varepsilon \text{Tr} \left\{ (\vec{u}^{(i)} \otimes \vec{u}^{(i)} - \mathbf{1}_3) (\vec{u}^{(j)} \otimes \vec{u}^{(j)} - \mathbf{1}_3) \right\} \quad (19)$$

$$= -\varepsilon \left[(\vec{u}^{(i)} \cdot \vec{u}^{(j)})^2 - \frac{1}{3} (\vec{u}^{(i)})^2 - \frac{1}{3} (\vec{u}^{(j)})^2 + \frac{1}{9} \right] = -\varepsilon (\vec{u}^{(i)} \cdot \vec{u}^{(j)})^2 + \text{cste} \quad (20)$$

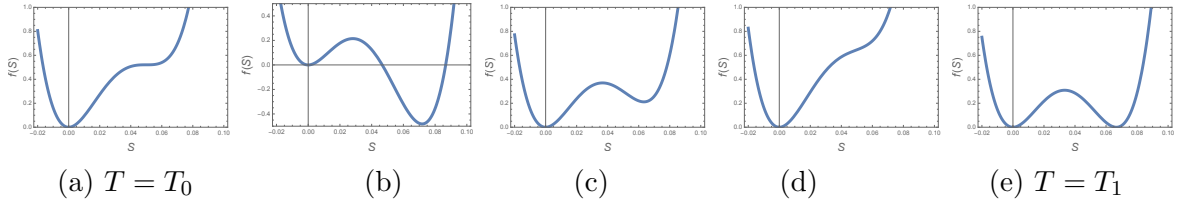
hence, for $\varepsilon > 0$, such interaction favors the cases where the two vectors are either aligned $\vec{u}^{(i)} = \vec{u}^{(j)}$ or anti-aligned $\vec{u}^{(i)} = -\vec{u}^{(j)}$. This is indeed a good model for the microscopic interaction.

B. Isotropic-nematic transition.— Within the Maier-Saupe model, one obtains the $S \rightarrow 0$ expansion

$$f(S) = \frac{1}{2} a(T) S^2 - \frac{b}{3} S^3 + \frac{c}{4} S^4 \quad \text{with } a(T) = \tilde{a} (T - T_*) \text{ and } \tilde{a}, b, c \text{ positive.} \quad (21)$$

for the Landau free energy (lengthy and painful calculation).

Contrary to the case of the para-ferro transition, no symmetry prevents from the presence of the term S^3 .

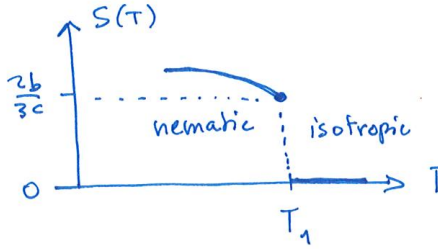


1/ As T decreases, a diminishes, hence $f(S)$ decreases in the intermediate region. The correct ordering is thus (d), (a), (c), (e), (b).

2/ $f'(S) = S(a + bS + cS^2)$. The temperature T_0 corresponds to the case where $a - bS + cS^2$ has one degenerate root, hence $\Delta = b^2 - 4ac = 0$, leading to $T_0 = T_* + \frac{b^2}{4ac}$. T_1 corresponds to the case where the two minima coincide, $f(S) = f(0)$. Hence we solve $f(S) = f(0)$ and $f'(S) = 0$, i.e. $a - bS + cS^2 = 0$ and $\frac{1}{2}a - \frac{1}{3}bS + \frac{1}{4}cS^2 = 0$, which is easy. We get $S = 2b/(3c)$ (or $S = 0$) and $a = 2b^2/(9c)$ i.e. $T_1 = T_* + \frac{2b^2}{9ac}$.

3/ The form of free energy describes a transition between a state $S = 0$ (isotropic) for $T > T_1$ (figures d, a, c), to a state where $S > 0$ for $T < T_1$ (figures e and b). This indeed describes the isotropic-nematic transition.

The order parameter S makes a jump from $S = 0$ for $T = T_1^+$ to $S = 2b/(3c)$ for $T = T_1^-$, hence the transition is first order.



C. Nematic phase and Ginzburg-Landau theory.— We describe a spatial dependent order parameter. We consider S uniform ($T < T_1$) and consider that the director is spatial dependent, i.e. the unit vector $\vec{n}(\vec{r})$.

We study below the case where the director is in the xOy plane, $\vec{n}(\vec{r}) = (\cos \psi(z), \sin \psi(z), 0)$, with the angle depending only on the coordinate z .

1/ Obviously $\vec{\nabla} \cdot \vec{n} = 0$. We find $\vec{\nabla} \times \vec{n} = -\psi'(z)\vec{n}$, thus

$$F[\psi(z)] = K_2 \int dz \left\{ \frac{1}{2} [\psi'(z)]^2 - \frac{1}{\xi^2} \sin^2 \psi(z) \right\} \quad (22)$$

with $g = K_2$ and $\xi^{-2} = \chi_a H^2 / (2K_2)$.

2/ We have $\frac{\delta F}{\delta \psi(z)} = -K_2 \psi''(z) - \frac{K_2}{\xi^2} \sin 2\psi(z)$. The field equation corresponds to the configuration which minimizes the free energy,

$$\psi''(z) + \frac{1}{\xi^2} \sin 2\psi(z) = 0 \quad (23)$$

3/ We can find a "constant of motion" by analogy with classical mechanics (field equation is similar to the Newton equation for a particle at position $\psi(z)$ at time z in a potential $V(\psi) \propto -\sin^2 \psi$).

We may also directly check that $\frac{d}{dz} \left\{ \frac{1}{2} [\psi'(z)]^2 + \xi^{-2} \sin^2 \psi(z) \right\} = 0$ thanks to the field equation.

4/ We consider the field configuration with $\psi(z) \rightarrow \pm\pi/2$ for $z \rightarrow \pm\infty$. Hence $\mathcal{E} = \xi^{-2}$ since $\psi'(z) \rightarrow 0$ at infinity. We can write

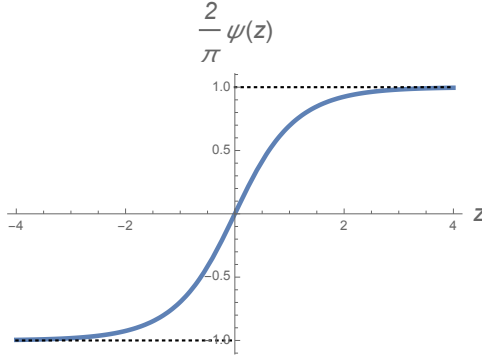
$$\frac{1}{2} [\psi'(z)]^2 + \xi^{-2} \sin^2 \psi(z) = \xi^{-2} \quad \Rightarrow \quad \frac{d\psi}{\cos \psi} = \frac{\sqrt{2}}{\xi} dz \quad (24)$$

thus

$$\int_0^{\psi(z)} \frac{d\psi}{\cos \psi} = \frac{\sqrt{2}}{\xi} z \quad (25)$$

for $\psi(0) = 0$. Using $\frac{d}{dt} \ln |\tan(t/2 + \pi/4)| = 1/\cos t$ one deduces

$$\tan\left(\frac{1}{2}\psi(z) + \frac{\pi}{4}\right) = e^{\sqrt{2}z/\xi} \quad (26)$$



The uniform configuration is $\psi = \pm\pi/2$ (the minimum of the "potential"), hence it has a free energy $F[\text{uniform}] = -K_2 \text{Volume}/\xi^2$.

The difference of the free energy of the configuration obtained above is

$$F[\psi] - F[\text{uniform}] = K_2 \int dz [\psi'(z)]^2 \sim K_2 \xi [1/\xi]^2 \sim K_2/\xi > 0 \quad (27)$$

where I made use of (24) ; I have used that $\psi'(z) \sim 1/\xi$ on a width $\sim \xi$.

The configuration for the non uniform field has a higher free energy due to the elastic cost.