3.6 Polymers

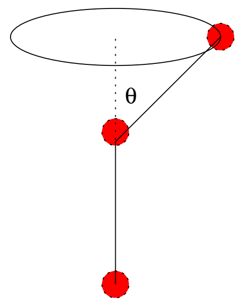

Figure 3.4: Bonds in a polymer constrained to have $\mathbf{r}_i \cdot \mathbf{r}_{i-1} = a^2 \cos\theta$.

Problem (2 marks): Consider a polymer chain with links constrained as in Fig. 3.4, but otherwise freely jointed.
(a) Write $\mathbf{r}_i = \mathbf{r}_{i-1}\cos\theta + \mathbf{w}_i$, for some unknown $\mathbf{w}_i$ and then show that $\langle \mathbf{r}_i \cdot \mathbf{r}_{i-n}\rangle = \langle \mathbf{r}_{i-1} \cdot \mathbf{r}_{i-n}\rangle \cos\theta$. Solve this to get

$$\langle \mathbf{r}_i \cdot \mathbf{r}_{i-n}\rangle = a^2 \cos^n \theta.$$

(b) What is $S_N^2 = \langle \left(\sum_{j=1}^N \mathbf{r}_j\right)^2 \rangle$.
(c) What effective persistence length can be introduced to make this equivalent to the freely jointed chain?

3.7 Brownian motion

In fluids, there are no equilibrium sites like in solids. Therefore there can be no forces pushing atoms back to equilibrium positions. Instead, atoms experience 'random' forces $\Gamma(t)$ from their neighboring atoms. This leads to the erratic motion of small particles in fluids as observed by the botanist Robert Brown. How can one describe these random forces and their effect on the dynamics of a particle?

It is important to realize that forces are not entirely random, i.e., if atom i experiences a force $\mathbf{F}$ at time t, then an extremely small time later, let's say 1 fs, this force will barely have changed. However, after sufficient time has passed by for the local structure to reorganize, it is safe to assume that forces are uncorrelated.

3.7.1 Langevin equation

Let us pretend for a moment that it is appropriate to have the random force rejuvinate on a very small time scale, i.e., $\Gamma(t^-)$ and $\Gamma(t^+)$ are uncorrelated. We also know that - on average - an atom will slow down with time or that it experiences a drag force when an external force is applied to it. For example, a sufficiently large colloidal particle immersed in a fluid consisting of small particles will reach a finite drift velocity as it sinks towards the ground or rises to the top (depending on the density difference). The situation just described can be mimicked by the Langevin equation

$$m\ddot{x} = F_c - \gamma m\dot{x} + \Gamma(t), \tag{3.134}$$

where F_c is a conservative force, γ a damping term with the unit of inverse time, and $\Gamma(t)$ the random force. $\Gamma(t)$ is not supposed to invoke a drift, thus

$$\langle \Gamma(t) \rangle = 0. \tag{3.135}$$

Moreover, $\Gamma(t)$ is meant to lose its memory very quickly, hence

$$\langle \Gamma(t)\Gamma(t') \rangle = \Gamma_0^2 \, \delta(t - t'). \tag{3.136}$$

How do we choose the amplitude Γ_0 for the random force? In order to address this question, it is conveniant to analyse Eq. (3.134) in the frequency domain. For this purpose, let us assume that we can approximate F_c to be a linear restoring force $F_c = -kx$, something appropriate for a particle in an optical trap centered at the origin. In reciprocal space, the Langevin equation reads

$$\tilde{x}(\omega) = a(\omega)\tilde{\Gamma}(\omega). \tag{3.137}$$

with

$$a(\omega) = \frac{1}{k - m\omega^2 + im\gamma\omega}. \tag{3.138}$$

Since Γ is random, it is not possible to predict the dependence of $\tilde{x}$ on ω. However, it is possible to make predictions about the expectation values of the various moments of $\tilde{x}(\omega)$. First, since $\langle \Gamma(t) \rangle$ is zero at all times, we can conclude that the expectation value in the frequency domain must have the same property

$$\langle \tilde{\Gamma}(\omega) \rangle = 0 \tag{3.139}$$

for every ω. As a consequence we can say that $\langle \tilde{x}(\omega) \rangle = 0$ and hence $\langle \tilde{x}(t) \rangle = 0$ at all times. This means that while $\tilde{\Gamma}$ and $\tilde{x}$ are generally different from zero for a single realization of an 'experiment', there is no reason for $\tilde{\Gamma}$ and $\tilde{x}$ to be positive or negative, if we average over many different realizations of the random process. (Throughout the present treatment, we assume that no controlled external force is applied, unless mentioned otherwise.)

In order to get more information on the dynamics, it will be necessary to calculate the second moment of $\tilde{\Gamma}$ in frequency space. With the convention of the Fourier transform to be

$$\Gamma(t) = \frac{1}{\sqrt{2\pi}} \int d\omega \, \tilde{\Gamma}(\omega) \exp(-i\omega t), \tag{3.140}$$

one can define the second moment of $\tilde{\Gamma}$ in the frequency domain as $I'_{\Gamma}(\omega, \omega')$:

$$\begin{aligned} I'_{\Gamma}(\omega, \omega') &= \langle \tilde{\Gamma}(\omega) \tilde{\Gamma}^*(\omega') \rangle, \\ &= \frac{1}{2\pi} \left\langle \int dt \, dt' \, \Gamma(t) \Gamma^*(t') \, e^{i(\omega t - \omega' t')} \right\rangle \\ &= \frac{1}{2\pi} \int dt dt' \underbrace{\langle \Gamma(t) \Gamma^*(t') \rangle}_{C_{\Gamma}(t-t')} e^{i(\omega t - \omega' t')}, \end{aligned} \tag{3.141}$$

where we have made use of the fact that the only random variables in the equation above are related to Γ. For a *stationary* process, the time autocorrelation function $C_{\Gamma} = \langle \Gamma(t) \Gamma(t') \rangle$ of a random signal only depends on the *time difference* $\Delta t = t - t'$. Eq. (3.141) can therefore be simplified to

$$I'_{\Gamma}(\omega, \omega') = \delta(\omega - \omega') \int d\Delta t \; C_{\Gamma}(\Delta t) \; e^{i\omega \Delta t} \tag{3.142}$$

$$= \sqrt{2\pi} \, \tilde{C}_{\Gamma}(\omega) \, \delta(\omega - \omega') \tag{3.143}$$

We recognize that the function $I'(\omega, \omega')$ is diagonal in frequency. This means that $\tilde{\Gamma}(\omega)$ is completely independent of (or uncorrelated with) $\tilde{\Gamma}^*(\omega')$ if $\omega \neq \omega'$. For the derivation of this property, we only made use of the stationarity of the process, but not of the specific choice for $\langle \Gamma(t) \Gamma(t') \rangle$. The full information of the spectrum of a random signal that is due to a stationary process is thus contained in the Fourier transform of $C_{\Gamma}(\Delta t)$. This is summarized in Eq. (3.143) which is also called the *Wiener-Khintchine theorem*. Note that this equation only holds for an ensemble of real or expected trajectories.

The Wiener-Khintchine theorem is not meaningful for a single realization of a random process.

We will now continue with the discussion of our specific case. Inserting Eq. (3.136) into Eq. (3.142), yields the spectrum

$$\tilde{C}_\Gamma(\omega) = \frac{1}{\sqrt{2\pi}}\,\Gamma_0^2, \tag{3.144}$$

which is independent of frequency. Since every frequency in the random force contributes on average with the same absolute square, one calls such a random force 'white noise'.

We can now proceed with the calculation of the expected dynamics of our particle. Although x is not δ correlated, it can be interpreted as a random variable with an underlying random process. Eq. (3.143) is therefore also valid if x is the index in the function instead of Γ. Realizing that

$$\langle \tilde{x}(\omega)\tilde{x}^*(\omega')\rangle = a(\omega)a^*(\omega)\ \langle \tilde{\Gamma}(\omega)\tilde{\Gamma}^*(\omega')\rangle \tag{3.145}$$

we can make use of the Wiener-Khintchine theorem and obtain the time autocorrelation function of x as

$$\begin{aligned} C_x(t) := \langle x(t)x(0)\rangle &= \frac{1}{\sqrt{2\pi}}\int d\omega\ e^{-i\omega t}\ a(\omega)a^*(\omega)\ \tilde{C}_\Gamma(\omega) \\ &= \frac{1}{2\pi}\int d\omega\ e^{-i\omega t}\frac{\Gamma_0^2}{(k-m\omega^2)^2+m^2\omega^2\gamma^2} \end{aligned} \tag{3.146}$$

The integral is most easily solved with the help of the residue theorem, which states that integration of an analytic function with a finite number of poles over a closed path yields $2\pi i\sum_j R_j$, where the R_j are the residues at the poles. In the present examples, poles are located at

$$\omega = \pm\frac{i}{2}\gamma \pm \omega_1,\ \text{where}\ \omega_1 = \sqrt{\frac{k}{m}-\frac{\gamma^2}{4}} \tag{3.147}$$

For positive times, we would integrate over the upper plane and for negative times, we would integrate over the lower plane. The time correlation function can now be written as

$$C_x(t) = \frac{\Gamma_0^2}{2mk\gamma}\left(\cos(\omega_1\mid t\mid) + \frac{\gamma}{2\omega_1}\sin(\omega_1\mid t\mid)\right)\ e^{-\gamma|t|/2}. \tag{3.148}$$

Note that $C_x(t)$ is time reversible. Generally, all (classical) time correlation functions are time reversible. We still have to determine the value for Γ_0 to know the full correlation function $C_x(t)$. If we want to obtain the correct equilibrium solution then, from equipartition, we may conclude that

$$\frac{1}{2}k_BT = \frac{1}{2}k\langle x^2(t)\rangle = \frac{1}{2}k\langle x^2(0)\rangle = \frac{1}{2}kC_x(0) = \frac{\Gamma_0^2}{2m\gamma}, \tag{3.149}$$

thus

$$\Gamma_0^2 = 2m\gamma k_BT. \tag{3.150}$$

This value is independent of k and also ensures proper 'thermostating' for $k = 0$, in which case $C_x(t)$ simply diverges. The calculation of correlation functions for fluids ($k = 0$) will be done in the problem set.

3.7.2 Fluctuation dissipation theorem

In most circumstances, we do not know the response functions or more generally speaking the susceptibility of a system. However, often we can measure the fluctuations of an observable. For example, when we run a computer simulation employing a thermostat, we can monitor the fluctuations of the energy $\langle \delta E^2\rangle$ and, as shown in a previous problem, predict the specific heat $C = dU/dT$ as $C/k_B = \beta^2\langle \delta E^2\rangle$ without actually having to change the temperature T. In the previous section, if we knew $C_x(0)$ (for example by measuring the fluctuations of a particle in an optical trap), then we could immediatly predict the corresponding strength k of the trap. Thus in both examples, we do not have to change the external parameters (temperature in the first case, external force or torque in the second case), in order to predict the response (specific heat, strength of the trap) of the system. Many more examples could be given, i.e., if we knew the fluctuations of the strain (which one can get from inelastic scattering experiments or in a computer simulation), we could predict the elastic constants, without actually having to stress the crystal, etc.

However, the fluctuations do not only contain information on the static susceptibilities. They also contain information on the dynamics of the system. Knowing the thermal autocorrelation function $C_x(t)$ allows one to determine the (linear) response of x to *any* (sufficiently small) *time*-dependent force. This relation is usually named the *fluctuation-dissipation* theorem. In the present case, we can find that

$$\begin{aligned}\Im[a_x(\omega)] &= \Im\left(\frac{1}{k - m\omega^2 + im\gamma\omega}\right) \\ &= \frac{-m\gamma\omega}{(k - m\omega^2)^2 + \gamma^2\omega^2} \qquad (3.151) \\ &= -2\beta\omega\,\tilde{C}_x(\omega). \qquad (3.152)\end{aligned}$$

The relation (3.152), which gives the imaginary part of the susceptibility as a function of the (F.T. of) the autocorrelation function is generally applicable for thermal, classical systems, i.e., it is also valid for generalized damping terms, which will be discussed below.

As a reminder from classical mechanics, one may add that imaginary and real part of a response function are related through the Kramers-Kronig relationship, namely

$$\Re[a(\omega)] = \mathcal{P}\int \frac{d\omega'}{\pi}\,\frac{\Im[a(\omega)]}{\omega - \omega'} \qquad (3.153)$$

where $\mathcal{P}$ denotes the principal value of the integral. Thus knowing the time correlation function $C_x(t)$ enables one to reconstruct the full response function.

3.7.3 Generalized Langevin dynamics and the 2$^{\text{nd}}$ fluq-diss theorem

As argued in the beginning to this chapter, random forces do not rejuvinate infinitely fast. One might argue that random forces have a *memory*, albeit it might be very short. A generalization for the random force would thus be to give up the idea of δ correlated forces and to simply require that the correlation function of the random force be stationary

$$\langle\Gamma(t)\Gamma(t')\rangle = C_\Gamma(t - t'). \qquad (3.154)$$

Since the damping and the random forces have the same atomistic origin, i.e., collision of a colloidal particle with solvent atoms, we should allow for the damping to have a memory as well. Keeping the linearity of the Langevin equation, the following generalization of Eq. (3.134) occurs quite naturally:

$$m\ddot{x} + m\int_{-\infty}^{t}\gamma'(t - t')\dot{x}(t')\,dt' + kx = \Gamma(t) + F(t) \qquad (3.155)$$

where $F(t)$ is an external force and where the present damping on the particle can only depend on the past and the current velocity but certainly not on the future velocity. This would violate causality. We may therefore require that

$$\gamma'(t < 0) = 0. \tag{3.156}$$

Deterministic and inertial forces remain instantaneous in Eq. (3.155). In the original Langevin dynamics, γ and $\Gamma(t)$ were not chosen independent from one another, see Eq. (3.150). A heuristic generalization of this equation would be to require that

$$C_\Gamma(t - t') = 2k_B T m\,\gamma(|\,t - t'\,|), \tag{3.157}$$

which contains the original Langevin dynamics unperturbed, i.e., $C_\Gamma(t-t') = \Gamma_0^2\,\delta(t-t')$ and due to the δ-correlation in $\gamma'(|\,t-t'\,|) = \gamma\delta(t-t')$, damping becomes instantaneous in Eq. (3.155).

Eq. (3.157) is known as the *second fluctuation-dissipation theorem*. It relates the time-dependent damping in a system to the non-explicitly considered (random) forces. The relation appears to be ad-hoc here, but it can be verified by making use of the partition function and Liouville operator formalism. One may actually say that the proper relation between stochastic and damping force turned out to be coincidentally correct in the original treatment by Langevin.

Let us reconsider Eq. (3.155). It is linear in x so that its Fourier transform reads

$$\left(k - m\omega^2 + im\omega\tilde{\gamma}[\omega]\right)\ \tilde{x}(\omega) = \tilde{\Gamma}(\omega) + \tilde{F}(\omega), \tag{3.158}$$

where $\tilde{\gamma}[\omega]$ is the Fourier transform as obtained by the integration over positive times only. We can see that the expectation value of the displacement x satisfies

$$\begin{aligned} \langle \tilde{x}(\omega) \rangle &= \frac{1}{a(\omega)}\ \tilde{F}(\omega) \\ &= \frac{1}{k - m\omega^2 + im\omega\tilde{\gamma}[\omega]}\ \tilde{F}(\omega). \end{aligned} \tag{3.159}$$

Similarly to the above derivation, we can calculate the autocorrelation function $C_x(t)$ to be

$$C_x(t) = \frac{1}{\sqrt{2\pi}} \int d\omega e^{-i\omega t} \frac{1}{a(\omega)a^*(\omega)} \tilde{C}_\Gamma(\omega), \tag{3.160}$$

and owing to the second fluctuation-dissipation theorem, Eq. (3.157), we can recuperate the original fluctuation-dissipation theorem as stated in Eq. (3.152).

3.7.4 Problems

1. (3 marks) Calculate the velocity autocorrelation function $C_v(t)$ for a particle in a fluid. For this purpuse, set $k = 0$ in Eq. (3.134) and find the proper velocity resoponse function $\mu(\omega)$ such that $\tilde{v}(\omega) = \mu(\omega)\tilde{F}(\omega)$, where $F(t)$ is a time-dependent force (externally imposed force and/or white thermal noise). Formulate and check the fluctuation-dissipation theorem for the 'mobility' $\mu(\omega)$.

2. (a) (1 mark) Show that $C_v(t) = -\partial_2^2 C_x(t)$. Hint: Use the Wiener-Khintchine theorem.
(b) (1 mark) Show that $\Delta C_x(t) := \langle \{x(t) - x(0)\}^2 \rangle$ can be written as $\Delta C_x(t) = 2\{C_x(0) - C_x(t)\}$.
(c) (2 marks) Consider again a particle in a fluid. What functional form do you expect for $\Delta C_x(t)$ in the limit $t \to \infty$? Use part a and b of this problem. You may assume that $C_v(t)$ decays exponentially with time, if you haven't solved 3.3.4.1. Determine the proportionality coefficients of the leading term by using Eq. (3.148) and by analyzing the limit $k \to 0$. Discuss briefly why the limits $\lim_{t\to\infty}$ and $\lim_{k\to 0}$ do not commute when calculating the required coefficient (which is called the diffusion coefficient).

3. (4 marks) Consider a linear, harmonic chain plus thermal noise:

$$m\ddot{x}_n + k(2x_n - x_{n+1} - x_{n-1}) = F_{\text{damping}} + \Gamma_n(t)$$

with two different realizations of the noise.

(a) Langevin dynamics:

$$F_{\text{damping}} = -m\gamma\dot{x}_n \quad \text{and} \quad \langle\Gamma_n(t)\Gamma_n(t)\rangle = \Gamma_0^2\delta(t')$$

(b) Dissipative particle dynamics:

$$F_{\text{damping}} = -m\gamma(\dot{x}_n - \dot{x}_{n+1}) - m\gamma(\dot{x}_n - \dot{x}_{n-1}) \quad \text{and} \quad \Gamma_n = \Gamma_{n,n+1} - \Gamma_{n-1,n},$$

where the random forces conserve the (local) momentum of the chain, i.e., the random forces can be written as

$$\Gamma_{n,n+1} = -\Gamma_{n+1,n} \quad \text{and} \quad \langle\Gamma_{n,n+1}(t)\Gamma_{n',n'+1}(t')\rangle = \Gamma_0^2\,\delta(t-t')\delta_{n,n'}$$

Transform the equations of motion into reciprocal space and frequency domain and find the proper condition for Γ_0 in either case. Draw a sketch of the phonon spectrum $\langle|\,\tilde{u}(q,\omega)\,|^2\rangle$ as a function of ω for a fixed, but small value of q. Which description is more realistic if our linear chain is meant to describe density fluctuations in a regular fluid?