Statistical Mechanics
E0415

Fall 2021, lecture 3
Correlations & Dissipation

Take home 2

2.t

Let us turn this into an exercise in gambling. You play heads and tails (toss a coin, and guess the outcome: win or lose the coin). Three questions: you start with 10 coins. Give an argument how the distribution of times it takes for you to lose all your coins looks like. What happens if you play till you have zero, or until you won all the 10 coins of your friend? Let us now consider the case where the coin is not fair: the fractional Brownian motion, where the subsequent outcomes are correlated (positively or negatively). How does that influence qualitatively those outcomes?

"-- the distribution of times it takes to lose all the money, must be zero when the number of tosses is less than 10, because it is impossible to lose 10 coins in less than 10 tosses. The distribution must also be zero when the number of tosses is odd."

"For random walk, the expectation value of distance from starting point after N steps is sqrt(N)*L_step. This would mean that the most likely number of throws and guesses would be N = 100. "

“If we were to forcefully play the game to an end, the game might in reality end much sooner, or much later than after 100 throws. The RMS relation is just a statistical estimate, and in reality the number of throws can vary a lot."

"Weighted coin has a considerable effect on the probability distribution especially in the no-win-scenario where long games allows even small correlations to be noticeable. If a win is more probable, then games without a win condition tend to go on way longer and to infinity perhaps. If loses are more probable, then long games tend to happen a lot less often."

"This problem is known as the “Gambler’s ruin” in stochastics. It can be modelled using Markov chains to calculate e.g., mean passage times through certain states of interest. "

Comments:

The first question is actually a so-called First Passage problem. For an unbounded domain (your friend is immensely rich so you can win ad infinitum) the average time is… infinite. That Is b/c the first passage time (to reach zero) τ scales with an exponent of -3/2 (is a power-law). You may note that this is related to the Gaussian distribution of -1/2 exponent, and the FP time is its derivative. “Diffusive flux”.

fBm: trends and anti-trends

Correlation functions

"Fields" s(x,y): how to find regularities?

$$C_t^{\mathrm{coar}}(\mathbf{r}) = \langle S(\mathbf{x},t)S(\mathbf{x}+\mathbf{r},t)\rangle$$

$$C(\mathbf{r},\tau) = \langle S(\mathbf{x},t)S(\mathbf{x}+\mathbf{r},t+\tau)\rangle.$$

s: height, magnetization, activity..

Limiting behaviors (τ, $\mathbf{x} \to \infty$)!

Scale-free behavior (2^{nd} order phase transitions).

Check Google Maps for s(x,y)… Retkeilypaikka…

Fig. 10.1 Phase separation in an Ising model, quenched (abruptly cooled) from high temperatures to zero temperature [124]. The model quickly separates into local blobs of up- and down-spins, which grow and merge, coarsening to larger blob sizes (Section 11.4.1).

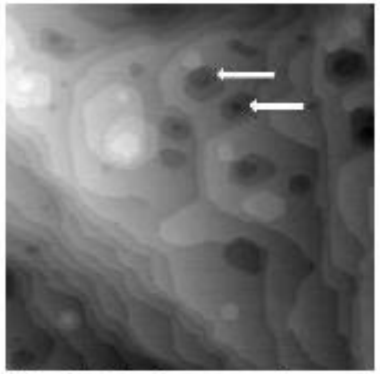


Fig. 10.2 Surface annealing. An STM image of a surface, created by bombarding a close-packed gold surface with noble-gas atoms, and then allowing the irregular surface to thermally relax (Tatjana Curcic and Barbara H. Cooper [32]). The figure shows individual atomic-height steps; the arrows each show a single step pit inside another pit. The characteristic sizes of the pits and islands grow as the surface evolves and flattens.

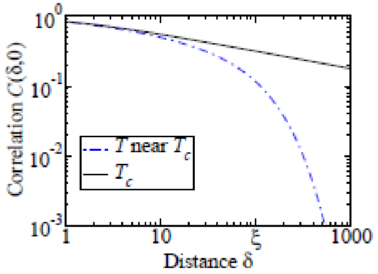
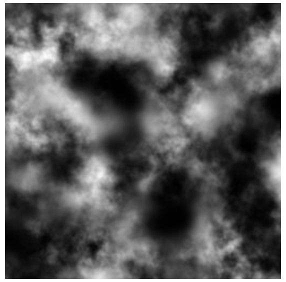
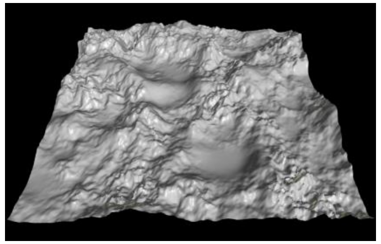


Fig. 10.5 Power-law correlations. The schematic correlation function of figure 10.4 on a log–log plot, both at T_c (straight line, representing the power law $C \sim r^{-(d-2+\eta)}$) and above T_c (where the dependence shifts to $C \sim e^{-r/\xi(T)}$ at distances beyond the correlation length $\xi(T)$). See Chapter 12.





Experimental measures

X-rays, neutrons scatter (from what? Electrons, Nuclear spins…) and produce… the Fourier Transform of the equal-time Correlation function. How?

$$\begin{aligned}
|\widetilde{\rho}(\mathbf{k})|^2 &= \widetilde{\rho}(\mathbf{k})^* \widetilde{\rho}(\mathbf{k}) = \int d\mathbf{x}'\, e^{i\mathbf{k}\cdot\mathbf{x}'} \rho(\mathbf{x}') \int d\mathbf{x}\, e^{-i\mathbf{k}\cdot\mathbf{x}} \rho(\mathbf{x}) \\
&= \int d\mathbf{x}\, d\mathbf{x}'\, e^{-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} \rho(\mathbf{x}')\rho(\mathbf{x}) \\
&= \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} \int d\mathbf{x}'\, \rho(\mathbf{x}')\rho(\mathbf{x}'+\mathbf{r}) \\
&= \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} V \langle \rho(\mathbf{x})\rho(\mathbf{x}+\mathbf{r}) \rangle = V \int d\mathbf{r}\, e^{-i\mathbf{k}\cdot\mathbf{r}} C(\mathbf{r}) \\
&= V \widetilde{C}(\mathbf{k}).
\end{aligned}$$

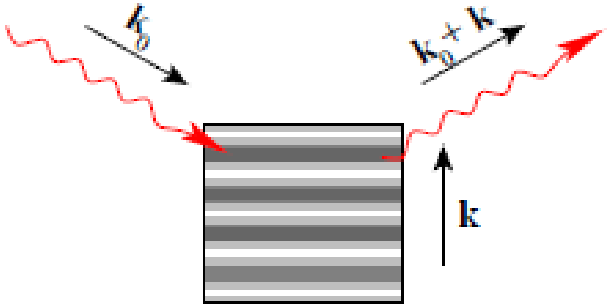


Fig. 10.6 X-ray scattering. A beam of wavevector $\mathbf{k}_0$ scatters off a density variation $\rho(\mathbf{x})$ with wavevector $\mathbf{k}$ to a final wavevector $\mathbf{k}_0 + \mathbf{k}$; the intensity of the scattered beam is proportional to $|\widetilde{\rho}(\mathbf{k})|^2$ [9, chapter 6].

Ideal gases: equal time correlations

Easiest, illustrative case (with no correlations). We need to compute from the FE free energy and density the fluctuations, and then consider what happens if we break the system into many sub-volumes (un-correlated).

Hemholtz' FE and its derivative

$$\mathcal{F}^{\rm ideal}(\rho(\mathbf{x}),T) = \rho(\mathbf{x}) k_B T \left[\log(\rho(\mathbf{x})\lambda^3) - 1\right]$$

$$\alpha = \left.\frac{\partial^2 \mathcal{F}}{\partial \rho^2}\right|_{\rho_0} = k_B T/\rho_0 = P_0/\rho_0^2$$

$$\mathcal{F}(\rho) = \frac{1}{2}\alpha(\rho - \rho_0)^2, \qquad P\{\rho(\mathbf{x})\} \propto \mathrm{e}^{-\beta \int \frac{1}{2}\alpha(\rho-\rho_0)^2\,\mathrm{d}\mathbf{x}}.$$

Distributions of free energy and density fluctuations in equilibrium

$$\langle(\rho - \rho_0)^2\rangle = \frac{1}{\beta\alpha\,\Delta V}$$

Dirac' delta-function: no correlations.

$$C^{\rm ideal}(\mathbf{r}, 0) = \frac{1}{\beta\alpha}\delta(\mathbf{r}).$$

Enter Onsager…

Lars Onsager

Lars Onsager (November 27, 1903 – October 5, 1976): Norvegian physicist/chemist.

Known for: electrolytes… phase transitions… Onsager relations….

Nobel prize (in Chemistry) in 1968.

Enter Onsager…

How to treat deviations from the equilibrium (read: correlations)?

O's regression hypothesis:

> …we may assume that a spontaneous deviation from the equilibrium decays according to the same laws as one that has been produced artificially.

Average over initial conditions, thermal history. We get for the C the diffusion equation, again:

$$\frac{\partial C^{\mathrm{ideal}}}{\partial t} = \left\langle \frac{\partial}{\partial t} \left[\rho(\mathbf{r},t)\right]_{\rho_i} (\rho_i(\mathbf{0}) - \rho_0) \right\rangle_{\mathrm{eq}}$$
$$= \left\langle D\nabla^2 \left[\rho(\mathbf{r},t)\right]_{\rho_i} (\rho_i(\mathbf{0}) - \rho_0) \right\rangle_{\mathrm{eq}}$$
$$= D\nabla^2 \left\langle \left[\rho(\mathbf{r},t)\right]_{\rho_i} (\rho_i(\mathbf{0}) - \rho_0) \right\rangle_{\mathrm{eq}}$$
$$= D\nabla^2 \left\langle (\rho(\mathbf{r},t) - \rho_0)(\rho(\mathbf{0},0) - \rho_0) \right\rangle_{\mathrm{ev}}$$
$$= D\nabla^2 C^{\mathrm{ideal}}(\mathbf{r},t).$$

$$\frac{\partial}{\partial t} \left[\rho(\mathbf{x},t)\right]_{\rho_i} = D\nabla^2 \left[\rho(\mathbf{x},t)\right]_{\rho_i} .$$

$$C(\mathbf{r},\tau) = \langle (\rho(\mathbf{x}+\mathbf{r},t+\tau) - \rho_0)(\rho(\mathbf{x},t) - \rho_0) \rangle_{\mathrm{ev}}$$
$$= \langle (\rho(\mathbf{r},\tau) - \rho_0)(\rho(\mathbf{0},0) - \rho_0) \rangle_{\mathrm{ev}}$$
$$= \left\langle (\left[\rho(\mathbf{r},\tau)\right]_{\rho_i} - \rho_0)(\rho_i(\mathbf{0}) - \rho_0) \right\rangle_{\mathrm{eq}} .$$

Example: 3D ideal gas from the DE

$$C^{\mathrm{ideal}}(\mathbf{r},\tau) = \frac{1}{\beta\alpha} G(\mathbf{r},\tau) = \frac{1}{\beta\alpha} \left(\frac{1}{\sqrt{4\pi D\tau}} \right)^3 \mathrm{e}^{-\mathbf{r}^2/4D|\tau|}.$$

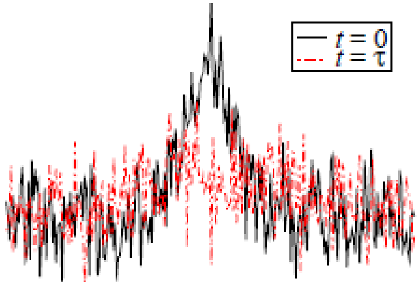


Fig. 10.7 Noisy decay of a fluctuation. An unusual fluctuation at $t = 0$ will slowly decay to a more typical thermal configuration at a later time τ.

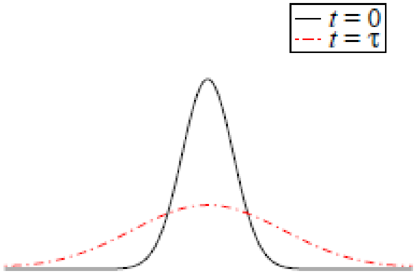


Fig. 10.8 Deterministic decay of an initial state. An initial condition with the same density will slowly decay to zero.

Susceptibility and linear response

The idea: define a measure for the response to a perturbation.

We assume that this can be measured "based on the past" via a response function χ. Note how and why this is linear (in f).

Then FT everything, and call χ as *the AC susceptibility* (language of magnets).

(Electricity: polarizability,

Magnetism: susceptibility again)

$$F_f(t) = -\int \mathrm{d}\mathbf{x}\, f(\mathbf{x},t) s(\mathbf{x},t).$$

$$s(\mathbf{x},t) = \int \mathrm{d}\mathbf{x}' \int_{-\infty}^{t} \mathrm{d}t'\ \chi(\mathbf{x}-\mathbf{x}', t-t') f(\mathbf{x}',t').$$

$$\widetilde{s}(\mathbf{k},\omega) = \widetilde{\chi}(\mathbf{k},\omega)\widetilde{f}(\mathbf{k},\omega),$$

Dissipation

χ splits into real and imaginary parts and Im χ relates to the “lag” of the response and to the dissipation per cycle (oscillatory force).

$$\tilde{\chi}(\mathbf{k},\omega) = \int \mathrm{d}\mathbf{x}\,\mathrm{d}t\ \mathrm{e}^{\mathrm{i}\omega t}\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{x}}\chi(\mathbf{x},t) = \chi'(\mathbf{k},\omega) + \mathrm{i}\chi''(\mathbf{k},\omega)$$

$$p(\omega) = \frac{\omega|f_\omega|^2}{2}\int_{-\infty}^{\infty}\mathrm{d}\tau\ \chi(\tau)\sin(\omega\tau) = \frac{\omega|f_\omega|^2}{2}\mathrm{Im}[\tilde{\chi}(\omega)]$$
$$= \frac{\omega|f_\omega|^2}{2}\chi''(\omega).$$

The zero-frequency limit (electrical analogue) relates the conductivity to limit of the polarizability.

$$\sigma = \lim_{\omega\to 0} \omega^2\ddot{\alpha}(\omega)$$

Static susceptibility

Define via perturbed equilibrium (no time-dependence).

$$s(\mathbf{x}) = \int \mathrm{d}\mathbf{x}' \, \chi_0(\mathbf{x} - \mathbf{x}') f(\mathbf{x}').$$

Fluctuation-dissipation relation: susceptibility vs. correlation function in the zero frequency limit.

$$\chi_0(\mathbf{r}) = \beta C(\mathbf{r}, 0).$$

$$\widetilde{\chi}_0(\mathbf{k}) = \widetilde{\chi}(\mathbf{k}, \omega = 0).$$

Relation of these to fluctuations in equilibrium and their (non-extensive) scaling.

$$\begin{aligned}
k_B T \, \widetilde{\chi}_0(\mathbf{k} = \mathbf{0}) &= \widehat{C}(\mathbf{k} = \mathbf{0}, t = 0) = \int \mathrm{d}\mathbf{r} \, \langle s(\mathbf{r} + \mathbf{x}) s(\mathbf{x}) \rangle \\
&= \int \mathrm{d}\mathbf{r} \, \frac{1}{V} \left\langle \int \mathrm{d}\mathbf{x} \; s(\mathbf{r} + \mathbf{x}) s(\mathbf{x}) \right\rangle \\
&= V \left\langle \frac{1}{V} \int \mathrm{d}\mathbf{r}' \; s(\mathbf{r}') \frac{1}{V} \int \mathrm{d}\mathbf{x} \; s(\mathbf{x}) \right\rangle \\
&= V \left\langle \langle s \rangle^2_{\text{space}} \right\rangle .
\end{aligned}$$

Fluctuation-dissipation theorem

Susceptibility χ relates to the correlations, thus the field and its fluctuations.

In frequency domain, the imaginary part does the same.

Thus also dissipated power: fluctuations are related to dissipation.

[FYI: there is a large universe of attempts to use this in out of equilibrium systems: measure χ and C, in order to define an effective temperature β_{eff}.]

$$\chi(\mathbf{x}, t) = -\beta \frac{\partial C(\mathbf{x}, t)}{\partial t} \quad (t > 0).$$

$$\chi''(\omega) = \frac{\beta\omega}{2} \widetilde{C}(\omega).$$

$$\begin{aligned} p(\omega) &= \frac{\omega |f_\omega|^2}{2} \chi''(\omega) = \frac{\omega |f_\omega|^2}{2} \frac{\beta\omega}{2} \widetilde{C}(\omega) \\ &= \frac{\beta\omega^2 |f_\omega|^2}{4} \widetilde{C}(\omega). \end{aligned}$$

Role of causality

The FT (frequency-dependent) susceptibility has real and imaginary parts: two functions instead of one (χ(t)).

This can used (Kramers-König –relation) to relate these to each other. The derivation follows from Cauchy’s theorem in complex analysis (with the K-K contour).

$$\chi'(\omega) = \mathrm{Re}[\widetilde{\chi}(\omega)] = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\mathrm{Im}[\widetilde{\chi}(\omega')]}{\omega' - \omega}\, \mathrm{d}\omega' = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\chi''(\omega')}{\omega' - \omega}\, \mathrm{d}\omega' .$$

$$\chi''(\omega) = -\frac{2\omega}{\pi}\int_{0}^{\infty} \chi'(\omega')\frac{1}{\omega'^2 - \omega^2}\, \mathrm{d}\omega' .$$

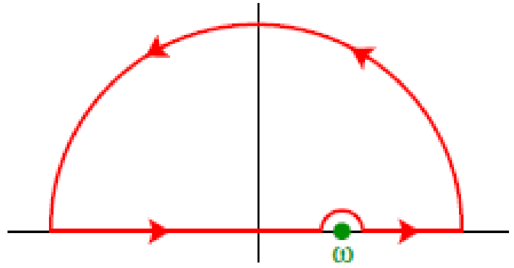


Fig. 10.12 Kramers–Krönig contour. A contour C_ω in the complex ω' plane. The horizontal axis is $\mathrm{Re}[\omega']$ and the vertical axis is $\mathrm{Im}[\omega']$. The integration contour runs along the real axis from $-\infty$ to ∞ with a tiny semicircular detour near a pole at ω. The contour is closed with a semicircle back at infinity, where $\chi(\omega')$ vanishes rapidly. The contour encloses no singularities, so Cauchy’s theorem tells us the integral around it is zero.

Homework

2.3 Generating random walks (Sethna 2.5 p. 28) HOMEWORK (5 points)

Please note that this exercise is computational, so in order to get help with possible problems, take a laptop to the exercise session or alternatively send your code and problem in advance to the TA. The preferred programming tool to use (from the point of view of debugging and getting TA help) is Python, but also others are acceptable.

(a) Write a routine to generate an N-step random walk in d dimensions, with each step uniformly distributed in the range $(-1/2, 1/2)$ in each dimension. (Generate the steps first as an $[N \times d]$ array, then do a cumulative sum.) Plot x_t versus t for a few 10 000-step random walks. Plot x versus y for a few two-dimensional random walks, with $N = 10, 1000, 100000$. (Try to keep the aspect ratio of the XY plot equal to one.) Does multiplying the number of steps by one hundred roughly increase the net distance by ten?

Each random walk is different and unpredictable, but the ensemble of random walks has elegant, predictable properties.

(b) Write a routine to calculate the endpoints of W random walks with N steps each in d dimensions. Do a scatter plot of the endpoints of 10000 random walks with $N = 1$ and 10, superimposed on the same plot. Notice that the longer random walks are distributed in a circularly symmetric pattern, even though the single step random walk $N = 1$ has a square probability distribution (arising from the single step range, see Fig 2.10 from Sethna p. 28).

This is an emergent symmetry; even though the walker steps longer distances along the diagonals of a square, a random walk several steps long has nearly perfect rotational symmetry. The most useful property of random walks is the central limit theorem. The endpoints of an ensemble of N step one-dimensional random walks with root-mean-square (RMS) step-size a has a Gaussian or normal probability distribution as $N \to \infty$,

$$\rho(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp(-x^2/2\sigma^2), \qquad (1)$$

with $\sigma = \sqrt{N}a$.

(c) Calculate the RMS step-size a for one-dimensional steps uniformly distributed in $(-1/2, 1/2)$. Write a routine that plots a histogram of the endpoints of W one-dimensional random walks with N steps and 50 bins, along with the prediction of above equation for x in $(-3\sigma, 3\sigma)$. Do a histogram with $W = 10000$ and $N = 1, 2, 3, 5$. How quickly does the Gaussian distribution become a good approximation to the random walk?

Take home

This lecture looks at the classical measures of correlations and their decay. We shall get back to these topics later on, but you should read through the chapter and think of conditional probabilities. Read first the Chapter and check then the lecture slides again.

The take home consists of answering to the following three questions:

Give an example of X and Y that are correlated but there is no causal relation (X because of Y or X because of Y happened before) between them.

Take a (time) series of the binary kind 0110110011000111.... (or subtract -1/2 from all the values so that the average might become zero). When would this be correlated?

Take instead a series like this: ...00001111111(...)111000.... This is clearly not a random one. Now start tossing a coin (0/1) and replace according to each toss one of the values with the new one. Does this correspond to the Onsager hypothesis and why? If the coin is biased, does the process relate to linear response?