# Tutorial 11, Statistical Mechanics: Concepts and applications
## 2019/20 ICFP Master (first year)

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*Tutorial exercises*

## I. WORKSHEET: HARMONIC SOLID

1. **The harmonic solid model**

   **Reminder:** The equipartition theorem states that the average energy for a simple harmonic oscillator is given by

   $$\langle E \rangle = \langle E_{\text{kinetic}} \rangle + \langle U_{\text{potential}} \rangle = D \left( \frac{k_B T}{2} + \frac{k_B T}{2} \right) = D k_B T, \tag{1}$$

   where $D$ is the dimensionality of the problem.

   **The model:** Consider a crystal in which the atoms are arranged in an ordered way: at $T = 0$, they are all located at their respective lattice sites $\vec{R}_j$. For the time being, let us assume the lattice to be a one-dimensional chain with periodic boundary conditions, so that $R_j = ja$, where $a$ is the lattice constant that we take to be 1, and $R_{j+N} = R_j$. At $T > 0$, the atoms positions deviate from the associated lattice sites by some displacement $x_j$:

   $$r(R_j) = R_j + x_j. \tag{2}$$

   The atoms have some sort of potential energy $U$, that we can expand in a Taylor series around the atoms' equilibrium positions $R_j$. The lowest order non-trivial contribution is going to be quadratic, resulting in the so-called harmonic approximation in which the systems energy is given by

   $$E = \frac{m}{2} \sum_j \dot{x}_j^2 + \frac{K}{2} \sum_j (x_j - x_{j+1})^2. \tag{3}$$

   (a) Explain why the linear term of the expansion does not appear in the potential.

   : *The linear term is gone because the potential energy is minimized when atoms are sitting at their equilibrium positions.*

   (b) Perform the Fourier transform of the position variables to find the normal modes of the system. Apply the FT to the potential energy and show how it enables us to factorize the problem.

   :

   $$U^{\text{harm}} = \frac{K}{2} \sum_n [u(na) - u((n+1)a]^2 \,, \tag{4}$$

*where $K$ is the spring constant and $a$ is the inter-ionic distance. The equations of motion read as*

$$M\ddot{u}(na) = -\frac{\partial U^{\text{harm}}}{\partial u(na)} = -K[2u(na) - u((n+1) - u((n-1)a)] \, .$$
<div align="right">(5)</div>

*For the sake of simplicity we assume periodic boundary conditions and seek for a solution of the form*

$$u(na,t) = u_k e^{ikna - i\omega(k)t} + \text{h.c.} \, ,$$
<div align="right">(6)</div>

*where we summed the complex conjugate because the displacement is real. Periodic boundary conditions imply $e^{ikNa} = 1$. By substituting this ansatz into the equations of motion we obtain*

$$\omega^2(k) = \frac{4K}{M} \sin^2 \frac{ka}{2} \, .$$
<div align="right">(7)</div>

*In this way we have found all the $N$ independent solutions ($k_j = \frac{2\pi j}{N}$). These are therefore wave propagating along the chain with dispersion*

$$\omega(k) = 2\sqrt{\frac{K}{M}} \left| \sin \frac{ka}{2} \right| \, .$$
<div align="right">(8)</div>

*At long wavelengths, i.e. small $k$, the dispersion is linear $\omega(k) \sim \sqrt{\frac{K}{M}} a|k|$ and the waves propagate at a finite speed (known as the sound velocity).*
*The solution has a simple form because the oscillators are uncoupled in the Fourier space defined as follows*

$$u(na) = \frac{1}{\sqrt{N}} \sum_j u_{k_j} e^{ik_j na} \qquad u_{k_j}^* = u_{-k_j} \, .$$
<div align="right">(9)</div>

*Indeed we have*

$$U^{\text{harm}} = \frac{K}{2} \sum_n [u(na) - u((n+1)a]^2 = \frac{K}{2N} \sum_{n,j,j'} [u_{k_j} e^{ik_j na} - u_{k_j} e^{ik_j(n+1)a}][u_{k_{j'}} e^{ik_{j'} na} - u_{k_{j'}} e^{ik_{j'}(n+1)a}]$$

$$= \frac{K}{2} \sum_j [u_{k_j} - u_{k_j} e^{ik_j a}][u_{-k_j} - u_{-k_j} e^{-ik_j a}] = 2K \sum_{j>0} |u_{k_j}|^2 (1 - \cos(k_j a)) = M \sum_{j>0} \omega^2(k) |u_{k_j}|^2$$
<div align="right">(10)</div>

(c) Compute the quadratic displacement of a given atom $\langle x_\ell^2 \rangle$, then the quadratic displacement between different atoms $\langle (x_\ell - x_m)^2 \rangle$. What is the physical meaning of the results?

: *If, for $k \geq 0$, we write*

$$u_k = u_k^{(R)} + i u_k^{(I)}$$
<div align="right">(11)</div>

*with $u_k^{(R,I)}$ real, we obtain*

$$u(na) = \frac{u_0^{(R)}}{\sqrt{N}} + \frac{2}{\sqrt{N}} \sum_{0 < ak_j < \pi} u_{k_j}^{(R)} \cos(k_j na) - u_{k_j}^{(I)} \sin(k_j na) + \frac{(-1)^n u_\pi^{(R)}}{\sqrt{N}}$$
<div align="right">(12)</div>

$$u_{k_j}^{(R)} = \frac{1}{\sqrt{N}} \sum_n u(na) \cos(k_j na) \qquad u_{k_j}^{(I)} = -\frac{1}{\sqrt{N}} \sum_n u(na) \sin(k_j na) \tag{13}$$

*and hence*

$$\prod_n \mathrm{d}u(na) = \mathrm{d}u_0^{(R)} \Big( \prod_{0 < ak_j < \pi} \mathrm{d}u_{k_j}^{(R)} \mathrm{d}u_{k_j}^{(I)} \Big) \mathrm{d}u_\pi^{(R)} \tag{14}$$

*The potential reads as*

$$U^{\mathrm{harm}} = M \sum_{j>0} \omega^2(k_j)[(u_{k_j}^{(R)})^2 + (u_{k_j}^{(I)})^2] \tag{15}$$

*and the contribution from the position variables to the canonical distribution is given by*

$$\frac{1}{Z} e^{-\beta U^{\mathrm{harm}}} = \frac{1}{Z} \Big( \prod_{0<ak_j<\pi} e^{-\beta M \omega^2(k_j)(u_{k_j}^{(R)})^2} e^{-\beta M \omega^2(k_j)(u_{k_j}^{(I)})^2} \Big) e^{-\beta 4K(u_\pi^{(R)})^2} \tag{16}$$

*From now on we ignore the zero mode, which is a by-product of periodic boundary conditions. From (16) it follows that $u_{k_j}^{(R)}$ and $u_{k_{j'}}^{(I)}$ are uncoupled, as well ad $u_k^{(R,I)}$ and $u_p^{(R,I)}$ for $k \neq p$. Thus $(k_j, k_{j'} > 0)$*

$$\langle u_{k_j} u_{k_{j'}} \rangle = \langle u_{k_j}^{(R)} u_{k_{j'}}^{(R)} \rangle - \langle u_{k_j}^{(I)} u_{k_{j'}}^{(I)} \rangle + i(\langle u_{k_j}^{(R)} u_{k_{j'}}^{(I)} \rangle + \langle u_{k_j}^{(I)} u_{k_{j'}}^{(R)} \rangle) = \delta_{jj'} \langle (u_{k_j}^{(R)})^2 \rangle - \langle (u_{k_j}^{(I)})^2 \rangle = 0$$

$$\langle u_{k_j} u_{k_{j'}}^* \rangle = \langle u_{k_j}^{(R)} u_{k_{j'}}^{(R)} \rangle + \langle u_{k_j}^{(I)} u_{k_{j'}}^{(I)} \rangle - i(\langle u_{k_j}^{(R)} u_{k_{j'}}^{(I)} \rangle - \langle u_{k_j}^{(I)} u_{k_{j'}}^{(R)} \rangle) = \delta_{jj'} \langle (u_{k_j}^{(R)})^2 \rangle + \langle (u_{k_j}^{(I)})^2 \rangle = \frac{\delta_{jj'} kT}{M\omega^2(k_j)} \tag{17}$$

*We first compute the quadratic displacement of a given atom:*

$$\langle u(na)^2 \rangle = \frac{1}{N} \sum_{j,j} e^{ik_j na} e^{ik_{j'} na} \langle u_{k_j} u_{k_{j'}} \rangle = \frac{(u_\pi^{(R)})^2}{N} + \frac{2}{N} \sum_{0<ak_j<\pi} \langle u_{k_j} u_{-k_j} \rangle = \frac{2kT}{NM} \sum_{k_j>0} \frac{1}{\omega^2(k_j)} \sim N \,. \tag{18}$$

*This diverges in the thermodynamic limit, so the system can not be considered a solid in the usual sense.*
*Let us compute the quadratic displacement between different atoms*

$$\langle [u(na) - u(ma)]^2 \rangle = \frac{1}{N} \sum_{j,j' \neq 0} (e^{ik_j na} - e^{ik_j ma})(e^{ik_{j'} na} - e^{ik_{j'} ma}) \langle u_{k_j} u_{k_{j'}} \rangle$$

$$\frac{kT}{NM} \sum_{j \neq 0} \frac{(e^{ik_j na} - e^{ik_j ma})(e^{-ik_j na} - e^{-ik_j ma})}{\omega^2(k_j)} = \frac{4kT}{NM} \sum_{k_j>0} \frac{1 - \cos(k_j(n-m)a)}{\omega^2(k_j)} \,. \tag{19}$$

*This time the function inside the sum is integrable at $k = 0$, so in the thermodynamic limit we can use the Euler-Maclaurin formula to transform the sum into an integral*

$$\frac{4kT}{NM} \sum_{k_j>0} \frac{1 - \cos(k_j(n-m)a)}{\omega^2(k_j)} \xrightarrow{N \to \infty} \frac{2kT}{M} \int_0^\pi \frac{\mathrm{d}k}{\pi} \frac{1 - \cos(k(n-m))}{\omega^2(k)} = \frac{kT}{MK} R \,. \tag{20}$$

*We see that the local deformations of the lattice are finite so, independently of the presence of infinite fluctuations for u(na), the assumption of harmonic forces between nearest neighbor atoms could in fact be satisfied. However, the quadratic displacement increases linearly with the distance, therefore there is no long range positional order. In other words, if an atom is close to the corresponding lattice site, a distant atom can be arbitrarily far away from its site.*

(d) Consider the $2D$ case, where the calculations are carried out in much the same way. Again, use the FT of $\vec{x}_\ell$ to find the normal modes and factorize the potential energy term.

: *We now repeat the same calculations in two and three dimensions. We assume a potential of the form (**??**). The equations of motion read as*

$$M\ddot{\vec{u}}(\vec{R}) = -\frac{\partial U^{\mathrm{harm}}}{\partial \vec{u}(\vec{R})} = -\sum_{\vec{R}'} \hat{D}(\vec{R} - \vec{R}')\vec{u}(\vec{R}') \tag{21}$$

*We seek for a solution of the form*

$$\vec{u}(\vec{R}) = \vec{u}_k e^{i\vec{k}\cdot\vec{R} - i\omega(k)t} + \mathrm{h.c.} \tag{22}$$

*and impose periodic boundary conditions*

$$\vec{u}(\vec{R} + N_i\vec{a}_i) = \vec{u}(\vec{R}), \tag{23}$$

*where $N_i$ and $\vec{a}_i$ are the number of sites and the vectors of elementary displacements, respectively. This gives*

$$e^{iN_i\vec{k}\cdot\vec{a}_i} = 1 \tag{24}$$

*so the vector $\vec{k}$ has the form*

$$\vec{k} = \sum_{i=1}^{d} \frac{n_i\vec{b}_i}{N_i} \tag{25}$$

*where $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}$, namely $\vec{b}_i$ are the reciprocal lattice vectors.*
*By plugging our ansatz into the equations of motion (for now, we can ignore the complex conjugate) we find*

$$M\omega^2(k)\vec{u}_k e^{i\vec{k}\cdot\vec{R} - i\omega(k)t} = \sum_{\vec{R}'} \hat{D}(\vec{R} - \vec{R}')\vec{u}_k e^{i\vec{k}\cdot\vec{R}' - i\omega(k)t} = \sum_{\vec{R}'} \hat{D}(\vec{R}')\vec{u}_k e^{i\vec{k}\cdot(\vec{R} + \vec{R}') - i\omega(k)t} \tag{26}$$

*that is to say*

$$M\omega^2(k)\vec{u}_k = \left[\sum_{\vec{R}'} \hat{D}(\vec{R}')e^{i\vec{k}\cdot\vec{R}'}\right]\vec{u}_k = \hat{D}_{\vec{k}}\vec{u}_k \tag{27}$$

*where we defined the so-called* dynamical matrix *as follows*

$$\hat{D}_{\vec{k}} = \sum_{\vec{R}'} \hat{D}(\vec{R}')e^{i\vec{k}\cdot\vec{R}'}. \tag{28}$$

We note that $\hat{D}_{\vec{k}}$ is a real, symmetric, and even matrix-function of $k$:

$$\hat{D}_{\vec{k}} = \sum_{\vec{R}'} \hat{D}(\vec{R}') \cos(\vec{k} \cdot \vec{R}') = -2 \sum_{\vec{R}'} \hat{D}(\vec{R}') \sin^2\left(\frac{\vec{k} \cdot \vec{R}'}{2}\right), \tag{29}$$

where we used $\sum_{\vec{R}} \hat{D}(\vec{R}) = 0$. The solutions $\vec{u}_k$ of (27) are the eigenvectors of the dynamical matrix and the corresponding dispersion relation is related to the eigenvalues $\lambda_{\vec{k},i}$ by the following relation

$$\omega_i(k) = \sqrt{\frac{\lambda_{\vec{k},i}}{M}} \tag{30}$$

Clearly the solution depends on the specific problem under investigation, however there are some general properties the hold for any dynamical matrix. In particular, if $\vec{k} \cdot \vec{R}$ is small for any $\vec{R}$ we have

$$\hat{D}_{\vec{k}} \approx -\frac{|\vec{k}|^2}{2} \sum_{\vec{R}'} \hat{D}(\vec{R}')(\hat{k} \cdot \vec{R}')^2, \tag{31}$$

and hence, in the limit of small $\vec{k}$, the dispersion relation turns is linear:

$$\omega_i(\vec{k}) \approx c_i(\hat{k})|\vec{k}|. \tag{32}$$

As in the 1D case, let us rewrite the potential in terms of the real vectors $\vec{u}_{k,i}$ that solve the eigenvalue problem

$$\hat{D}_{\vec{k}}\hat{u}_{\vec{k},i} = M\omega_i^2(\vec{k})\hat{u}_{\vec{k},i} \qquad \hat{u}_{-\vec{k},i} = \hat{u}_{\vec{k},i} \ \ real \tag{33}$$

$$\vec{u}(\vec{R}) = \frac{1}{\sqrt{\prod_{i=1}^{d} N_i}} \sum_{j=1}^{d} \sum_{\vec{k}} \vec{u}_{\vec{k},j} e^{i\vec{k}\cdot\vec{R}} \qquad u^*_{-\vec{k},j} = u_{\vec{k},j} \tag{34}$$

where

$$\vec{u}_{\vec{k},i} = u_{\vec{k},i}\hat{u}_{\vec{k},i}. \tag{35}$$

$$U^{\mathrm{harm}} = \frac{1}{2} \sum_{\vec{R},\vec{R}'} \vec{u}^t(\vec{R})\hat{D}(\vec{R}-\vec{R}')\vec{u}(\vec{R}') = \frac{1}{2\prod_{i=1}^{d}N_i} \sum_{j,j'} \sum_{\vec{k},\vec{p}} \sum_{\vec{R}'} \vec{u}^t_{\vec{k},j}\hat{D}_{\vec{k}}\vec{u}_{\vec{p},j'} e^{i(\vec{k}+\vec{p})\cdot\vec{R}'} \tag{36}$$

Let us consider the sum over $\vec{R}$:

$$\frac{1}{\prod_{i=1}^{d}N_i} \sum_{\vec{R}} e^{i(\vec{k}+\vec{p})\cdot R} = \prod_{i=1}^{d}\left(\frac{1}{N_i}\sum_{n_i=1}^{N_i}\right) e^{i(\vec{k}+\vec{p})\cdot\sum_{j=1}^{d}n_j\vec{a}_j} = \prod_{i=1}^{d}\left(\frac{1}{N_i}\sum_{n_i=1}^{N_i}\right) e^{i\sum_{i'=1}^{d}\frac{\ell_i+m_i}{N_i}\vec{b}_i\cdot\sum_{j=1}^{d}n_j\vec{a}_j}$$

$$= \prod_{i=1}^{d}\left(\frac{1}{N_i}\sum_{n_i=1}^{N_i}\right) e^{2\pi i\sum_{j=1}^{d}\frac{\ell_j+m_j}{N_j}n_j} = \delta_{\vec{k},-\vec{p}}. \tag{37}$$

*Thus we have*

$$U^{\mathrm{harm}} = \frac{1}{2}\sum_{j,j'}\sum_{\vec{k}}\vec{u}^t_{\vec{k},j}\hat{D}_{\vec{k}}\vec{u}_{\vec{k},j'} = M\sum_{\vec{k}/\pm}\sum_{j}\omega_j^2(\vec{k})|u_{\vec{k},j}|^2 = M\sum_{\vec{k}/\pm}\sum_{j}\omega_j^2(\vec{k})((u^R_{\vec{k},j})^2 + (u^I_{\vec{k},j})^2)$$

(38)

(e) Find the quadratic displacement of a given atom in a given direction $\langle(\hat{n}\cdot\vec{x}_\ell)^2\rangle$. Can you guess the solution for $D > 2$? Is there any difference between $D = 2$ and $D = 3$?

:

$$\langle(\hat{r}\cdot\vec{u}(\vec{R}))^2\rangle = \frac{1}{\prod_{i=1}^d N_i}\sum_{j,j'=1}^d\sum_{\vec{k},\vec{p}}e^{i\vec{k}\cdot\vec{R}}e^{i\vec{p}\cdot\vec{R}}\hat{r}\cdot\hat{u}_{\vec{k},j}\hat{r}\cdot\hat{u}_{\vec{p},j'}\langle u_{\vec{k},j}u_{\vec{p},j'}\rangle = \frac{kT}{M\prod_{i=1}^d N_i}\sum_j^d\sum_{\vec{k}}\frac{(\hat{r}\cdot\hat{u}_{\vec{k},j})^2}{\omega_j^2(\vec{k})}\,.$$

(39)

*In more than two dimensions ($d > 2$) we can use the Euler-Maclaurin formula, which yields*

$$\langle(\hat{r}\cdot\vec{u}(\vec{R}))^2\rangle \to \frac{kT}{M}\sum_j\int_{[-\pi,\pi]^d}\frac{\mathrm{d}^d k}{(2\pi)^d}\frac{(\hat{r}\cdot\hat{u}_{\vec{k},j})^2}{\omega_j^2(k)} < \infty\,.$$

(40)

*Here we used that $\omega_j(\vec{k}) \propto |\vec{k}|$ and hence the integral is convergent as long as $d > 2$. This means that the atoms have finite fluctuations about their equilibrium positions (the Bravais lattice), consistently with the crystal structure that we originally assumed. In $d = 2$ instead the expectation value diverges logarithmically in $N$ (it is not possible to find $\hat{r}$ orthogonal to all three versors $\hat{u}_{\vec{0},j}$):*

*$\vec{u}(\vec{R})$ has infinite fluctuations and the system is not a solid in the usual sense.*

(f) Calculate the quadratic displacement between different atoms in a given direction $\langle(\hat{n}\cdot(\vec{x}_\ell - \vec{x}_m)^2\rangle$. Is there long range positional order in $D = 2$? And in $D = 3$?

: *The next question is whether or not long range positional order arises. To that aim we compute the quadratic displacement between different atoms in a given direction $\hat{n}$*

$$\langle(\hat{n}\cdot(\vec{u}(\vec{R}) - \vec{u}(\vec{R}')))^2\rangle = \frac{1}{\prod_{i=1}^d N_i}\sum_{j,j'=1}^d\sum_{\vec{k},\vec{p}}(e^{i\vec{k}\cdot\vec{R}}-e^{i\vec{k}\cdot\vec{R}'})(e^{i\vec{p}\cdot\vec{R}}-e^{i\vec{p}\cdot\vec{R}'})\hat{n}\cdot\hat{u}_{\vec{k},j}\hat{n}\cdot\hat{u}_{\vec{p},j'}\langle u_{\vec{k},j}u_{\vec{p},j'}\rangle$$

$$= \frac{2kT}{M\prod_{i=1}^d N_i}\sum_{j=1}^d\sum_{\vec{k}}\frac{1-\cos(\vec{k}\cdot(\vec{R}-\vec{R}'))}{\omega_j^2(\vec{k})}(\hat{n}\cdot\hat{u}_{\vec{k},j})^2 \xrightarrow{N\to\infty} \frac{2kT}{M}\sum_{j=1}^d\int_{[-\pi,\pi]^d}\frac{\mathrm{d}k^d}{(2\pi)^d}\frac{1-\cos(\vec{k}\cdot(\vec{R}-\vec{R}'))}{\omega_j^2(\vec{k})}(\hat{n}\cdot\hat{u}_{\vec{k},j})^2$$

(

*For $d > 2$ the last term is finite, so the entire integral is finite. On the other hand, for $d = 2$ one can show that the integral grows logarithmically with $r$. This shows that in 2D long range positional order is not present.*

(g) Consider the following expectation value

$$\langle(\vec{r}(\vec{R}_\ell + \vec{a}) - \vec{r}(\vec{R}_\ell))\cdot(\vec{r}(\vec{R}_m + \vec{a}) - \vec{r}(\vec{R}_m))\rangle$$

(42)

where $\vec{a}$ is one of the primitive vectors that generate the Bravais lattice. This is a measure of the spatial correlation of the "local orientation" of the system. If this correlation vanishes in the limit of large distance, it means that thermal fluctuations had spoiled the long-range propagation of the local crystalline orientation.

:

$$\langle(\vec{r}(\vec{R}+\vec{a}_s)-\vec{r}(\vec{R}))\cdot(\vec{r}(\vec{R}'+\vec{a}_s)-\vec{r}(\vec{R}'))\rangle = |\vec{a}_s|^2 + \langle(\vec{u}(\vec{R}+\vec{a}_s)-\vec{u}(\vec{R}))\cdot(\vec{u}(\vec{R}'+\vec{a}_s)-\vec{u}(\vec{R}'))\rangle$$

$$= |\vec{a}_s|^2 + \frac{1}{\prod_{i=1}^d N_i}\sum_{j,j'=1}^d \sum_{\vec{k},\vec{p}}(e^{i\vec{k}\cdot\vec{R}+i\vec{k}\cdot a_s}-e^{i\vec{k}\cdot\vec{R}})(e^{i\vec{p}\cdot\vec{R}'+i\vec{p}\cdot a_s}-e^{i\vec{p}\cdot\vec{R}'})\hat{u}_{\vec{k},j}\cdot\hat{u}_{\vec{p},j'}\langle u_{\vec{k},j}u_{\vec{p},j'}\rangle$$

$$= |\vec{a}_s|^2 + \frac{kT}{M\prod_{i=1}^d N_i}\sum_{j=1}^d \sum_{\vec{k}}e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\frac{(e^{i\vec{k}\cdot a_s}-1)(e^{-i\vec{k}\cdot a_s}-1)}{\omega_j^2(\vec{k})}|\hat{u}_{\vec{k},j}|^2$$

$$= |\vec{a}_s|^2 + \frac{2kT}{M\prod_{i=1}^d N_i}\sum_{j=1}^d \sum_{\vec{k}}e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\frac{1-\cos(\vec{k}\cdot\vec{a}_s)}{\omega_j^2(\vec{k})}|\hat{u}_{\vec{k},j}|^2 \xrightarrow{|\vec{R}-\vec{R}'|\to\infty} |\vec{a}_s|^2 \quad (43)$$

*where in the last step we used the Riemann-Lebesgue lemma. If thermal fluctuations had spoiled the long-range propagation of the local crystalline orientation, this correlation would have vanished in the limit of large distance. Instead, it approaches $|\vec{a}_s|^2$ independently of the dimension, as if particles were frozen at their equilibrium sites. This reveals that even in 2D, there is long-range orientational order.*