Harmonic Oscillator. Normal modes and quantization:

Consider a one dimensional chain of Hamiltonian:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{l=1}^{N} \frac{c}{2}(u_l - u_{l+1})^2 \qquad u_{N+1} = u_1 \text{ (periodic boundary conditions).}$$

Normal mode decomposition:

$$u_l = \frac{1}{\sqrt{N}} \sum_k \left(Q_k e^{ikla} e^{-i\omega_k t} + Q_k^* e^{-ikla} e^{i\omega_k t} \right) \qquad a: \text{ lattice spacing}$$

Adding the complex conjugate ensures that u_l is real.

For ease of manipulation we write:

$$u_l = \sum_k \left(\lambda_k e^{ikla} + \lambda_k^* e^{-ikla} \right) \quad \text{with } \lambda_k = \frac{Q_k}{\sqrt{N}} e^{-i\omega_k t}$$

We also transform the momentum into the normal modes:

$$p_l = m\dot{q}_l = \sum_k \left(\Pi_k e^{ikla} + \Pi_k^* e^{-ikla} \right) \quad \text{with } \Pi_k = -i\omega_k \lambda_k \cdot m$$

We first transform the kinetic energy:

$$T = \sum_l \frac{p_l^2}{2m} = \frac{1}{2m} \sum_l \sum_k \sum_{k'} \left(\Pi_k e^{ikla} + \Pi_k^* e^{-ikla} \right)\left(\Pi_{k'} e^{ik'la} + \Pi_{k'}^* e^{-ik'la}\right.$$

We will use the orthogonality of the exponential functions:

$$\sum_l e^{i(k+k')la} = N\delta_{kk'}$$

We find:

$$T = \frac{N}{2m} \sum_k \left(\Pi_k \Pi_{-k} + \Pi_k \Pi_k^* + \Pi_k^* \Pi_k + \Pi_k^* \Pi_{-k}^* \right)$$

We now transform the potential energy:

$$V = \frac{c}{2} \sum (u_l - u_{l+1})^2 = \frac{c}{2} \sum \left(\underbrace{u_l^2 + u_{l+1}^2}_{\substack{\text{same contribution due to periodic}\\ \text{boundary conditions}}} - u_l u_{l+1} - u_{l+1} u_l \right)$$

Compute $V_1 = c \sum_{l=1}^{N} u_l^2 = c \sum_l \sum_k \sum_{k'} \left(\lambda_k e^{ikla} + \lambda_k^* e^{-ikla} \right)\left(\lambda_{k'} e^{ik'la} + \lambda_{k'}^* e^{-ik'la} \right) =$

$$= Nc \sum_k \left(\lambda_k \lambda_{-k} + \lambda_k^* \lambda_k + \lambda_k \lambda_k^* + \lambda_k^* \lambda_{-k}^* \right)$$

Similarly:

$$V_2 = -\frac{c}{2}\sum_l u_{l-1}u_l = -\frac{Nc}{2}\sum_k\left(\lambda_k\lambda_{-k}e^{-ika} + \lambda_k\lambda_k^* e^{-ika} + \lambda_k^*\lambda_k e^{ika} + \lambda_k^*\lambda_{-k}^* e^{ika}\right)$$

$$V_3 = -\frac{c}{2}\sum_l u_{l+1}u_l = -\frac{Nc}{2}\sum_k\left(\lambda_k\lambda_{-k}e^{ika} + \lambda_k\lambda_k^* e^{ika} + \lambda_k^*\lambda_k e^{-ika} + \lambda_k^*\lambda_{-k}^* e^{-ika}\right)$$

Therefore:

$$\begin{aligned} V = Nc\sum_k\Big[&\lambda_k\lambda_{-k} + \lambda_k^*\lambda_k + \lambda_k\lambda_k^* + \lambda_k^*\lambda_{-k}^* \\ &-\frac{1}{2}\left(\lambda_k\lambda_{-k}e^{-ika} + \lambda_k\lambda_k^* e^{-ika} + \lambda_k^*\lambda_k e^{ika} + \lambda_k^*\lambda_{-k}^* e^{ika}\right) \\ &-\frac{1}{2}\left(\lambda_k\lambda_{-k}e^{ika} + \lambda_k\lambda_k^* e^{ika} + \lambda_k^*\lambda_k e^{-ika} + \lambda_k^*\lambda_{-k}^* e^{-ika}\right)\Big] \end{aligned}$$

$$\begin{aligned} = Nc\sum_k\Big[&\left(1-\frac{1}{2}e^{-ika}-\frac{1}{2}e^{ika}\right)\lambda_k\lambda_{-k} + \left(1-\frac{1}{2}e^{-ika}-e^{ika}\right)\lambda_k\lambda_k^* + \\ &+\left(1-\frac{1}{2}e^{ika}-\frac{1}{2}e^{-ika}\right)\lambda_k^*\lambda_k + \left(1-\frac{1}{2}e^{ika}-\frac{1}{2}e^{-ika}\right)\lambda_k^*\lambda_{-k}^*\Big] \end{aligned}$$

Same factor appears in all:

$$1-\frac{1}{2}\left(e^{ika}+e^{-ika}\right) = 1-\frac{1}{\cancel{2}}\cancel{2}\cos ka = (1-\cos ka)$$

Hence: $$\boxed{V = Nc\sum_k(1-\cos ka)\left(\lambda_k\lambda_{-k} + \lambda_k\lambda_k^* + \lambda_k^*\lambda_k + \lambda_k^*\lambda_{-k}^*\right)}$$

Recalling that $\Pi_k = -i\omega_k m\lambda_k$, the kinetic energy can be written:

$$\boxed{T = \frac{Nm^2}{2m}\sum_k\left[-\omega_k^2\lambda_k\lambda_{-k} + \omega_k^2\lambda_k\lambda_k^* + \omega_k^2\lambda_k^*\lambda_k - \omega_k^2\lambda_k^*\lambda_{-k}^*\right]}$$

The total Hamiltonian is $H=T+V$. Remember that the dispersion relation for the linear chain is: $\omega_k^2 = \frac{2C}{m}(1-\cos ka)$

Most of the terms cancel, except: two common terms: $\left(\frac{m\omega_k^2}{2}+\frac{m\omega_k^2}{2}\right)$

$$H = N\sum_k\frac{m\omega_k^2}{2}2\left(\lambda_k\lambda_k^* + \lambda_k^*\lambda_k\right)$$

$$\rightarrow \boxed{H = \sum_k m\omega_k^2\left(Q_k^*Q_k + Q_kQ_k^*\right)}$$

This is the Hamiltonian written in normal mode coordinates.

As long as the normal modes are classical variables, the partition function is:

$$Z = \int \left(\prod_k d^2 Q_k\right) e^{-\beta \sum_k m\omega_k^2 (Q_k^* Q_k + Q_k Q_k^*)}$$

($d^2 Q_k$): the "2" signifies that Q_k is a complex variable and for each k the integral over $d^2 Q_k$ is on the complex plane.

Note that the energy is quadratic: $|Q_k|^2$, and therefore the integral is Gaussian, and can be done exactly. In particular, equipartition holds and $\langle E\rangle = N\left(\frac{1}{2}k_BT + \frac{1}{2}k_BT\right) = Nk_BT$ (again, by computing Gaussian integrals).

Quantization

We have now a system of harmonic oscillators (one for each k) and therefore the usual quantization rules apply. If one starts from the commutation rules for position and momentum:

$$\begin{cases} [u_i, u_j] = 0 \\ [p_i, p_j] = 0 \\ [u_i, p_j] = i\hbar\,\delta_{ij} \end{cases}$$

the commutation rules extend now to Q_k as they are functions of position and velocity (inverting their definition, writing them in terms of u_i and p_i). It is customary to rewrite them as:

$$Q_k = \sqrt{\frac{\hbar}{2m\omega_k}}\, a_k \quad \text{so that} \quad \bullet\ [a_k, a_{k'}] = [a_k^*, a_{k'}^*] = 0 \qquad \bullet\ [a_k, a_{k'}^*] = \delta_{kk'}$$

and the Hamiltonian becomes:

$$H = \sum_k \frac{\hbar\omega_k}{2}\left[a_k a_k^* + a_k^* a_k\right]$$

This is precisely the Hamiltonian for a set of harmonic oscillators of frequency ω_k. It is rewritten as:

$$\boxed{H = \sum_k \hbar\omega_k\left(\frac{1}{2} + a_k^* a_n\right)}$$

Of course, we have N oscillators (independent in this normal mode representation), each with its own frequency ω_k. Therefore, the energy of <u>each</u> oscillator is given by:

$$E_k = \left(n_k + \frac{1}{2}\right)\hbar\omega_k \qquad n_n = 0, 1, 2, \ldots$$

depending ~~it~~ on the particular occupancy of each level n_k.

This is, of course, the same for each of the oscillators.

Since ~~they~~ the oscillators (once quantized are called "phonons") are all independent, ~~the parti~~ and bosons, the partition function can be computed exactly by computing the "single oscillator" partition function.