SIF40AH/DIF4997
Nano-particle and polymer physics I
SOLUTION of EXERCISE 1

Eq. (x.x) refers to version AM11sep02 of lecture notes: "Nano-particle and polymer physics". Equations pertinent to this exercise you will find in Eq. (2.45) - (2.54).

A) The Rouse chain consists of N segments (beads) connected by $N-1$ segment vectors (springs). We assume that there are no other forces than the spring force and that the end beads are free. We also assume that all springs obey Hooke's law with Hooke's constant H. Relative to the laboratory coordinate system the position of bead ν is r_ν $(\nu = 1, 2, \ldots N)$, and we define $r_0 = r_1$ and $r_{N+1} = r_N$. Note that for the one-dimensional chain the coordinates r_ν are scalars and not vectors.

Newtons law for bead ν reads:

$$m\ddot{r}_\nu = H \cdot [(r_{\nu+1} - r_\nu) - (r_\nu - r_{\nu-1})] \tag{1}$$

Changing coordinate system from the laboratory system to cm-system with origo in the chain of mass $r_c = \sum_{\nu=1}^{N} r_\nu/N$, that is $r_\nu = r_c + R_\nu$. Eq. (1) transforms to

$$m\ddot{R}_\nu = H \cdot [(R_{\nu+1} - R_\nu) - (R_\nu - R_{\nu-1})] = H \cdot [(R_{\nu+1} - 2R_\nu) + R_{\nu-1})], \tag{2}$$

or on vector form

$$m\ddot{\vec{R}} = -H\cdot \overset{\Rightarrow}{\boldsymbol{A}}{}' \cdot \vec{R}, \quad \text{where} \quad \overset{\Rightarrow}{\boldsymbol{A}}{}' = \begin{bmatrix} 1 & -1 & & & & \\ -1 & 2 & -1 & & & \\ & -1 & 2 & -1 & & \\ & & & \ddots & & \\ & & & & & \\ & & & & -1 & 1 \end{bmatrix}. \tag{3}$$

Note that matrix $\overset{\Rightarrow}{\boldsymbol{A}}{}'$ is not the Rouse matrix. Also note that in this one-dimensional chain the components of the vector $\vec{R} = [R_1, R_2, \ldots, R_N]$ are scalars, but for a three-dimensional chain the components are vectors.

The essence now is to rewrite Eq. (2) to be expressed by the segment vectors $Q_\nu = R_{\nu+1} - R_\nu$ $(\nu = 1, 2, \ldots (N-1))$. From the above defined $r_0 = r_1$ and $r_{N+1} = r_N$ follows $Q_0 = 0$ and $Q_N = 0$. We obtain

$$m\ddot{Q}_\nu = H \cdot [(Q_{\nu+1} + Q_{\nu-1} - 2Q_\nu)], \tag{4}$$

or on vector form

$$m\ddot{\vec{Q}} = -H\cdot \overset{\Rightarrow}{\boldsymbol{A}} \cdot \vec{Q}, \quad \text{where} \quad \overset{\Rightarrow}{\boldsymbol{A}} = \begin{bmatrix} 2 & -1 & & & & \\ -1 & 2 & -1 & & & \\ & -1 & 2 & -1 & & \\ & & & \ddots & & \\ & & & & & \\ & & & & -1 & 2 \end{bmatrix}. \tag{5}$$

Now the $(N-1) \times (N-1)$-matrix $\overset{\Rightarrow}{\boldsymbol{A}}$ is precisely the Rouse-matrix (see Eq. (2.52)). We have thus easily obtained the Rouse matrix from Newtons law using the relative coordinates $\vec{Q}$.

(The following is not part of the question:) Further analysis shows, where $\overset{\Rightarrow}{\bar{\boldsymbol{B}}}$ and $\overset{\Rightarrow}{\boldsymbol{B}}$ are as defined in lecture notes

$$\vec{Q} = \overset{\Rightarrow}{\bar{\boldsymbol{B}}} \cdot \vec{R} \quad \text{and} \quad \vec{R} = \overset{\Rightarrow}{\boldsymbol{B}} \cdot \vec{Q} \tag{6}$$

$$\Rightarrow \qquad \overset{\Rightarrow}{\bar{\boldsymbol{B}}} \cdot \overset{\Rightarrow}{\boldsymbol{B}} = \overset{\Rightarrow}{\boldsymbol{\delta}} \quad \text{and} \quad \overset{\Rightarrow}{\boldsymbol{B}} \cdot \overset{\Rightarrow}{\bar{\boldsymbol{B}}} = \overset{\Rightarrow}{\boldsymbol{\delta}}, \tag{7}$$

but note that $\overset{\Rightarrow}{\boldsymbol{B}}$ and $\overset{\Rightarrow}{\bar{\boldsymbol{B}}}$ have different dimensions. Eq. (2) can be expressed

$$m\ddot{R}_\nu = H(Q_\nu - Q_{\nu-1}) \tag{8}$$

or, by introducing $\overset{\Rightarrow}{\bar{\boldsymbol{B}}}$

$$m\ddot{\vec{R}} = -H\, \overset{\Rightarrow}{\bar{\boldsymbol{B}}}^{T} \cdot \vec{Q}. \tag{9}$$

Comparing with

$$m\ddot{\vec{R}} \overset{(6)}{=} m\, \overset{\Rightarrow}{\boldsymbol{B}} \cdot \ddot{\vec{Q}} \overset{(5)}{=} -H\, \overset{\Rightarrow}{\boldsymbol{B}}\overset{\Rightarrow}{\boldsymbol{A}} \cdot \vec{Q} \tag{10}$$

we obtain

$$\overset{\Rightarrow}{\bar{\boldsymbol{B}}}^{T} = \overset{\Rightarrow}{\boldsymbol{B}} \cdot \overset{\Rightarrow}{\boldsymbol{A}} \quad \Rightarrow \quad \overset{\Rightarrow}{\boldsymbol{A}} = \overset{\Rightarrow}{\boldsymbol{B}}^{-1} \cdot \overset{\Rightarrow}{\bar{\boldsymbol{B}}}^{T} = \overset{\Rightarrow}{\bar{\boldsymbol{B}}} \cdot \overset{\Rightarrow}{\bar{\boldsymbol{B}}}^{T} \quad \text{or} \quad A_{ij} = \sum_{\nu=1}^{N} \bar{B}_{i\nu}\bar{B}_{j\nu}. \tag{11}$$

This is precisely the mathematical definition of the Rouse matrix! It is now trivial to show that the Rouse matrix $\overset{\Rightarrow}{\boldsymbol{A}}$ and the Kramer matrix $\overset{\Rightarrow}{\boldsymbol{C}}$ are inverse, since

$$\overset{\Rightarrow}{\boldsymbol{A}} \cdot \overset{\Rightarrow}{\boldsymbol{C}} = (\overset{\Rightarrow}{\bar{\boldsymbol{B}}} \cdot \overset{\Rightarrow}{\bar{\boldsymbol{B}}}^{T}) \cdot (\overset{\Rightarrow}{\boldsymbol{B}}^{T} \cdot \overset{\Rightarrow}{\boldsymbol{B}}) = \overset{\Rightarrow}{\bar{\boldsymbol{B}}} \cdot \left(\overset{\Rightarrow}{\boldsymbol{B}} \cdot \overset{\Rightarrow}{\bar{\boldsymbol{B}}}\right)^{T} \cdot \overset{\Rightarrow}{\boldsymbol{B}} = \overset{\Rightarrow}{\bar{\boldsymbol{B}}} \cdot \left(\overset{\Rightarrow}{\boldsymbol{\delta}}\right) \cdot \overset{\Rightarrow}{\boldsymbol{B}} = \overset{\Rightarrow}{\boldsymbol{\delta}}\ . \tag{12}$$

B) Let $\varepsilon = |Q|$ be the length of each segment. In the limit $N \to \infty$ the length $L = N\varepsilon$ of the chain must be kept constant, so $\varepsilon \to 0$. It is thus natural to expand in a series in ε. Coordinate x is used as space coordinate:

$$R_\nu \equiv R(x), \quad R_{\nu\pm1} \equiv R(x \pm \varepsilon). \tag{13}$$

Taylor expansion to second order of Eq. (2) yields

$$mR_{tt} = H\varepsilon^2 \cdot \left[R_{xx} + \frac{\epsilon^2}{12}R_{xxxx} + \cdots\right], \tag{14}$$

where $R_x \equiv \frac{\partial R}{\partial x}$, $R_{xx} \equiv \frac{\partial^2 R}{\partial x^2}$, etc. In the limit $\varepsilon \to 0$ we obtain the wave equation of zeroth order with the wave velocity c given by $c^2 = H\varepsilon^2/m$.

C1) In the *continuous case* ($N \to \infty$) the eigenvectors of the Rouse matrix are trivial. A vibrating rod has the quantization properties (standing wave in the rod with fixed endpoints: a whole number of $\lambda/2$ along the rod):

$$j\frac{\lambda}{2} = L, \quad j = 1, 2, \ldots. \tag{15}$$

The eigenvalues of the matrix $\overset{\Rightarrow}{\boldsymbol{A}}$ are given by $\overset{\Rightarrow}{\boldsymbol{A}} \cdot \vec{Q} = a_j\vec{Q}$. From Eq. (5) and using the continuous standing wave solution $Q \propto \exp\{i(\omega t - kx)\}$ we obtain

$$\overset{\Rightarrow}{\boldsymbol{A}}\,\vec{Q} = -\frac{m}{H}\ddot{\vec{Q}} = \frac{m}{H}\omega^2\vec{Q}. \tag{16}$$

Further, using the relation $c^2 = H\varepsilon^2/m$, expressing the wave velocity $c = \lambda\frac{\omega}{2\pi}$, using Eq. (15) and $\varepsilon = L/N$, the eigenvalues a_j can be expressed

$$a_j = \frac{m}{H}\omega^2 = \varepsilon^2\left(\frac{2\pi}{\lambda}\right)^2 = \frac{\pi^2 j^2}{N^2}. \tag{17}$$

This is precisely the same as obtained taking the limit $N \to \infty$ of the eigenvalues of the Rouse matrix in the discrete case: Holding L constant we obtain for the Rouse eigenvalues:

$$a_j = \lim_{N\to\infty} 4 \cdot \sin^2\left(\frac{j\pi}{2N}\right) = \lim_{\varepsilon\to0} 4 \cdot \sin^2\left(\frac{j\pi\varepsilon}{2L}\right) = \frac{\pi^2 j^2 \epsilon^2}{L^2} = \frac{\pi^2 j^2}{N^2} \tag{18}$$

C2) Now we calculate the eigenvalues in the *discrete case* (finite N). In place of finding the N eigenvalues by zeroing the determinant of the equation, we do an alternative approach:

The eigenvalues represent the characteristic resonance modes. At resonance all beads oscillates with the same frequency ω but different phase. Therefore the general wave function is given by

$$Q_k = f_k \exp\{i\omega t\}, \qquad \text{where} \quad f_k = C\exp\{ikn\} + D\exp\{-ikn\}, \tag{19}$$

and C and D are constants given by the boundary conditions for $Q_0 = Q_N = 0$, that is $f_0 = f_N = 0$.

This yields

$$\begin{aligned} C+D &= 0 \qquad (20)\\ C\exp\{iNn\}+D\exp\{-iNn\} &= 0 \qquad (21)\end{aligned}$$

Inserting Eq. (19) into Eq. (4) and defining $a=\frac{m}{H}\omega^2$, we find that the function f_k must fulfil

$$f_{k-1}+f_{k+1}=(2-a)f_k \qquad (22)$$

Using the trial solutions of Eq. (18) in Eq. (22) and $D=-C$ yields

$$\begin{aligned}(e^{i(k-1)n}-e^{-i(k-1)n})+(e^{i(k+1)n}-e^{-i(k+1)n}) &= (2-a_n)(e^{ikn}-e^{-ikn})\\ e^{ikn}(e^{in}+e^{-in})-e^{-ikn}(e^{in}+e^{-in}) &= (2-a_n)(e^{ikn}-e^{-ikn})\\ e^{-in}+e^{in}-2 &= a_n\\ \underline{a_n}=2-2\cos n &= 4\frac{1-\cos n}{2}=\underline{4\sin^2\left(\frac{n}{2}\right)}. \qquad (23)\end{aligned}$$

Using the boundary condition Eq. (21) we obtain

$$\begin{aligned} C\exp\{-iNn\}[\exp\{2iNn\}-1] &= 0\\ \text{fulfilled only for}\qquad \exp\{2iNn\}=1 &\Rightarrow \underline{n=\frac{j\pi}{N}} \qquad (24)\end{aligned}$$

Conclusion: The eigenvalues of the Rouse matrix fulfills

$$\underline{a_j=4\sin^2\left(\frac{j\pi}{2N}\right)}$$

Comments:

1) Note that the for the contiuous vibration we do not accept dispertion: After disturbing the system all frequency components will move with the same velocity $c=\varepsilon\sqrt{H/m}$. This is not the case for the discrete case, when the wave velocity equals ω/k and $\omega^2=\frac{H}{m}\sin^2\left(\frac{j\pi}{2N}\right)$. The continuous limit corresponds to limiting to the *linear* part of the dispertion relation of the rod: We study waves with wavelengths much larger than the distance ε.

2) You may perhaps not like that the wave velocity $c=\varepsilon\sqrt{H/m}$ seems to diverge to zero when $\varepsilon\to 0$. Remember that the mass and the spring constant are given by $m=\rho\varepsilon$ and $H=T/\varepsilon$, where ρ is mass per length unit and T is the spring constant for the complete spring. From these variables we obtain $c^2=T/\rho$, as for a "macroscopic" spring.

3) Including the next order approximation of the forces, we get for instance

$$m\ddot{R}_\nu=H\cdot[(R_{\nu+1}-R_\nu)-(R_\nu-R_{\nu-1})]+H\varepsilon_1\cdot\left[(R_{\nu+1}-R_\nu)^2-(R_\nu-R_{\nu-1})^2\right],$$

and in the continuous limit we will get the wave equation (14) plus something. This something gives a variation about the usual wave solution given by the KdV-equation, $R_t+RR_x+R_{xxx}=0$. This equation is non-linear and has dispertion, and accounts for the socalled *soliton* solutions. Such solitons are funny. They keep the asymptotic shape and velocity after a collision with other solitons (as it is for the solutions of the usual wave solution), something not to be expected of a solution of a non-linear equation!

4) Both free and constricted boundary conditions yield the same quantization conditions for the finite chain, and the same eigenvalues of the Rouse matrix. For constricted ends the amplitudes are zeroat the ends, but for free ends the relative amplitudes are zero at the ends. When additionally the differential equation is the same for the amplitude and the relative amplitude, we surely obtain the same quantization conditions. (For periodic boundary conditions it is somewhat different, as the eigenfrequency has doble degeneration.)