FY8201 / TFY8 **Nanoparticle and polymer physics I**
SOLUTION of EXERCISE 1

Eq. (x.x) refers to version AM24nov05 of lecture notes: "Nanoparticle and polymer physics". Equations pertinent to this exercise you will find in Ch. 2.3.

A) The Rouse chain consists of N segments (beads) connected by $N-1$ segment vectors (springs). We assume that 1) there are no other forces than the spring force, 2) the end beads are free, 3) 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 no. ν reads:

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

We change the coordinate system from the laboratory system to cm-system with origo in the center of mass $r_{\rm cm} = \sum_{\nu=1}^{N} r_\nu/N$. The coordinates in cm-system then aren $R_\nu = r_\nu - r_{\rm cm}$ and 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 $Q_N = 0$, and 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. (2.46). We have thus easily obtained the Rouse matrix from Newtons law using the relative coordinates $\vec{Q}$.

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:

$$R_\nu \equiv R(x), \quad R_{\nu\pm1} \equiv R(x \pm \varepsilon). \tag{6}$$

Taylor expansion to fourth order yields

$$R_{\nu\pm1} = R(x \pm \varepsilon) = R(x) \pm \frac{\partial R}{\partial x}\varepsilon + \frac{1}{2}\frac{\partial^2 R}{\partial x^2}\varepsilon^2 \pm \frac{1}{6}\frac{\partial^3 R}{\partial x^3}\varepsilon^3 + \frac{1}{24}\frac{\partial^4 R}{\partial x^4}\varepsilon^4 + \cdots \tag{7}$$

Using this, Eq. (2) may be expressed

$$m\frac{\partial^2 R}{\partial t^2} = H\varepsilon^2 \cdot \left[\frac{\partial^2 R}{\partial x^2} + \frac{\varepsilon^2}{12}\frac{\partial^4 R}{\partial x^4} + \cdots\right]. \tag{8}$$

In the limit $\varepsilon \to 0$ we obtain the wave equation of zeroth order with the wave velocity c given by $c^2 = H\varepsilon^2/m$:

$$\frac{\partial^2 R}{\partial t^2} = \frac{H\varepsilon^2}{m} \cdot \frac{\partial^2 R}{\partial x^2}. \tag{9}$$

C) 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):

$$j\frac{\lambda}{2} = L, \quad j = 1, 2, \ldots. \tag{10}$$

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

$$\overset{\Rightarrow}{\boldsymbol{A}}\,\vec{Q} = -\frac{m}{H}\ddot{\vec{Q}} = \frac{m}{H}\omega^2\vec{Q}. \tag{11}$$

Further, using the relation $c^2 = H\varepsilon^2/m$, expressing the wave velocity $c = \lambda\frac{\omega}{2\pi}$, using Eq. (10) and $\varepsilon = L/N$, the eigenvalues a_j can be expressed

$$a_j = \frac{m}{H}\omega^2 = \varepsilon^2\left(\frac{\omega}{c}\right)^2 = \varepsilon^2\left(\frac{2\pi}{\lambda}\right)^2 = \frac{\pi^2 j^2}{N^2}. \tag{12}$$

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:

$$a_j = \lim_{N\to\infty} 4 \cdot \sin^2\left(\frac{j\pi}{2N}\right) = \lim_{\varepsilon\to 0} 4 \cdot \sin^2\left(\frac{j\pi\varepsilon}{2L}\right) = \frac{\pi^2 j^2 \varepsilon^2}{L^2} = \frac{\pi^2 j^2}{N^2}. \tag{13}$$

D) In the *discrete case* (finite N) the most direct method would be to find the N eigenvalues by zeroing the determinant of the equation, but we do an alternative approach.

The eigenvalues represent the characteristic resonance modes. Each resonance mode $j = 1, 2, 3, \cdots$ is a longitudinal standing wave where all beads oscillate with the same frequency ω_j but different phases. A standing wave in a chain of length L may be represented by

$$f_j(x,t) = A\sin\left(\frac{2\pi}{2L}j \cdot x\right) \cdot \cos\omega_j t. \tag{14}$$

The function is fulfilling the end constriction $f_j(0,t) = f_j(L,t) = 0$, c.f. Eq. (10). For our discrete chain the position x is given by bead number ν and $L \to N$ = total no. of beads. The function $f_j(x,t)$ is represented by connector Q_ν (should strictly be denoted $Q_{\nu,j}$ = connector Q_ν in mode j), given by

$$Q_\nu = A\sin\left(\frac{2\pi}{2N}j \cdot \nu\right) \cdot \cos\omega_j t. \tag{15}$$

Using complex notation: $\sin\phi = \frac{1}{2i}(\mathrm{e}^{i\phi} - \mathrm{e}^{-i\phi})$ and for simplicity defining $n = \frac{2\pi}{2N}j$, we obtain

$$Q_\nu = B\left[\mathrm{e}^{in\nu} - \mathrm{e}^{-in\nu}\right]\mathrm{e}^{i\omega_n t}. \tag{16}$$

Inserting this expression in Eq. (4), we obtain:

$$\begin{aligned}
m\ddot{Q}_\nu &= H \cdot [Q_{\nu+1} + Q_{\nu-1} - 2Q_\nu] \\
m(-\omega_n^2)(\mathrm{e}^{in\nu} - \mathrm{e}^{-in\nu}) &= H\left[(\mathrm{e}^{i(\nu+1)n} - \mathrm{e}^{-i(\nu+1)n}) + (\mathrm{e}^{i(\nu-1)n} - \mathrm{e}^{-i(\nu-1)n}) - 2(\mathrm{e}^{i\nu n} - \mathrm{e}^{-i\nu n})\right] \\
-\frac{m\omega_n^2}{H}(\mathrm{e}^{in\nu} - \mathrm{e}^{-in\nu}) &= \mathrm{e}^{i\nu n}(\mathrm{e}^{in} + \mathrm{e}^{-in}) - \mathrm{e}^{-i\nu n}(\mathrm{e}^{in} + \mathrm{e}^{-in}) - 2(\mathrm{e}^{i\nu n} - \mathrm{e}^{-i\nu n}) \\
-a_n(\mathrm{e}^{in\nu} - \mathrm{e}^{-in\nu}) &= (\mathrm{e}^{i\nu n} - \mathrm{e}^{-i\nu n})(\mathrm{e}^{in} + \mathrm{e}^{-in}) - 2(\mathrm{e}^{i\nu n} - \mathrm{e}^{-i\nu n}) \\
-a_n &= (\mathrm{e}^{in} + \mathrm{e}^{-in}) - 2\,,
\end{aligned} \tag{17}$$

where we have defined $a_n = \frac{m\omega_n^2}{H}$, determined to be

$$a_n = 2 - (\mathrm{e}^{in} + \mathrm{e}^{-in}) = 2 - 2\cos(in) = 4\frac{1-\cos(in)}{2} = 4\sin^2\left(\frac{n}{2}\right) , \tag{18}$$

or, more directly

$$a_n = -(\mathrm{e}^{in} - 2 + \mathrm{e}^{-in}) = -\left(\mathrm{e}^{in/2} + \mathrm{e}^{-in/2}\right)^2 = 4\left(\frac{\mathrm{e}^{in/2} + \mathrm{e}^{-in/2}}{2i}\right)^2 = 4\sin^2\left(\frac{n}{2}\right) . \tag{19}$$

Now $n = \frac{2\pi}{2N}j$ and the conclusion is that 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 continous 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, then the wave velocity equals ω_n/k where $\omega^2 = \frac{H}{m}\sin^2\left(\frac{j\pi}{2N}\right)$. 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 $c^2 = \varepsilon^2 H/m$ seems to diverge to zero when $\varepsilon \to 0$. Remember that the mass and the spring constant are given by $m = \lambda\varepsilon$ and $H = F/\varepsilon$, where λ is mass per length unit and F is the force (stretch) of the spring. From these variables we obtain $c^2 = F/\lambda$, as for a "macroscopic" spring.

3) 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 zero at 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.)