SIF40AH/DIF4997
Nano-particle and polymer physics I
SOLUTION of EXERCISE 4

Equilibrium probability distribution of a three-bead Kramer's chain

Eq. (x.x) refers to version AM11sep02 of lecture notes: "Nano-particle and polymer physics".

A. The chain in two dimensions with bead 1 being fixed to origo

There are two internal generalized coordinates: The angle θ_1 between segment vector 1 and the y-axis and the angle θ_2 between segment vector 2 and the y-axis. The Cartesian coordinates of the three beads are:

$$\begin{aligned} x_0 &= 0 & y_0 &= 0 \\ x_1 &= a_1 \sin\theta_1 & y_1 &= a_1 \cos\theta_1 \\ x_2 &= x_1 + a_2 \sin\theta_2 & y_2 &= y_1 + a_2\cos\theta_2 \\ &= a_1\sin\theta_1 + a_2\sin\theta_2 & &= a_1\cos\theta_1 + a_2\cos\theta_2 \end{aligned} \tag{1}$$

As given we use $m_1 = m_2 = m = 2$ and $a_1 = a_2 = a = 1$. In a Kramer's chain there is only kinetic energy $\mathcal{K}$, being equal

$$\begin{aligned} \mathcal{K}(\theta_1,\theta_2,\dot\theta_1,\dot\theta_2) &= \frac{1}{2}m(\dot x_1^2 + \dot y_1^2 + \dot x_2^2 + \dot y_2^2) \\ &= (\cos\theta_1\cdot\dot\theta_1)^2 + (-\sin\theta_1\cdot\dot\theta_1)^2 \\ &\quad +(\cos\theta_1\cdot\dot\theta_1)^2 + 2(\cos\theta_1\cdot\dot\theta_1)(\cos\theta_2\cdot\dot\theta_2) + (\cos\theta_2\cdot\dot\theta_2)^2 \\ &\quad +(-\sin\theta_1\cdot\dot\theta_1)^2 + 2(-\sin\theta_1\cdot\dot\theta_1)(-\sin\theta_2\cdot\dot\theta_2) + (-\sin\theta_2\cdot\dot\theta_2)^2 \\ &= \dot\theta_1^2 + \dot\theta_1^2 + \dot\theta_2^2 + 2(\sin\theta_1\cdot\sin\theta_2 + \cos\theta_1\cos\theta_2)\cdot\dot\theta_1\dot\theta_2 \\ &= 2\dot\theta_1^2 + \dot\theta_2^2 + 2\dot\theta_1\dot\theta_2\cdot\cos\xi \end{aligned} \tag{2}$$

where $\xi = \theta_2 - \theta_1$ equals the included angle.

The Hamiltonian $\mathcal{H}$ and the Lagrangian $\mathcal{L}$ are given by

$$\mathcal{H}(\theta_1,\theta_2,p_1,p_2) = \mathcal{K} + V = \mathcal{K}(\theta_1,\theta_2,p_1,p_2) \tag{3}$$

$$\mathcal{L}(\theta_1,\theta_2,p_1,p_2) = \mathcal{K} - V = \mathcal{K}(\theta_1,\theta_2,p_1,p_2) \tag{4}$$

since there is no potential energy V involved. The kinetic energy has to be expressed by the generalized coordinates $(\theta_1,\theta_2,p_1,p_2)$. The generalized momenta are

$$p_1 = \frac{\partial\mathcal{L}}{\partial\dot\theta_1} = 4\dot\theta_1 + 2\dot\theta_2\cos\xi \tag{5}$$

$$p_2 = \frac{\partial\mathcal{L}}{\partial\dot\theta_2} = 2\dot\theta_2 + 2\dot\theta_1\cos\xi \tag{6}$$

Solving with respect to $\dot\theta_1$ and $\dot\theta_2$ yields

$$\dot\theta_1 = \frac{1}{2(2-\cos^2\xi)}(p_1 - p_2\cos\xi) = \frac{\gamma}{2}(p_1 - p_2\cos\xi) \tag{7}$$

$$\dot\theta_2 = \frac{1}{2(2-\cos^2\xi)}(2p_2 - p_1\cos\xi) = \frac{\gamma}{2}(2p_2 - p_1\cos\xi), \tag{8}$$

defining for simplicity $\gamma = (2-\cos^2\xi)^{-1}$. Inserted in Eqs. (15) and (16) we obtain after some basic calculation

$$\mathcal{H}(\xi,p_1,p_2) = \frac{\gamma}{4}(p_1^2 + 2p_2^2 - 2p_1p_2\cos\xi) \tag{9}$$

The probability density in configuration space is determined by integrating out the momenta of the probability distribution function given by the Boltzmann factor $\exp\{-\mathcal{H}/k_{\mathrm{B}}T\}$:

$$\Psi(\xi) = C \int\int_{-\infty}^{\infty} \exp\{-\mathcal{H}/k_{\mathrm{B}}T\} \mathrm{d}p_1 \mathrm{d}p_2 \tag{10}$$

where C is the normalization constant.

Before integration we rewrite the exponent to complete quadratic expressions:

$$\begin{aligned}
\gamma(2p_2^2 - 2p_1p_2\cos\xi + p_1^2) &= 2\gamma(p_2 - \frac{1}{2}p_1\cos\xi)^2 + \gamma(p_1^2 - \frac{1}{2}p_1^2\cos^2\xi) \\
&= \gamma(p_2 - \frac{1}{2}p_1\cos\xi)^2 + \gamma p_1^2 \frac{1}{2\gamma} \\
&= \gamma u^2 + \frac{1}{2}p_1^2,
\end{aligned} \tag{11}$$

where we have defined $u = p_2 - \frac{1}{2}p_1\cos\xi$ and recalled $\gamma = (2 - \cos^2\xi)^{-1}$. Integration using $\int_{-\infty}^{\infty} \exp\{-bu^2\}\mathrm{d}u = \sqrt{\frac{\pi}{b}}$, yields

$$\underline{\underline{\Psi(\xi)}} = C'\sqrt{\frac{1}{\gamma}} = \underline{\underline{C'\sqrt{2-\cos^2\xi} = C''\sqrt{1 - \frac{1}{2}\cos^2\xi}}} \tag{12}$$

where C' and C'' are new normalization constants.

Because of the ξ-dependence the Kramers Chain is *not* a random-walk configuration. Note especially that

$$\frac{\Psi(\xi = \pi/2)}{\Psi(\xi = 0)} = \sqrt{2} \approx 1.41 \tag{13}$$

indicating that there is 41 % larger probability to find the segment vectors orthogonal than parallell.

B. The chain in three dimensions with no fixed point

We recall the expression of kinetic energy of a three-bead Kramers chain in two dimensions from lecture notes Ch. 3.2.3 (Eq. (3.40) of AM11sep02):

$$\mathcal{K} = \frac{1}{2}m_p \dot{\vec{\boldsymbol{r}}}_c^{\,2} + \frac{1}{6}a^2 m \begin{pmatrix} \dot\theta_1 \\ \dot\theta_2 \end{pmatrix}^T \cdot \begin{pmatrix} 2 & \cos\xi \\ \cos\xi & 2 \end{pmatrix} \cdot \begin{pmatrix} \dot\theta_1 \\ \dot\theta_2 \end{pmatrix}, \tag{14}$$

where $\xi = \theta_2 - \theta_1$ equals the included angle.

The kinetic energy of center of mass is decoupled from the rest and i snot included in the following analysis. As noted we simplify by choosing $m = 2$ and $a = 1$. Multiplication of Eq. (14) yields

$$\mathcal{K} = \frac{1}{3}\left(2\dot\theta_1^2 + \cos\xi\dot\theta_1\dot\theta_2 + \cos\xi\dot\theta_1\dot\theta_2 + 2\dot\theta_2^2\right) = \frac{2}{3}\left(\dot\theta_1^2 + \cos\xi\dot\theta_1\dot\theta_2 + \dot\theta_2^2\right) \tag{15}$$

The Hamiltonian $\mathcal{H}$ and the Lagrangian $\mathcal{L}$ are given by

$$\mathcal{H}(\theta_1, \theta_2, p_1, p_2) = \mathcal{K} + V = \mathcal{K}(\theta_1, \theta_2, p_1, p_2) \tag{16}$$

$$\mathcal{L}(\theta_1, \theta_2, p_1, p_2) = \mathcal{K} - V = \mathcal{K}(\theta_1, \theta_2, p_1, p_2) \tag{17}$$

since there is no potential energy V involved. The kinetic energy has to be expressed by the generalized coordinates $(\theta_1, \theta_2, p_1, p_2)$. The generalized momenta are

$$p_1 = \frac{\partial\mathcal{L}}{\partial\dot\theta_1} = \frac{4}{3}\dot\theta_1 + \frac{2}{3}\dot\theta_2\cos\xi \tag{18}$$

$$p_2 = \frac{\partial\mathcal{L}}{\partial\dot\theta_2} = \frac{4}{3}\dot\theta_2 + \frac{2}{3}\dot\theta_1\cos\xi \tag{19}$$

Solving with respect to $\dot{\theta}_1$ and $\dot{\theta}_2$ yields

$$\dot{\theta}_1 = \frac{3}{2(4-\cos^2\xi)}(2p_1 - p_2\cos\xi) = \frac{3}{2}\gamma(2p_1 - p_2\cos\xi) \tag{20}$$

$$\dot{\theta}_2 = \frac{3}{2(4-\cos^2\xi)}(2p_2 - p_1\cos\xi) = \frac{3}{2}\gamma(2p_2 - p_1\cos\xi), \tag{21}$$

defining for simplicity $\gamma = (4-\cos^2\xi)^{-1}$. Inserted in Eqs. (15) and (16) we obtain

$$\begin{aligned}
\mathcal{H}(\xi, p_1, p_2) &= \frac{2}{3}\cdot\frac{9}{4}\gamma^2(4p_1^2 - 4p_1p_2\cos\xi + p_2^2\cos^2\xi) \\
&+ \frac{2}{3}\cdot\cos\xi\frac{9}{4}\gamma^2(4p_1p_2 - 2p_1^2\cos\xi - 2p_2^2\cos\xi + p_1p_2\cos^2\xi) \\
&+ \frac{2}{3}\cdot\frac{9}{4}\gamma^2(4p_2^2 - 4p_1p_2\cos\xi + p_1^2\cos^2\xi) \\
&= \frac{3}{2}\gamma^2\left\{p_1^2(4-\cos^2\xi) + p_2^2(4-\cos^2\xi) - p_1p_2\cos\xi(4-\cos^2\xi)\right\} \\
&= \frac{3}{2}\gamma\left\{p_1^2 + p_2^2 - p_1p_2\cos\xi\right\}
\end{aligned} \tag{22}$$

The probability density in configuration space is determined by integrating out the momenta of the probability distribution function given by the Boltzmann factor $\exp\{-\mathcal{H}/k_{\mathrm{B}}T\}$:

$$\Psi(\xi) = C\int\int_{-\infty}^{\infty}\exp\{-\mathcal{H}/k_{\mathrm{B}}T\}\mathrm{d}p_1\mathrm{d}p_2 \tag{23}$$

where C is the normalization constant.

Before integration we rewrite the exponent to complete quadratic expressions:

$$\begin{aligned}
\gamma(p_2^2 - p_1p_2\cos\xi + p_1^2) &= \gamma(p_2 - \frac{1}{2}p_1\cos\xi)^2 + \gamma(p_1^2 - \frac{1}{4}p_1^2\cos^2\xi) \\
&= \gamma(p_2 - \frac{1}{2}p_1\cos\xi)^2 + \gamma p_1^2\frac{1}{4\gamma} \\
&= \gamma u^2 + \frac{1}{8}p_1^2,
\end{aligned} \tag{24}$$

where we have defined $u = p_2 - \frac{1}{2}p_1\cos\xi$ and recalled $\gamma = (4-\cos^2\xi)^{-1}$. Integration using $\int_{-\infty}^{\infty}\exp\{-bu^2\}\mathrm{d}u = \sqrt{\frac{\pi}{b}}$, yields

$$\underline{\underline{\Psi(\xi)}} = C'\sqrt{\frac{1}{\gamma}} = \underline{\underline{C'\sqrt{4-\cos^2\xi} = C''\sqrt{1-\frac{1}{4}\cos^2\xi}}} \tag{25}$$

where C' and C'' are new normalization constants.

Because of the ξ-dependence the Kramers Chain is *not* a random-walk configuration. Note especially that

$$\frac{\Psi(\xi=\pi/2)}{\Psi(\xi=0)} = \sqrt{\frac{4}{3}} \approx 1.15, \tag{26}$$

indicating that there is 15 % larger probability to find the segment vectors orthogonal than parallell.

C. The chain in three dimensions with no fixed point

In three dimensions we need two more generalized coordinates to give the three-bead Kramers chain, namely the two angles (ϕ, θ) which define the plane of the chain. However, using the same procedure as given above for two dimensions, the rotation of this plane yields general momenta being orthogonal to the plane of the chain. Thus there is no coupling between these velocities (momenta) and the momenta analysed above for the two-dimensional problem. The momenta can therefore easily be integrated out, and the conclusion is that the probability distribution for the included angle for the 3-dimensional three-bead Kramers chain effectively is identical to a two-dimensional problem.

For a formal analysis we have to use the three-dimensional spherical coordinates $(\phi_1, \theta_1, \phi_2, \theta_2)$ for the orientation of the two segment vectors. It can easily be shown that the included angle ξ (geometrically the same as in the two-dimensional chain) is expressed

$$\cos\xi = \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) + \cos\theta_1 \cos\theta_2 \tag{27}$$

Because of the properties of the spherical coordinates the factors $\sin\theta_1 \sin\theta_2$ enters the probability distribution:

$$\Psi(\theta_1, \theta_2, \xi) = C \cdot \sin\theta_1 \sin\theta_2 \sqrt{1 - \frac{1}{4}\cos^2\xi} \tag{28}$$

Also note that all configuration probilities found are temperature independent.

Normalization

$$C^{-1} = \int\int\int\int \sin\theta_1 \sin\theta_2 \sqrt{1 - \frac{1}{4}\cos^2\xi}\, \mathrm{d}\theta_1 \mathrm{d}\phi_1 \mathrm{d}\theta_2 \mathrm{d}\phi_2 \tag{29}$$

Take the first integration on θ_1, ϕ_1, in which we choose to fix segment vector 2 along z-axis ($\theta_2 = 0$). Then $\xi = \theta_1$ and

$$\begin{aligned}
C^{-1} &= \int\int \sin\theta_2 \left[\int_0^{2\pi}\int_0^{\pi} \sin\theta_1 \sqrt{1 - \frac{1}{4}\cos^2\theta_1}\, \mathrm{d}\theta_1 \mathrm{d}\phi_1\right] \mathrm{d}\theta_2 \mathrm{d}\phi_2 \\
&= \left[\int\int \sin\theta_2 \mathrm{d}\theta_2 \mathrm{d}\phi_2\right] \left[2\pi \int_{\pi/3}^{2\pi/3} 2 \cdot \sin x \sqrt{1 - \cos^2 x}\, \mathrm{d}x\right] \\
&= \left[\int_0^{2\pi} \mathrm{d}\phi_2 \int_0^{\pi} \sin\theta_2 \mathrm{d}\theta_2\right] \left[2\pi \int_{\pi/3}^{2\pi/3} 2\sin^2 x\, \mathrm{d}x\right] \\
&= [4\pi] \left[2\pi \cdot (x - \frac{1}{2}\sin 2x)\right]_{\pi/3}^{2\pi/3} \\
&= 4\pi \left[2\pi \cdot (\frac{\pi}{3} + \frac{\sqrt{3}}{2})\right] \\
&= (4\pi)^2 \cdot \left(\frac{\pi}{6} + \frac{\sqrt{3}}{4}\right).
\end{aligned} \tag{30}$$

The normalized probability equals

$$\Psi(\theta_1, \theta_2, \xi) = \frac{\sin\theta_1 \sin\theta_2}{(4\pi)^2} \cdot \frac{\sqrt{1 - \frac{1}{4}\cos^2\xi}}{\pi/6 + \sqrt{3}/4} \tag{31}$$

Compare to the random walk distribution (that is, both segments free to rotate in any direction):

$$\Psi(\theta_1, \theta_2) = \frac{\sin\theta_1 \sin\theta_2}{(4\pi)^2} \tag{32}$$

and the distribution of "included angle" ξ is uniform on the sphere, and the same probability to find the two segments orthogonal as parallell.