UNIVERSITY OF IOANNINA
DEPARTMENT OF PHYSICS
PHYSICS SOCIETY OF IOANNINA (PSI)
PLANCKS examination (Greece)
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1. Mass in a tube

A tube of mass M and length ℓ is free to swing around a pivot at its left end. A mass m is positioned inside the (frictionless) tube at this point. The tube is held horizontal and then released (see Fig. 1). Let θ be the angle of the tube regarding the horizontal, and x be the distance the mass has travelled along the tube.

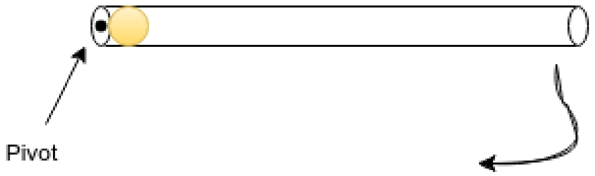


Figure 1: A mass m in a tube of length ℓ and mass M.

a) Find the equations of motion for θ and x and write them in terms of θ and $\eta = x/\ell$ (the fraction of the distance along the cube).

[10 marks]

b) You probably see that these differential equations cannot be solved analytically. What to do? A numerical solution is a possible strategy. Write a constructive program in a language of your choice (Python, C++, Fortran, ...) without built-in functions or unknown subroutine calls, that produce the value of η when the tube is vertical ($\theta = \pi/2$). Give this value of η for a few values of the mass ratio $\zeta \equiv m/M$.

Hint: It is very useful, before writing the code or even before trying something analytically, to investigate with simple arguments whether η depends on ℓ or the acceleration constant g.

[10 marks]

Solution

a) The inertial moment of the tube is $\frac{1}{3}M\ell^2$ as we can easily find. Adding up (rotational and linear) kinetic and potential energies for both tube M and particle m, we find the Lagrangian

$$\mathcal{L} \;=\; \frac{1}{2}\left(\frac{1}{3}M\ell^2\right)\dot{\theta}^2 + \left(\frac{1}{2}mx^2\dot{\theta}^2 + \frac{1}{2}m\dot{x}^2\right) + mgx\sin\theta + Mg\left(\frac{\ell}{2}\right)\sin\theta \;. \tag{1}$$

Euler-Lagrange equations are then

$$\begin{aligned}\frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{\theta}}\right) = \frac{\partial\mathcal{L}}{\partial\theta} &\Rightarrow \frac{d}{dt}\left(\frac{1}{3}M\ell^2\dot{\theta} + mx^2\dot{\theta}\right) = \left(mgx + \frac{Mg\ell}{2}\right)\cos\theta \\ &\Rightarrow \left(\frac{1}{3}M\ell^2 + mx^2\right)\ddot{\theta} + 2mx\dot{x}\dot{\theta} = \left(mgx + \frac{Mg\ell}{2}\right)\cos\theta \;, \end{aligned}\tag{2}$$

$$\frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{x}}\right) = \frac{\partial\mathcal{L}}{\partial x} \Rightarrow m\ddot{x} = mx\dot{\theta}^2 + mg\sin\theta \;. \tag{3}$$

In terms of $\eta = x/\ell$, $\zeta = m/M$ and also $\tilde{g} = g/\ell$ equations of motion become

$$(1+3\zeta\eta^2)\ddot{\theta} = \left(3\zeta\tilde{g}\eta + \frac{3}{2}\tilde{g}\right)\cos\theta - 6\zeta\eta\dot{\eta}\dot{\theta} \;, \tag{4}$$

$$\ddot{\eta} = \eta\dot{\theta}^2 + \tilde{g}\sin\theta \;. \tag{5}$$

b) The coupled system of non-linear differential equations (4) and (5) are impossible to be solved analytically. I give a `Python` program below (trivially adapted to any other computer language) where it calculates η when the tube is vertical, i.e. $\theta = \pi/2$ for the case of adjustable ζ-values (I will set $\zeta = 1$ for the intended purpose).

Before doing so, here is an observation: Since η is dimensionless, it cannot depend on g, the only parameter that contains time. Nor, it depends on ℓ, the only length parameter encountered in the problem. The only dimensionless parameter is the ratio between mass scales m and M, that is η can only be a function of $\zeta = m/M$.

```

import math

l = 1.  # length of the tube
g = 10. # acceleration constant
n = 0.  #value of eta
n1 =0.  #initial value of dot(eta)
q = 0.  #initial theta value
q1 = 0. #initial dot(theta) value
e = 0.0001 # small time increment
gt= g/l #value of gtilde = g/l
z=1.    #valuue of zeta=m/M
```

```python
while q<1.57079 : # do the following loop until angle theta =pi/2
    n2=n*q1**2 + gt*math.sin(q) #E-L eq.(5)
    q2=((3*z*gt*n+3*gt/2)*math.cos(q) - 6*z*n*n1*q1)/(1+3*z*n**2) #E_L eq.(4)
    n=n+e*n1 # n changes slightly
    n1=n1+e*n2 # n1 changes
    q=q+e*q1 # q changes slightly
    q1=q1+e*q2 # q1 changes


print(n) # print the value of eta when the tube is vertical
```

Listing 1: A suggestive `Python` code for the problem ”Mass in a tube”.

If computers are not allowed in class, marking this problem finishes here. It is interesting, however, to write the code on your computer and check if your physics expectations meet. You will find

$$\eta(\theta = \pi/2) = 0.378\ . \tag{6}$$

If you change the length of the tube value to say, $\ell = 1000$ you must see no change (up to the increment value you have chosen) according to the dimensional analysis argument above. Here are some results for variables η with different values of parameters ζ: Had we

ζ	$\eta\ (\theta = \pi/2)$
0.1	0.352
1	0.378
10	0.872
11.3	1.004
20	3.290
50	18893027

had extended the tube, we see that when $\zeta \to \infty$ then as well $\eta \to \infty$. In this case, the “heavy” mass m drops quickly down and forces the tube to swing quickly to vertical.

2. α Spectroscopy of Super-Heavy Nuclei

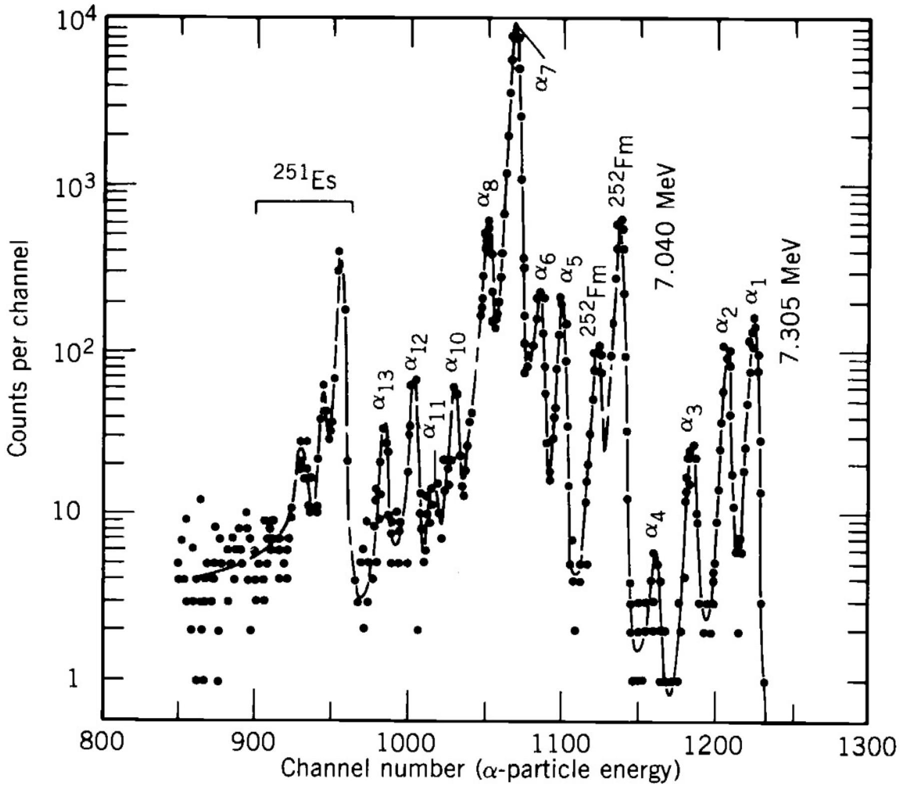
The energy spectrum of the α particles emitted from the decay of ^{251}Fm is depicted in Figure below.

a) Determine the Q value of the decay processes populating the ground state of the daughter nucleus, as well as the first two excited states. Assume that the parent nuclei are initially at rest. Determine the energies of the first two excited states of the daughter nucleus. The energies of the first three groups of α particles are given as α_1= 7305 keV, α_2 = 7251 keV, α_3 = 7184 keV

[5 marks]

b) Based on the decay spectrum, determine the angular momentum assignments of the ground and first two excited states of the daughter nucleus. Assume that the daughter nucleus is a deformed nucleus and that the ground state, as well as the first two excited states, belong to the same rotational band.

[15 marks]



Solution

a)

Conservation of momentum:

$$\vec{P}_{in} = \vec{P}_{fin} = 0 \tag{7}$$

Conservation of mass/energy:

$$m_p c^2 = m_d c^2 + T_d + T_\alpha + m_\alpha c^2 \tag{8}$$
$$Q = m_p c^2 - m_d c^2 - m_\alpha c^2 \tag{9}$$

No need for relativistic equations (denoting P the momentum):

$$Q = \frac{P^2}{2m_d} + \frac{P^2}{2m_\alpha} \tag{10}$$

$$Q = \frac{P^2}{2m_\alpha}\left(\frac{m_\alpha}{m_d} + 1\right) \tag{11}$$

For the kinetic energies of the three α groups (α_1= 7305 keV, α_2 = 7251 keV, α_3 = 7184 keV), and by considering the masses multiples of the atomic mass unit, we get:

$$Q_0 = 7.305\left(\frac{4}{247} + 1\right) = 7423.3\ keV \tag{12}$$

$$Q_1 = 7251\left(\frac{4}{247} + 1\right) = 7368.4\ keV \tag{13}$$

$$Q_2 = 7184\left(\frac{4}{247} + 1\right) = 7300.3\ keV \tag{14}$$

$$\Delta E_{1-0} = Q_0 - Q_1 = 55\ keV \tag{15}$$

$$\Delta E_{2-0} = Q_0 - Q_2 = 123\ keV \tag{16}$$

b) For the same rotational band the energy levels should follow:

$$E_n = \frac{\hbar^2}{2I} j(j+1) \tag{17}$$

We consider:

a)The ground, the first, and second excited states of the daughter nucleus belong to the same rotational band.

b) k the angular momentum of the ground state.

Accordingly, the ratio of the energy difference between these levels is:

$$\frac{\Delta E_{2-0}}{\Delta E_{1-0}} = \frac{\frac{\hbar^2}{2I}(k+2)(k+3) - \frac{\hbar^2}{2I}k(k+1)}{\frac{\hbar^2}{2I}(k+1)(k+2) - \frac{\hbar^2}{2I}k(k+1)} \tag{18}$$

Taking into account the results of the energy level differences as obtained from a), we have:

$$\frac{\Delta E_{2-0}}{\Delta E_{1-0}} = \frac{4k+6}{2k+2} = \frac{123}{55} \tag{19}$$

From the previous equation it is concluded that:

$$k \simeq 3.2 \tag{20}$$

The angular momentum of the ground state of daughter nucleus (odd-even nucleus) should be a half integer. Therefore:

$$k = 3.5 = \frac{7}{2} \tag{21}$$

Accordingly, we conclude that the angular momentum assignments of the ground and first two excited states of the daughter nucleus ^{247}Cf are: 7/2, 9/2, 11/2.

This result aligns well with the experimental observations.

3. Coaxial Conductor

Calculate the resistance between the center conductor of radius a and the coaxial conductor of radius b for a cylinder of length $l \gg b$, which is filled with a dielectric of permittivity ε and conductivity σ (10 pts). Also calculate the capacitance between the inner and outer conductors (10 pts).

Solution

1. Electric Field Calculation

Let V be the voltage difference between the inner and outer conductors. In the dielectric medium:

- The electric displacement field $\vec{D}$ is related to the electric field $\vec{E}$ by $\vec{D} = \varepsilon\vec{E}$
- Due to cylindrical symmetry, fields depend only on radial distance r
- From Gauss's law: $\oint \vec{D} \cdot d\vec{A} = Q_{enclosed}$

For a cylindrical Gaussian surface of radius r and length l:

$$\oint \vec{D} \cdot d\vec{A} = D(r)(2\pi r l) = Q_{enclosed} \tag{22}$$

$$\varepsilon E(r)(2\pi r l) = Q_{enclosed} \tag{23}$$

Therefore:

$$E(r) = \frac{Q_{enclosed}}{2\pi r l \varepsilon} \tag{24}$$

The potential difference V is:

$$V = -\int_a^b \vec{E} \cdot d\vec{r} = -\int_a^b \frac{Q_{enclosed}}{2\pi r l \varepsilon} dr \tag{25}$$

$$V = -\frac{Q_{enclosed}}{2\pi l \varepsilon} [\ln(r)]_a^b \tag{26}$$

$$V = -\frac{Q_{enclosed}}{2\pi l \varepsilon} \ln(b/a) \tag{27}$$

Solving for $Q_{enclosed}$:

$$Q_{enclosed} = -\frac{2\pi l \varepsilon V}{\ln(b/a)} \tag{28}$$

Therefore, the electric field is:

$$\vec{E}(r) = \frac{V}{r \ln(b/a)} \hat{e_r} \tag{29}$$

2. Current and Resistance Calculation

Using Ohm's law in the dielectric medium, $\vec{J} = \sigma \vec{E}$:

$$\vec{J} = \sigma \frac{V}{r \ln(b/a)} \hat{e_r} \tag{30}$$

The total current through any cylindrical surface is:

$$I = \oint \vec{J} \cdot d\vec{A} = \sigma \frac{V}{r \ln(b/a)} (2\pi r l) \tag{31}$$

$$I = \frac{2\pi \sigma l V}{\ln(b/a)} \tag{32}$$

The resistance is:

$$R = \frac{V}{I} = \frac{\ln(b/a)}{2\pi l \sigma} \tag{33}$$

3. Capacitance Calculation

At the surface of the inner conductor, the boundary condition gives:

$$\vec{D} = \omega \hat{e_r} \tag{34}$$

where ω is the surface charge density.

Therefore:

$$\varepsilon E(a) = \omega \tag{35}$$

Substituting the electric field at $r = a$:

$$\omega = \frac{\varepsilon V}{a \ln(b/a)} \tag{36}$$

The total charge on the inner conductor is:

$$Q = \omega(2\pi a l) = \frac{2\pi\varepsilon l V}{\ln(b/a)} \tag{37}$$

The capacitance is thus:

$$C = \frac{Q}{V} = \frac{2\pi\varepsilon l}{\ln(b/a)} \tag{38}$$

Physical Interpretation

The presence of the dielectric:

- Modifies the electric field through ε
- Affects the charge distribution on conductors
- Increases the capacitance by a factor of $\varepsilon/\varepsilon_0$ compared to vacuum
- Provides a conduction path that determines resistance through σ

The solution is valid for $l \gg b$, allowing us to ignore edge effects.

4. Stretching a Rubber Bar

Rubber is an amorphous, lightly cross-linked polymer whose macromolecules are long chains of isoprene molecules held together by carbon-carbon bonds. To construct a toy model for rubber, we start with a single chain consisting of n links, with each link having length ℓ (for now, picture a link as a thin rigid rod). Let $\mathbf{r} = \mathbf{r}_n$ be the end-to-end vector connecting the start of the first link to the end of the n-th link. In a real polymer, the direction of each link can vary in 3-dimensional space, leading to highly complicated entangled shapes. For simplicity, we will start by considering the toy model of a one-dimensional such chain.

1. Calculate the entropy $S_{\text{chain}}(n, x, \ell)$ of a single such one-dimensional chain, where x is the end-point of the chain (assuming it started at the origin). You may apply Stirling's approximation as needed.

   [5 pts]

2. Construct the one-dimensional probability density $P(x)$ for the chain's endpoint being x. From this, derive the 3-dimensional probability density $P(x, y, z)$ to have a 3-dimensional chain end within an infinitesimal volume d^3x around (x, y, z), by assuming that the "random walks" (traced by the chain's shape) in different dimensions are uncorrelated and isotropic. Use your result to calculate the total entropy S_{poly} of a polymer consisting of N chains.

   [5 pts]

3. One of the well-known properties of rubber is its elasticity. Take a rubber bar of square cross section, with base width w and height L and suppose we slowly (and reversibly) apply a stretching force along its long side, so that $L \to L' = \lambda L$, where $\lambda > 1$ is the dimensionless stretch factor. Taking into account rubber's incompressibility (i.e. the volume of the bar is preserved under the stretch), calculate the entropy change of the polymer as a function of λ. Is the sign of your result reasonable? Provide a physical interpretation. Assume that no chains break or glue together under the deformation.

   [5 pts]

4. For an ideal polymer, such as the one we are modelling here, there is no interaction between the chains and the elastic force is entropic. Use this fact, together with thermodynamical arguments to calculate the elastic force $\sigma = \sigma(\lambda)$ of the rubber bar.

   [5 pts]

Solution

1. A 1-dimensional chain starting at 0 and ending at position $x = x_n$, can be constructed using n links by combining n_+ links going to the right and $n_- = n - n_+$ links going to the left. Since the link length is ℓ, this means that $x = (n_+ - n_-)\ell$. Clearly, these equations determine

$$n_\pm = \frac{n}{2}\left(1 \pm \frac{x}{n\ell}\right) . \tag{39}$$

The entropy of the chain $S_{\text{chain}}(n, x, \ell) = k \log \Omega$, where $\Omega = \Omega(n, x, \ell)$ is the number of ways in which the n links can be arranged to form the chain. This is equal to the number of ways we can choose n_+ links out of the total number of links, namely $\Omega = n!/(n_+!n_-!)$.

We next calculate the entropy

$$\begin{aligned}
S_{\rm chain} &= k\log n! - k\log n_+! - k\log n_-! \\
&\simeq nk\log 2 - \frac{nk}{2}\left[(1+\tfrac{x}{n\ell})\log(1+\tfrac{x}{n\ell}) + (1-\tfrac{x}{n\ell})\log(1-\tfrac{x}{n\ell})\right] \\
&\simeq nk\left(\log 2 - \frac{x^2}{2n^2\ell^2}\right),
\end{aligned} \tag{40}$$

where we used Stirling's approximation $a! = a\log a - a$ for large a, and the Taylor expansion of the logarithm $\log(1\pm x) \simeq \pm x - x^2/2$.

2. The probability density of having a chain ending at x is proportional to the number of microstates

$$P(x) = Ae^{-\frac{x^2}{2n\ell^2}} \sim e^{S_{\rm chain}(x)/k}\,. \tag{41}$$

The normalisation constant is determined from the requirement $\int_{-\infty}^{\infty} dx P(x) = 1$ and found to be

$$A = \sqrt{2\pi n\ell^2}\,. \tag{42}$$

Therefore, the 1-dimensional probability element is

$$P(x)dx = \frac{1}{\sqrt{2\pi n\ell^2}}\,e^{-\frac{x^2}{2n\ell^2}}\,dx\,. \tag{43}$$

Since the 'random walks' of the chain in the x, y, z directions are uncorrelated, the 3-dimensional probability element is

$$P(x,y,z)d^3x = \frac{1}{\sqrt{n_x n_y n_z}}\frac{1}{(2\pi\ell^2)^{3/2}}\,e^{-\frac{(x/n_x)^2+(y/n_y)^2+(z/n_z)^2}{2\ell^2}}\,d^3x\,, \tag{44}$$

where n_x, n_y, n_z are the number of chain links in the x, y, z directions, respectively. Obviously, $n_x + n_y + n_z = n$. Isotropy then implies $n_x = n_y = n_z = n/3$. As a result, the 3-dimensional probability is

$$P(x,y,z)d^3x = \left(\frac{3}{2\pi n\ell^2}\right)^{3/2}\,e^{-\frac{3}{2}\frac{x^2+y^2+z^2}{n\ell^2}}\,d^3x\,. \tag{45}$$

From this, we infer that the entropy of a 3-dimensional chain is

$$S_{\rm chain} = S_{\rm chain}(x) + S_{\rm chain}(y) + S_{\rm chain}(z) = nk\left(\log 2 - \tfrac{3}{2}\frac{(x^2+y^2+z^2)}{n^2\ell^2}\right). \tag{46}$$

If there are N chains in total, the number of chains with endpoints between $\mathbf{r}$ and $\mathbf{r}+d\mathbf{r}$ is

$$dN = NP(x,y,z)d^3x\,. \tag{47}$$

We may now calculate the total entropy of the polymer as

$$S_{\rm poly} = \int dN\;S_{\rm chain} = N\int d^3x\;S_{\rm chain}P(x,y,z) = N\left\langle nk\log 2 - \frac{3}{2}nk\frac{x^2+y^2+z^2}{n^2\ell^2}\right\rangle, \tag{48}$$

where in the last equality we have conveniently expressed the result in terms of the average with respect to a single (3-dimensional) chain. This can be written as

$$S_{\text{poly}} = Nnk \log 2 - \frac{3}{2} Nnk \, \frac{\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle}{n^2 \ell^2} \,. \tag{49}$$

For the mean squared positions, we have

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3} \langle r^2 \rangle = \frac{1}{3} \left(\frac{3}{2\pi n \ell^2} \right)^{3/2} 4\pi \int_0^\infty dr \; r^4 \, e^{-\frac{3r^2}{2n\ell^2}} = \frac{1}{3} n \ell^2 \,. \tag{50}$$

The fact that $\sqrt{\langle r^2 \rangle} = \sqrt{n}\ell$ is basically the well-known result of Brownian motion, where the root mean square distance grows with the square root of time (here, the role of time is played by the number of steps n of the random walk). Plugging this into the expression for the entropy, we find

$$S_{\text{poly}} = Nnk \log 2 - \frac{3}{2} Nk \,. \tag{51}$$

3. Since the volume of the rubber bar is preserved under the stretch, the sides of the bar satisfy $L'(w')^2 = Lw^2$. Therefore, if the long side scales as $L' = \lambda L$, then the sides of the base should scale as $w' = w/\sqrt{\lambda}$. The number of chains N does not change under stretching and we assume no chains break or glue into longer ones. The stretching of the rod will cause a corresponding straightening of the chains, meaning that the entropy of a chain will be

$$S'_{\text{chain}}(\lambda) = nk \log 2 - \frac{3}{2} nk \frac{\lambda^2 x^2 + (y^2 + z^2)/\lambda}{n^2 \ell^2} \,. \tag{52}$$

As a result, the total entropy of the stretched polymer becomes

$$S'_{\text{poly}}(\lambda) = Nnk \log 2 - \frac{3}{2} Nnk \, \frac{\lambda^2 \langle x^2 \rangle + (\langle y^2 \rangle + \langle z^2 \rangle)/\lambda}{n^2 \ell^2} = Nnk \log 2 - \frac{1}{2} Nk \, (\lambda^2 + 2/\lambda) \,. \tag{53}$$

The change in entropy due to the stretch is

$$\Delta S_{\text{poly}} = S'_{\text{poly}}(\lambda) - S'_{\text{poly}}(1) = -\frac{1}{2} Nk \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \,. \tag{54}$$

The quantity in the brackets is positive and monotonically increasing with λ. Therefore, the change of entropy is negative and decreases as we stretch the rubber bar. This is expected, since the stretching of the rubber bar aligns the chains in the direction of the stretch and disentangles them. As the chains are stretched, the number of microstates drops and the system becomes less disordered.

4. The first law of thermodynamics for the rubber bar is $dU = \delta Q + \sigma dL$, where δQ is the heat received by the system and σdL is the work done on the rubber bar by the tensile force. Since we assume that the process is reversible, the second law of thermodynamics allows us to write $\delta Q = TdS$. In terms of the free energy $F = U - TS$, we then write

$$dF = -SdT + \sigma dL \,. \tag{55}$$

Since F is a state function, we now have

$$\sigma = \frac{\partial F}{\partial L} = \frac{\partial U}{\partial L} - T\frac{\partial S}{\partial L} \,. \tag{56}$$

However, for an ideal polymer there is no interaction between the chains and, therefore, the internal energy $U = U(T)$ is a function of temperature alone. As a result, $\partial U/\partial L = 0$ and the elastic force is entirely entropic:

$$\sigma = -T\frac{\partial S}{\partial L} \,. \tag{57}$$

The situation parallels the case of the ideal gas where the molecules are non-interacting, the internal energy is a function of the temperature alone (and not volume), and the pressure that develops is entirely due to entropy variations.

Using our result for the polymer entropy from Question 3, we may now calculate the elastic force

$$\sigma(\lambda) = \frac{NkT}{L_0}\left(\lambda - \frac{1}{\lambda^2}\right) \,, \tag{58}$$

where L_0 is the original (unstretched) length of the rubber bar.

5. Measurement of forces at the molecular level

Kevlar is a tough polymeric fiber with a chemical composition shown in Fig. 2a. When mechanical stress is applied to the material, the center wavenumber of some Raman scattering bands is shifted. This is particularly evident in bands corresponding to vibrations of covalent bonds along the main chain, such as the C-C bond of the aromatic ring. This vibration is centered at 1611 cm^{-1} when no force is applied, but is shifted to lower wavenumber under tensile stress.

a) Discuss briefly the origin of the effect shown in Fig. 2b. Hint: How does an external force change the energy landscape? (5 pts)

b) Calculate the cross-sectional area per polymer chain. The bulk density of Kevlar is $\rho = 1.44$ g cm^{-3} . Note that most C and H atoms are not shown explicitly in Fig. 2a. What force is applied to a single chain when the macroscopic stress is equal to $\sigma = 1$ GPa? Avogadro's constant $N_A = 6.022 \cdot 10^{23}$ mol^{-1} . (5 pts)

c) Find the Morse potential that best describes the C-C bond in the aromatic ring. Its equilibrium length is $R = 140$ pm. For calculations, you can assume that this bond is isolated. The form of the Morse potential is $U(x) = D\left(1 - e^{-a(x-R)}\right)^2$, where D, a are the parameters to be determined. Hint: Fig. 2b shows only the linear regime of the $\bar{\nu}(\sigma)$ dependence. (10 pts)

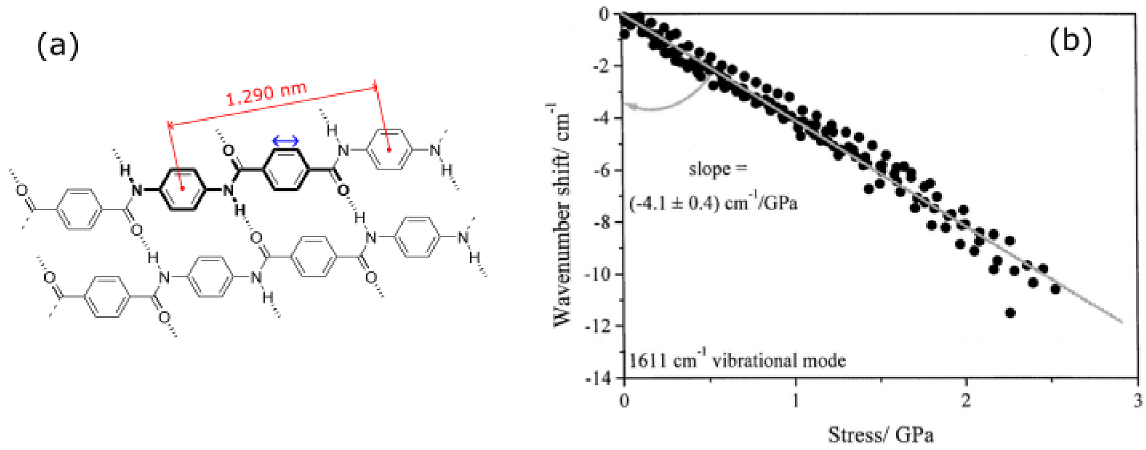


Figure 2: (a) Molecular structure of Kevlar. The length of the repeating unit is equal to 1.290 nm. A strong Raman band at 1611 cm^{-1} is attributed mainly to the stretching of aromatic ring C-C bonds shown in blue. (b) Raman wavenumber shift as a function of applied stress.

Solution

a) The origin of the effect is the anharmonicity of molecular bonds. The spring constant of the bond can be determined by the second derivative of $U(x)$. External forces add energy $U_{ext} = -Fx$ to this landscape. Under force, the equilibrium position is shifted to a longer bond length, where the curvature of the landscape $U(x)$ is different.

b) We can calculate the mass and the volume of the repeating unit (thicker lines in Fig. 2a). The length is known, so we get the cross-sectional area. The repeating unit includes 14 carbon, 2 nitrogen, 2 oxygen, and 10 hydrogen atoms. Their total mass is approx. $m_U = (14*12+2*14+2*16+10*1)$ g mol^{-1} / $N_A \approx 3.95 \cdot 10^{-22}$ g. The volume occupied by the repeating unit is $V_U = m_U/\rho = 2.74 \cdot 10^{-28}$ m^3. Thus, the cross-sectional area per chain is $A_{chain} = V_U/(1.290 \text{ nm}) = 2.13 \cdot 10^{-19}$ m^2. The force per chain at $\sigma = 1$ GPa is $F = \sigma A_{chain} = 2.13 \cdot 10^{-10}$ N.

c) It is possible to solve the Schrödinger equation for the Morse potential analytically and apply perturbation theory, but it is sufficient to treat the problem classically.

The maximum shift of vibrational frequency is about 2-3 orders of magnitude lower than the unperturbed frequency, and the dependence on stress is linear. Thus, first-order approximations can be made, greatly simplifying the solution.

The C-C bond of the ring can be treated as a system of two equal masses, each equal to $m_C = 12$ g mol$^{-1}/N_A = 1.99 \cdot 10^{-26}$ kg. The reduced mass of the system is $\mu = m_C/2 = 9.96 \cdot 10^{-27}$ kg. The effective force constant of the bond is

$$k = \left.\frac{\partial^2 U}{\partial x^2}\right|_{\frac{\partial U}{\partial x}=0} \tag{59}$$

The respective wavenumber of the Raman band is

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{60}$$

In general,

$$\frac{\partial^2 U}{\partial x^2} = 2Da^2 e^{-a(x-R)} \left(2e^{-a(x-R)} - 1\right) \tag{61}$$

At $F = 0$ we have $\partial U/\partial x = 0 \Rightarrow x = R$ and $k = 2Da^2$. Thus

$$Da^2 = 4\pi^2 c^2 \bar{\nu}_0^2 \mu \tag{62}$$

.

The dependence $\bar{\nu}(\sigma)$ will give the second relation between D, a. Setting $\frac{\partial U_{tot}}{\partial x} = 0$ gives

$$e^{-a(x-R)} = \frac{1}{2} + \frac{1}{2}\sqrt{1 - \frac{2F}{Da}} \approx \frac{1}{2} + \frac{1}{2}\left(1 - \frac{F}{Da}\right) = 1 - \frac{F}{2Da} \tag{63}$$

Substituting into the above equations yields

$$k \approx 2Da^2\left(1 - \frac{F}{2Da}\right)\left(1 - \frac{F}{Da}\right) \approx 2Da^2\left(1 - \frac{3F}{2Da}\right) \tag{64}$$

and, finally,

$$\bar{\nu} = \frac{1}{2\pi c\sqrt{\mu}}\sqrt{2Da^2\left(1 - \frac{3F}{2Da}\right)} \approx \frac{a\sqrt{2D}}{2\pi c\sqrt{\mu}}\left(1 - \frac{3F}{4Da}\right) = \bar{\nu}_0\left(1 - \frac{3F}{4Da}\right) \tag{65}$$

This result explains the observed linear dependence $\bar{\nu}(\sigma)$.

$$\Delta\bar{\nu} = -\bar{\nu}_0 \frac{3F}{4Da} \tag{66}$$

The final result is

$$D = \frac{9}{64\pi^2 c^2 \mu}\left(\frac{F}{\Delta\bar{\nu}}\right)^2 \tag{67}$$

and

$$a = \frac{16}{3}\pi^2 c^2 \bar{\nu}_0 \mu \frac{\Delta\bar{\nu}}{F} \tag{68}$$

The force exerted on this bond is half of that in the previous question, because the aromatic ring contains two such bonds connected in parallel. The values of the parameters are $D = 1.07 \cdot 10^{-18}$ J $= 6.7$ eV and $a = 29.2$ nm^{-1}. Other experimental methods yield more accurate results, but these values have the correct order of magnitude, demonstrating the effect of bond anharmonicity.