

PROBLEMS

PION

2024

SMALL PION
BIG IMPACT

 COMSOL



UNIVERSITY OF AMSTERDAM
Institute of Physics

SPIN
Studenten
Physica
in Nederland



Rules

**Please make every exercise on a separate sheet of paper stating your team's name!
Please answer all questions in English.**

There are 8 questions on 14 pages, with a total of 90 points.

Rules during test

- It is not allowed to use any (study)books, notes, etc. other than BINAS and a dictionary.
- It is not allowed to communicate (about the problems) via any means with anyone other than team members.
- It is allowed to use a scientific, graphical calculator (Ti-83, Ti-84 or a similar model).
- Mobile phones are tolerated, but can only be used for emergencies, during the duration of the competition.
- If it is brought to the invigilators' attention that a team has been cheating, breaking the rules or misbehaving, they will be disqualified. Disqualification can happen post submission.

Handing in your work

- All answers must be submitted in English.
- After the 3 hours for the test, the participants are expected to hand in their work to the committee as soon as they enter their room.
- If your team encounters problems with handing in your work, please let the committee (or a volunteer) known as soon as possible! If nothing is heard before the deadline and you hand in nothing, you will be disqualified.
- **Make every exercise on a separate sheet of paper!**
- Make sure your team name is written on every page! The question number should be written on the sheet as well.

The winner of PION2024 is the team with the most points. The second place goes to the best bachelor team, except if the winner of PION is already a bachelor team. In that case, the second place goes to the team with the second most points (bachelor or master). The third place goes to whichever team has the next most points (bachelor or master). The first place will get tickets to PLANCKS; for second and third place, tickets will be requested, but are not guaranteed.

In cases where these rules do not provide, the PION2024-committee will decide.

PION 2024 would not have been possible without help. For this we would like to thank the following companies and institutions.



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We would also like to thank the different universities who contributed to making PION 2024 possible.

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1 Tilted Butter

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Physics of Fluids - University of Twente
 10 points

A piece of butter with length L , height h , width w (directed into the page), and density ρ is placed on a heated slope, see figure 1. The slope is hot enough to melt the bottom of the butter, resulting in a thin layer of liquid butter below the solid butter. Because of the liquid layer the solid butter will move down the ramp. We aim to find the terminal velocity U of the butter and the thickness δ of the thin uniform layer of liquid butter. To solve this we will need to simplify the problem and use thermodynamics, fluid dynamics, and classical dynamics.

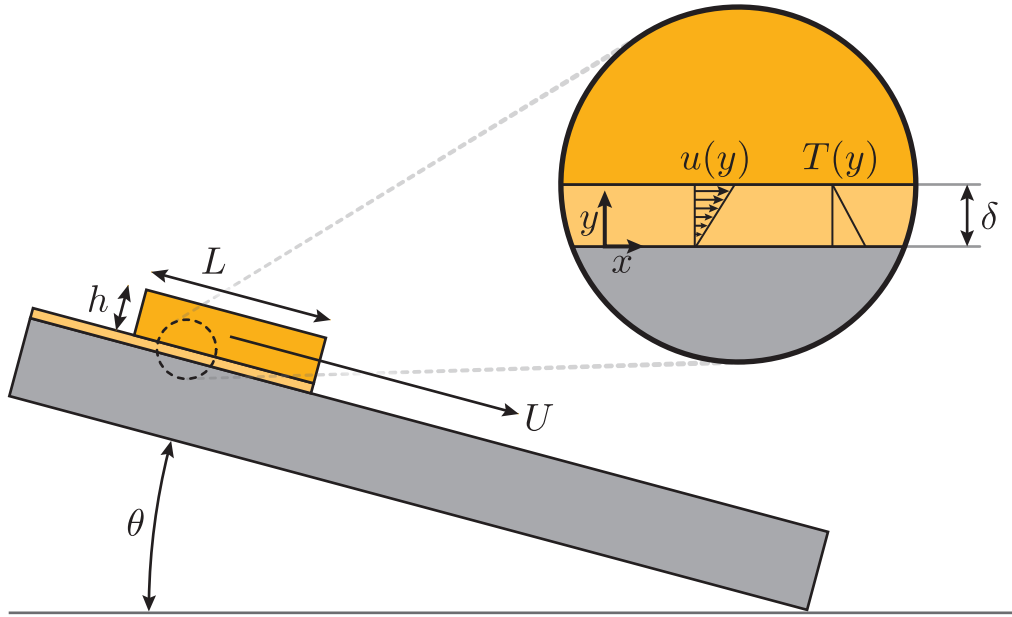


Figure 1: A block of butter (orange) is placed on a heated inclined (angle θ) plate. A thin liquid layer (pale orange) of thickness δ is formed between the solid butter and the ramp. Zoom: (rotated) detail of the thin liquid layer. From left to right we have the coordinate system and the velocity and temperature profiles (both plotted horizontally).

a - 2 pts The piece of butter experiences 3 forces: gravity, a normal force, and a frictional force due to viscosity. To find the drag force we need to consider the shear stress τ at the bottom boundary of the solid butter which is given by:

$$\tau = \frac{F_{\text{drag}}}{A} = \nu \rho \left. \frac{du}{dy} \right|_{y=\delta} \quad (1)$$

where F_{drag} is the force acting in the (negative) x direction, A the bottom area of the piece of butter, ν the kinematic viscosity of the butter, and $u = u(y)$ is the profile of the horizontal velocity. Fluid mechanics tells us that the velocity at the boundaries (wall–liquid–butter and liquid–butter–solid–butter) should follow the speed of this boundary, and since the melted butter is viscous and the melted layer thin, the velocity profile is assumed to be linear in y (as sketched in figure 1). After the initial transient the piece of butter will attain a terminal velocity U where the forces are balanced. **Find the velocity profile $u(y)$ and write down the balance relating gravity and drag forces and solve for U .**

The velocity profile is linear means that $u = ay + b$, we know that $u(0) = 0$ and $u(\delta) = U$ from

the boundary conditions, which gives $u = yU/\delta$. We look at the forces in the x direction:

$$F_{g,\text{eff}} = F_{\text{drag}} \quad (2)$$

$$\underbrace{\overbrace{hLw}^{\text{volume}} \rho}_{\text{mass}} \underbrace{g \sin(\theta)}_{\substack{\text{component of} \\ \text{gravity in the} \\ x \text{ direction}}} = \underbrace{Lw}_{\text{area}} \underbrace{\nu \rho \frac{U}{\delta}}_{\text{shear stress}} \quad (3)$$

we cancel terms and solve for U :

$$U = \frac{hg \sin(\theta) \delta}{\nu} \quad (4)$$

b - 2 pts After all transients have passed (apart from the mass of the solid butter, which we will assume to be constant, though it is slowly melting and ‘producing’ liquid butter), the butter moves down the slope at a constant speed U . As the butter moves forward enough material has to melt from the bottom to create a fresh new layer of thickness δ . We will assume this will come from the entire area under the butter in a uniform manner. We will call the volumetric melt rate of the butter \dot{V} (units m^3/s). **Write down the equation (mass balance) relating \dot{V} and U and the geometry, and solve for U .**

The melted rate should be equal to the newly created thin layer which has a width w and a height δ , and this front is growing with a speed U , this volume-flux should equal to the volumetric melt rate:

$$\dot{V} = U \delta w \quad (5)$$

$$U = \frac{\dot{V}}{\delta w} \quad (6)$$

If students have a factor $1/2$ in this answer because part of the fluid gets dragged along with the butter and thus does not have to be recreated, also correct.

c - 2 pts Now that we have used classical dynamics and fluid dynamics, we will now look at the thermodynamics: the melting. We will assume the solid butter is at its melting point T_{mp} but still solid. Now in order to melt, the temperature of the slope has to be higher than this, as sketched in the zoom of figure 1. Since the layer is thin we can assume the temperature profile is fully defined by thermal diffusion and that it instantly satisfies this equation (no transients):

$$\frac{\partial^2 T}{\partial y^2} = 0 \quad (7)$$

and of course this has to satisfy the boundary conditions that the plate is at temperature T_{plate} and the butter at its melting point. **Find the temperature profile $T(y)$.**

We integrate the equation twice to obtain:

$$\frac{\partial T}{\partial y} = a \quad (8)$$

$$T = ay + b \quad (9)$$

Now satisfying the boundary conditions we find:

$$T = \frac{y}{\delta} (T_{\text{mp}} - T_{\text{plate}}) + T_{\text{plate}} \quad (10)$$

d - 2 pts For any material to melt a “latent heat of fusion” or “enthalpy of fusion”, called \mathcal{L} , has to be supplied to go from solid to liquid (i.e. melting). The units of this enthalpy \mathcal{L} is J/kg, i.e. the amount of Joules needed per kilogram of material to go from solid to liquid. Since there is a thermal gradient, Fourier’s law tells us the heat flux:

$$\vec{q} = -k\vec{\nabla}T \quad (11)$$

where q is the heat flux (units W/m²) and k the thermal conductivity (units W/(Km)). The heat flux from plate to butter is solely used to melt the solid butter. **Relate the volumetric melt rate \dot{V} to the heat flux in equation 11.**

We use equation 11 and the found temperature profile (equation 10) and relate that to the volumetric rate and the latent heat:

$$\underbrace{Lw}_{\text{area}} \overbrace{q}^{\text{power}} = -Lwk \frac{T_{\text{mp}} - T_{\text{plate}}}{\delta} = \dot{V} \rho \mathcal{L} \quad (12)$$

e - 2 pts We now want to combine the results from questions a, b, and d. **Find the speed of the solid butter U and the thickness of the liquid layer δ expressed in terms of temperatures T_{mp} and T_{plate} , latent heat \mathcal{L} , gravity g , angle θ , viscosity ν , thermal conductivity k , density ρ , and dimensions h , L , and w , and show that both U and δ scale as $L^{1/3}$.**

First we find the velocity U . We multiply the square of equation 4 with equation 6:

$$U^3 = \frac{\dot{V} h^2 g^2 \sin(\theta)^2 \delta}{\nu^2 w} \quad (13)$$

and solving equation 12 for \dot{V} :

$$\dot{V} = \frac{Lwk (T_{\text{plate}} - T_{\text{mp}})}{\rho \mathcal{L} \delta} \quad (14)$$

and filling this in in equation 13 and solving for U :

$$U = \sqrt[3]{\frac{Lh^2k (T_{\text{plate}} - T_{\text{mp}}) g^2 \sin(\theta)^2}{\rho \mathcal{L} \nu^2}} \quad (15)$$

Finding δ can now be done by solving equation 4 for δ and filling in the result for U :

$$\delta = \frac{U\nu}{hg \sin(\theta)} \quad (16)$$

$$\delta = \frac{\nu}{hg \sin(\theta)} \sqrt[3]{\frac{Lh^2k (T_{\text{plate}} - T_{\text{mp}}) g^2 \sin(\theta)^2}{\rho \mathcal{L} \nu^2}} \quad (17)$$

$$\delta = \sqrt[3]{\frac{\nu Lk (T_{\text{plate}} - T_{\text{mp}})}{\rho \mathcal{L} hg \sin(\theta)}} \quad (18)$$

2 Frictionless Ball

dr. R.J.A.M. Stevens
Physics of Fluids - University of Twente
10 points

Consider a frictionless ball under the influence of gravity on a slope. Determine the shape of the slope track that minimizes the descent time. That is, determine the path the ball takes from point $A(x_a, y_a)$ to point $B(x_b, y_b)$ with gravity $\mathbf{g} = g\mathbf{e}_y$. You may assume $y_a > y_b$.

Note: there may be various ways of solving this problem. Any complete answer arriving at a mathematical expression for the path the ball takes from point A to B should receive the full 10 points. Any answer falling short of the full answer, should receive partial marks, to be determined by the exam checker. Contact committee in case of doubt.

Specifically, for a track shaped by $y(x)$ with $y(0) = 0$ and $y(L) = L$, so considering the y -axis is downwards. The first thing to do is to express the time of descent as an integral involving $y(x)$. Let $v = ds/dt$ be the speed of the ball along the track, where $ds = \sqrt{(dx)^2 + (dy)^2} = \sqrt{1 + (y')^2}dx$ is arc length along $y(x)$. From conservation of energy we obtain the relationship between velocity v , gravitational acceleration g , and height y , which is given by **(1pt)**:

$$\frac{1}{2}v^2 = gy, \quad v = \sqrt{2gy} \quad (19)$$

The expression for the time of descent T is given by the integral over the path as **(1.5pt)**:

$$T = \int dt = \int \frac{ds}{v} = \int \frac{1}{\sqrt{2g}} \frac{\sqrt{dx^2 + dy^2}}{\sqrt{y}} \quad (20)$$

that is, the definite integral for time T is given by **(1pt)**:

$$T = \frac{1}{\sqrt{2g}} \int_0^L \frac{\sqrt{1 + (y'(x))^2}}{\sqrt{y(x)}} dx. \quad (21)$$

Now we have to find, among all possible functions $y(x)$ satisfying the boundary conditions $y(0) = 0$, $y(L) = L$, the one that minimizes T . To solve this, we use Euler and Lagrange method, which, given a function $f(x, y, p)$, find the function $y(x)$ (satisfying given 'boundary conditions' $y(a) = y_a$, $y(b) = y_b$ for the integral

$$F[y] = \int_a^b f(x, y(x), y'(x)) dx \quad (22)$$

has the smallest value, which can be obtained from the Euler-Lagrange equation:

$$\frac{\partial F}{\partial y} = \frac{d}{dx} \left(\frac{\partial F}{\partial p} \right) \quad (23)$$

The right-hand side is understood as follows: take partial derivatives of F with respect to the argument p , evaluate the resulting function of (x, y, p) at the point $(x, y(x), y'(x))$ to obtain a function of x only, then take its (one-variable) derivative with respect to x . For this problem we have, ignoring the constant $\sqrt{2g}$, for the right-hand side **(1pt)**:

$$F(x, y, p) = \sqrt{\frac{1 + p^2}{y}}, \quad \frac{\partial F}{\partial p} = \frac{p}{\sqrt{y(1 + p^2)}}, \quad (24)$$

$$\frac{d}{dx} \left(\frac{\partial F}{\partial p} \right) = \frac{1}{\sqrt{y(1 + (y')^2)}} \left(\frac{y''}{1 + (y')^2} - \frac{1}{2} \frac{(y')^2}{y} \right). \quad (25)$$

and the left-hand side equals

$$\frac{\partial F}{\partial y} = -\frac{\sqrt{1 + (y')^2}}{2y^{3/2}} \quad (26)$$

Thus combining equations (25) and (26) Euler-Lagrange gives **(1.5pt)**

$$y'' = -\frac{1 + (y')^2}{2y} \quad (27)$$

The solution to this gives the path to minimizing the time for the ball to descend.

Rewrite equation (27) as

$$2yy'' + 1 + (y')^2 = 0 \quad (28)$$

Reduce to the first-order equation by multiplying by y'

$$2yy'y'' + y' + (y')^3 = 0 \quad (29)$$

and rewrite this as

$$\left[y + y(y')^2 \right]' = 0 \quad (30)$$

meaning that **(1pt)**

$$y(1 + (y')^2) = C \quad (31)$$

Now using

$$\frac{dy}{dx} = \sqrt{\frac{C-y}{y}}, \quad \frac{dx}{dy} = \sqrt{\frac{y}{C-y}} \quad (32)$$

Make change of variables from x to ϕ , the angle the tangent to the curve makes to the vertical, such that **(1.5pt)**

$$\frac{dx}{dy} = \tan \phi \quad (33)$$

so

$$\frac{y}{C-y} = \frac{\sin^2 \phi}{\cos^2 \phi} \quad (34)$$

or

$$y = y \cos^2 \phi - y \sin^2 \phi = C \sin^2 \phi \quad (35)$$

Differentiation with respect to ϕ

$$\frac{dy}{d\phi} = 2C \sin \phi \cos \phi \quad (36)$$

Therefore

$$\frac{dx}{d\phi} = \sqrt{\frac{y}{C-y}} \frac{dy}{d\phi} = 2C \sin^2 \phi = C(1 - \cos 2\phi) \quad (37)$$

This can be integrated to

$$x = C \int (1 - \cos 2\phi) d\phi = \frac{C}{2} (2\phi - \sin 2\phi) \quad (38)$$

So we finally obtain

$$x = \frac{C}{2} (2\phi - \sin 2\phi), \quad y = \frac{C}{2} (1 - \cos 2\phi) \quad (39)$$

This is a cycloid, which can also be represented as **(1.5pt)**

$$x = \frac{C}{2} \theta - \frac{C}{2} \sin \theta, \quad y = \frac{C}{2} - \frac{C}{2} \cos \theta \quad (40)$$

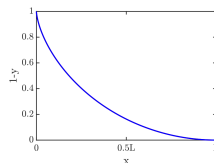


Figure 2: Trajectory that minimizes decent time for frictionless ball (sketch not required!)

3 Quantum description of electron spin at a topological surface

prof. dr. ir. A. Brinkman

Quantum Transport in Matter - University of Twente

10 points

Three-dimensional topological insulators are materials with an electrically insulating bulk and conducting surfaces. The electrons at this topological surface state have the special property that the spin expectation value is coupled to the momentum direction. In this problem we will model this behavior and explore some of its consequences. The Hamiltonian of the electrons at the topological surface is given by

$$H = v\boldsymbol{\sigma} \cdot \mathbf{p} \quad (41)$$

where v is a scalar value, \mathbf{p} is the momentum, given by $\mathbf{p} = \frac{\hbar}{i}\nabla$, and $\boldsymbol{\sigma}$ is the vector with the three Pauli matrices as components,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (42)$$

For the two-dimensional surface we can assume $p_z = 0$.

a - 2 pts Write the Hamiltonian as a matrix. Use $\psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix} e^{ik_x x} e^{ik_y y}$ as an Ansatz (trial solution) for the eigenstates of H and, from the time-independent Schrödinger equation derive the allowed energy eigenvalues $E(k)$, where $k = \sqrt{k_x^2 + k_y^2}$. Make a sketch of E as function of k_x and k_y .

$$H = v(\sigma_x p_x + \sigma_y p_y) \quad (43)$$

$$= v \begin{pmatrix} 0 & p_x \\ p_x & 0 \end{pmatrix} + v \begin{pmatrix} 0 & -ip_y \\ ip_y & 0 \end{pmatrix} \quad (44)$$

$$= v \begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix} = \hbar v \begin{pmatrix} 0 & -i\frac{\partial}{\partial x} - \frac{\partial}{\partial y} \\ -i\frac{\partial}{\partial x} + \frac{\partial}{\partial y} & 0 \end{pmatrix} \quad (45)$$

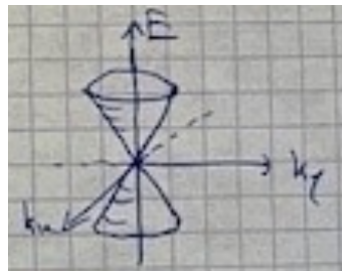
$H\psi = E\psi$ with $\psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix} e^{ik_x x} e^{ik_y y}$ gives

$$\hbar v \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} \begin{pmatrix} \phi \\ \chi \end{pmatrix} e^{ik_x x} e^{ik_y y} = E \begin{pmatrix} \phi \\ \chi \end{pmatrix} e^{ik_x x} e^{ik_y y} \quad (46)$$

$$\Rightarrow \begin{cases} \hbar v(k_x - ik_y)\chi = E\phi \\ \hbar v(k_x + ik_y)\phi = E\chi \end{cases} \quad (47)$$

$$\Rightarrow E^2 = (\hbar v)^2 (k_x - ik_y)(k_x + ik_y) \quad (48)$$

$$\Rightarrow E = \pm \hbar v k \quad \text{with} \quad k = \sqrt{k_x^2 + k_y^2} \quad (49)$$



b - 2 pts Derive expressions for ϕ and χ (and make sure that you normalize the spinor part of the eigenstate).

Hint: it is useful to use polar coordinates, i.e. $k_x = k \cos(\theta)$ and $k_y = k \sin(\theta)$, where θ is the angle of the momentum with respect to the positive k_x -axis.

For $E = +\hbar v k$: $\hbar v k e^{-i\theta} \chi = \hbar v k \phi$

$$\Rightarrow \frac{\chi}{\phi} = e^{i\theta} \Rightarrow A \begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix} \text{ is eigenstate} \quad (50)$$

$$\text{normalize: } A^2 (1, e^{-i\theta}) \begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix} = 1 \Rightarrow A = \frac{1}{\sqrt{2}} \quad (51)$$

$$\Rightarrow \text{eigenstate } \psi_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix} \quad (52)$$

Likewise, for $E = -\hbar v k$ we get

$$\psi_- = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{-i\theta} \end{pmatrix} \quad (53)$$

c - 2 pts For an eigenstate with $E_0 > 0$, calculate $\langle S_x \rangle$ and $\langle S_y \rangle$, where the electron spin operator is given by $\mathbf{S} = \frac{\hbar}{2} \boldsymbol{\sigma}$. On the contour of constant energy E_0 , plot the spin expectation value for different momentum directions. This sketch represents the famous spin-momentum locking at topological surfaces.

For $E = E_0 > 0$ we have $\psi = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{i\phi} \end{pmatrix}$

$$\langle S_x \rangle = \psi^* \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \psi \quad (54)$$

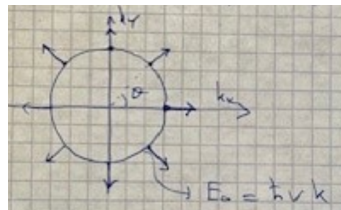
$$= \frac{\hbar}{4} (1, e^{-i\theta}) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix} \quad (55)$$

$$= \frac{\hbar}{4} (e^{i\theta} + e^{-i\theta}) = \frac{\hbar}{2} \cos \theta \quad (56)$$

$$\langle S_y \rangle = \frac{\hbar}{4} (1, e^{-i\theta}) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix} \quad (57)$$

$$= \frac{\hbar}{4} (1, e^{-i\theta}) \begin{pmatrix} -ie^{i\theta} \\ i \end{pmatrix} \quad (58)$$

$$= \frac{\hbar}{4} (ie^{-i\theta} - ie^{i\theta}) = \frac{\hbar}{2} \sin \theta \quad (59)$$



Indeed, the spin expectation value components are coupled to the momentum direction.

One of the consequences of the spin-momentum locking is the fact that electrons can pick up a so-called geometric Berry phase, ϕ_B , when changing direction. The Berry phase can be found by integrating over the Berry connection, $\int d\mathbf{k} \cdot \mathbf{A}$ where $\mathbf{A} = i \langle \psi | \nabla_{\mathbf{k}} \psi \rangle$. Note, that $\nabla_{\mathbf{k}}$ refers to polar coordinates in k -space.

d - 1 pt For the spinor-part of the electron eigenstates at the topological surface, give an expression for the Berry connection \mathbf{A} (Hint: the gradient in polar coordinates in k -space is given by $\nabla_{\mathbf{k}} = \hat{k} \frac{\partial}{\partial k} + \hat{\theta} \frac{1}{k} \frac{\partial}{\partial \theta}$)

$$\mathbf{A} = i \langle \psi | \nabla_{\mathbf{k}} \psi \rangle \quad \text{where} \quad \nabla_{\mathbf{k}} = \hat{k} \frac{\partial}{\partial k} + \hat{\theta} \frac{1}{k} \frac{\partial}{\partial \theta} \quad (60)$$

$$= i \frac{1}{\sqrt{2}} (1, e^{-i\theta}) \frac{1}{k} \frac{\partial}{\partial \theta} \left[\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix} \right] \hat{\theta} \quad (61)$$

$$= i \frac{1}{2} \frac{1}{k} (1, e^{-i\theta}) \cdot \begin{pmatrix} 0 \\ ie^{i\theta} \end{pmatrix} \hat{\theta} = -\frac{1}{2k} \hat{\theta} \quad (62)$$

e - 1 pt Assume that an electron on the constant energy contour with $E = E_0 > 0$ rotates over an angle of 2π , calculate the corresponding Berry phase.

$$\phi_B = \int d\mathbf{k} i \langle \psi | \nabla_{\mathbf{k}} \psi \rangle \quad (63)$$

$$= \int_0^{2\pi} k d\theta \cdot A_{\theta} = \int_0^{2\pi} k d\theta \frac{-1}{2k} = -\frac{1}{2} \int_0^{2\pi} d\theta = -\pi \quad (64)$$

Another, related, consequence of spin-momentum locking is the fact that electrons cannot back-scatter.

f - 2 pts For an incoming electron with $\psi_{in}(\theta_{in} = 0)$ calculate the scattering probability $|\langle \psi_{out} | \psi_{in} \rangle|^2$ as function of the angle θ_{out} of the outgoing electron. Sketch the scattering probability in a polar plot and verify that back-scattering ($\theta_{out} = \pi$) is indeed forbidden.

$$\psi_{in} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}; \quad \psi_{out} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ e^{i\theta} \end{pmatrix} \quad (65)$$

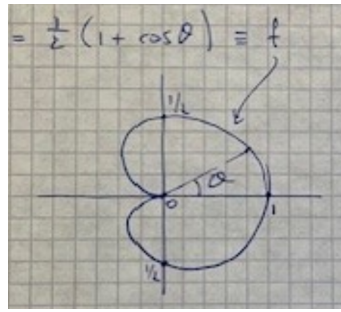
$$\Rightarrow |\langle \psi_{out} | \psi_{in} \rangle|^2 = \left| \frac{1}{\sqrt{2}} (1, e^{-i\theta}) \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \right|^2 \quad (66)$$

$$= \frac{1}{4} |1 + e^{-i\theta}|^2 \quad (67)$$

$$= \frac{1}{4} (1 + e^{-i\theta})(1 + e^{i\theta}) \quad (68)$$

$$= \frac{1}{4} (2 + e^{i\theta} + e^{-i\theta}) = \frac{1}{4} (2 + 2 \cos \theta) \quad (69)$$

$$= \frac{1}{2} (1 + \cos \theta) \equiv f \quad (70)$$



4 Plasmon-enhanced molecular biosensing

dr. O.S. Ojambati
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10 points

The recent COVID-19 pandemic has shown the world the importance of sensitive, reliable, and easy-to-use sensors in medical diagnosis and point-of-care testing. The goal of this exercise is to model a molecular spectroscopic technique that gives specific vibrational signatures of a molecule and how to enhance the spectroscopic signal. We consider an exemplar protein, which could be the spike protein of the COVID-SARS virus. The protein is a long polymer chain, made from repetitive units of amino acid residues and has 45,000 atoms.

Useful formula; Hermite polynomials

$$H_n(x) = n! \sum_{m=0}^{\lfloor \frac{n}{2} \rfloor} \frac{(-1)^m}{m!(n-2m)!} (2x)^{n-2m} \quad (71)$$

a - 1 pts Determine the number of degrees of freedom for translation, rotational, and vibrational motions of the protein.

Translation: 3 degrees of freedom (DoF), 3 DoF for rotation, and $3 \cdot 45000 - 6 = 134994$

b - 1 pts We now consider two of the vibrational degrees of freedom, namely, the stretching mode of the hydrogen and the oxygen atoms (see figure 3 that shows a part of the peptide link in the protein). Sketch the potential energy of the vibrational motion of each of the two atoms and explain any differences between the two potential energies.

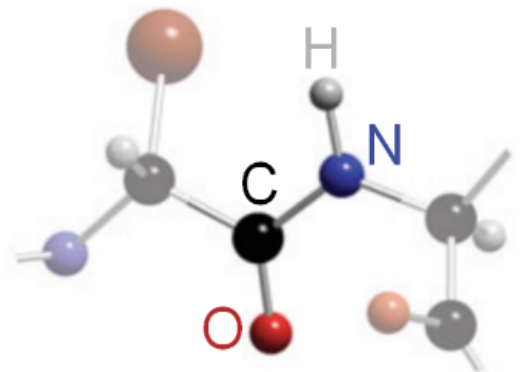
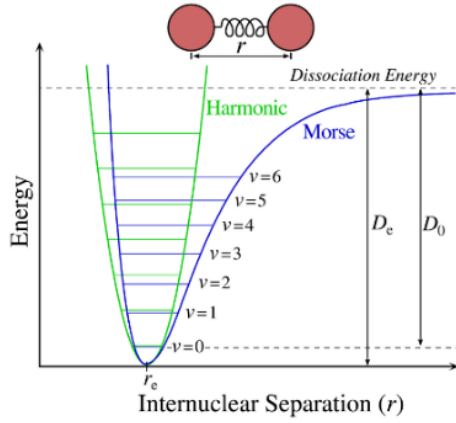


Figure 3: A part of the peptide link

The potential energy of the hydrogen atom in the peptide backbone can be approximated to a harmonic oscillator, consisting of a light mass that is attached to a fixed support. This approximation is valid since hydrogen is much lighter than the other atoms. The potential energy of the CO stretching mode can be described using the Morse potential.



	Harmonic	Morse
$V(x)$	$\frac{1}{2} kx^2$	$D_e(1 - e^{-\beta x})^2$
shape	symmetric	asymmetric
small x	does not account for nuclei interactions	nuclei repel each other
large x	no bond breaking	bond breaking can occur

c - 1 pts From the potential energy considered in b), an analytical solution of the Schrödinger equation can be obtained for the stretching motion. Without showing a detailed solution, what do you expect for the vibrational energy E_n of one of the molecular bonds in the protein (n is the vibrational quantum number)?

The energy of a harmonic oscillator is

$$E_n = \left(n + \frac{1}{2}\right) h\nu \quad (72)$$

d - 3 pts Determine which of these transitions are allowed: transition from (i) the ground state to the first excited state and (ii) the ground state to the second excited state.

A transition is allowed if the transition dipole moment is nonzero. $M_{nn'} \propto \int \psi_n^* x \psi_n dx$

$$\psi_n = N_n H_n(y) \exp\left(-\frac{y^2}{2}\right) \quad (73)$$

$$\text{and } N_n = \left(\frac{1}{\alpha\pi^{1/2}2^n n!}\right)^{1/2} \quad \text{and } H_0 = 1, H_1 = 2y, H_2 = 4y^2 - 2 \quad (74)$$

$$\psi_0 = \left(\frac{1}{\alpha\pi^{1/2}}\right)^{1/2} \exp\left(-\frac{y^2}{2}\right), \psi_1 = \left(\frac{1}{2\alpha\pi^{1/2}}\right)^{1/2} (2y) \exp\left(-\frac{y^2}{2}\right), \text{ and } \quad (75)$$

$$\psi_2 = \left(\frac{1}{16\alpha\pi^{1/2}}\right)^{1/2} (4y^2 - 2) \exp\left(-\frac{y^2}{2}\right) \quad (76)$$

Substituting $x = \alpha y$ and $dx = \alpha dy$

$$M_{01} \propto \int_{-\infty}^{\infty} \left(\frac{1}{\alpha\pi^{1/2}}\right)^{1/2} \exp\left(-\frac{y^2}{2}\right) \alpha y \left(\frac{1}{2\alpha\pi^{1/2}}\right)^{1/2} (2y) \exp\left(-\frac{y^2}{2}\right) \alpha dy \quad (77)$$

$$M_{01} \propto \frac{2\alpha^2}{\alpha(2\pi)^{1/2}} \int_{-\infty}^{\infty} y^2 \exp(-y^2) dy \quad (78)$$

where we used $\int_{-\infty}^{\infty} y^2 \exp(-y^2) dy = \sqrt{\pi}$

$$M_{01} \propto \frac{2\alpha^2}{\alpha(2\pi)^{1/2}} \sqrt{\pi} = 2/\sqrt{2}\alpha \quad (79)$$

Since $M_{01} \neq 0$, the transition is allowed.

$$M_{02} \propto \int_{-\infty}^{\infty} \left(\frac{1}{\alpha\pi^{1/2}} \right)^{1/2} \exp\left(-\frac{y^2}{2}\right) \alpha y \left(\frac{1}{16\alpha\pi^{1/2}} \right)^{1/2} (4y^2 - 2) \exp\left(-\frac{y^2}{2}\right) \alpha dy \quad (80)$$

$$M_{02} \propto \left(\frac{1}{\alpha\pi^{1/2}} \right)^{1/2} \left(\frac{1}{16\alpha\pi^{1/2}} \right)^{1/2} \alpha^2 \int_{-\infty}^{\infty} \exp(-y^2) (4y^3 - 2y) dy \quad (81)$$

$$\int_{-\infty}^{\infty} y \exp(y^2) dy = \int_{-\infty}^{\infty} y^3 \exp(-y^2) dy = 0 \quad (82)$$

$M_{02} = 0$, transition is not allowed.

e - 2 pts Now we consider that an electromagnetic radiation with frequency ν interacts with the protein and this interaction results in a time-dependent induced dipole moment $\mu_{ind}(t)$. Using only classical considerations, derive an expression for $\mu_{ind}(t)$ for a particular molecular vibration with frequency ν_0 . Explain the physical meaning of each component of μ_{ind} and show the components on an energy level diagram. Identify the components that are needed in molecular biosensing.

Induced dipole moment $\mu_{ind} = \alpha E_{ex}(t)$, α is the polarizability. $E_{ex}(t) = E_0 \cos(2\pi\nu t)$ is the applied electric field with frequency ν and amplitude E_0 . The optical electric field causes an oscillation of the α

$$\alpha = \alpha_0 + (\Delta\alpha) \cos(2\pi\nu_0 t) \quad (83)$$

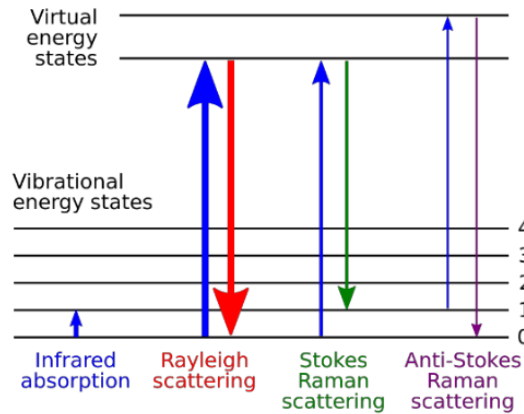
Substituting both α and $E_{ex}(t)$

$$\mu_{ind}(t) = [\alpha_0 + (\Delta\alpha) \cos(2\pi\nu_0 t)] [E_0 \cos(2\pi\nu t)] \quad (84)$$

Expanding gives

$$\mu_{ind}(t) = \alpha_0 E_0 \cos 2\pi\nu t + \frac{1}{2} \Delta\alpha E_0 \left\{ \cos [2\pi(\nu + \nu_0)t] + \cos [2\pi(\nu - \nu_0)t] \right\} \quad (85)$$

where we used $\cos \theta \cos \phi = \frac{1}{2} [\cos(\theta + \phi) + \cos(\theta - \phi)]$. The first term of $\mu_{ind}(t)$ is due to Rayleigh scattering and the second and third terms are the Stokes and anti-Stokes Raman scattering, and they are useful for molecular sensing since they contain the molecular vibration frequency ν_0 .



f - 1 pts Localized surface plasmons on a metallic nanoparticle can enhance the optical field to increase the spectroscopic signature of the protein. From classical

electrodynamics in the quasi-static limit, a conducting sphere in a uniform field has an electric potential Φ outside the sphere is given as

$$\Phi = -E_0 r \cos \theta + E_0 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \frac{a^3}{r^2} \cos \theta \quad (86)$$

where E_0 the amplitude of the incident electric field, ϵ_1 and ϵ_2 are the dielectric functions inside and outside of the metallic nanoparticle, respectively, a is the radius of the sphere, and r is the radial position from the center of the particle.

Derive an expression for the electric field \mathbf{E} and determine the resonance condition where the protein experiences the highest electric field. (*Hint: The gradient of a scalar function is defined as $\nabla F = \frac{\partial F}{\partial \rho} \mathbf{e}_\rho + \frac{1}{\rho \sin \phi} \frac{\partial F}{\partial \theta} \mathbf{e}_\theta + \frac{1}{\rho} \frac{\partial F}{\partial \phi} \mathbf{e}_\phi$*)

The electric field vector is $\mathbf{E} = -\nabla \Phi$

The gradient of a scalar function is defined as

$$\nabla F = \frac{\partial F}{\partial \rho} \mathbf{e}_\rho + \frac{1}{\rho \sin \phi} \frac{\partial F}{\partial \theta} \mathbf{e}_\theta + \frac{1}{\rho} \frac{\partial F}{\partial \phi} \mathbf{e}_\phi \quad (87)$$

Applying the gradient to the potential gives the electric field

$$= E_0 (\cos \theta \mathbf{n}_r - \sin \theta \mathbf{n}_\theta) + \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \frac{a^3}{r^3} E_0 (2 \cos \theta \mathbf{n}_r + \sin \theta \mathbf{n}_\theta). \quad (88)$$

The resonance condition is when $\epsilon_1 = -2\epsilon_2$.

5 Feeling Hot Hot Hot

prof. dr. F.G. Mugele

Physics of Complex Fluids - University of Twente

10 points

The heat capacity provides information about the ability of internal degrees of freedom of physical systems to absorb energy. Therefore, heat capacity measurements played an important role in the development of our understanding of both gaseous and – in particular – condensed phases of matter.

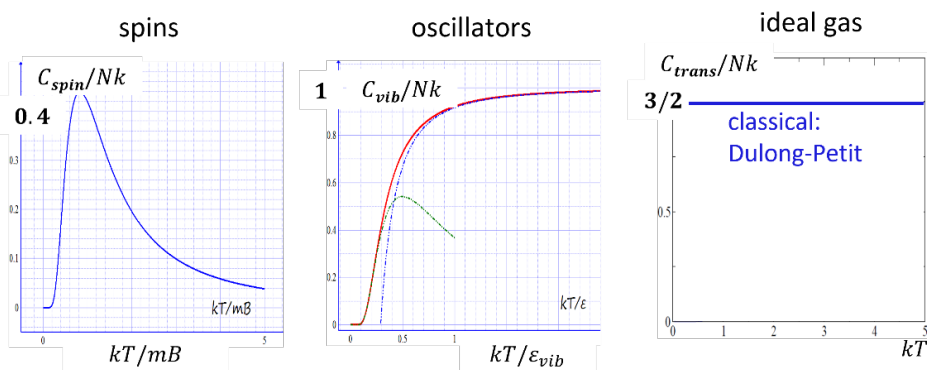
a - 1 pts Provide a general formula for the thermodynamic definition of a heat capacity, making suitable choices for constant thermodynamic variables. If you consider a fixed volume of matter, say 1 cm^3 , would the heat capacity of a gas be higher or lower than the one of a liquid of the same substance at standard pressure and temperature? Why?

$C_V = \left. \frac{\partial U}{\partial T} \right|_{N,V}$ or alternatively $C_P = \left. \frac{\partial U}{\partial T} \right|_{N,P}$ or $C_{V;P} = T \left. \frac{\partial S}{\partial T} \right|_{N,V \text{ or } P}$ (0.5 pt). The liquid has the higher heat capacity because it (a) has a lot higher density and (b) hence more degrees of freedom per volume that can absorb heat (0.5 pt).

b - 3 pts Sketch the specific heat as a function of temperature for three classical model systems:

1. N non-interacting spins (magnetic moment m) in an external magnetic field B as an example of a two-level system.
2. a system of N identical independent quantum mechanical harmonic oscillators with an energy spacing $\Delta\epsilon = hf$ as Einstein's simplified model of an insulating solid.
3. a classical monatomic ideal gas (N atoms).

3 pts, 1.5 for correct graphs, 1.5 for correct energy units.

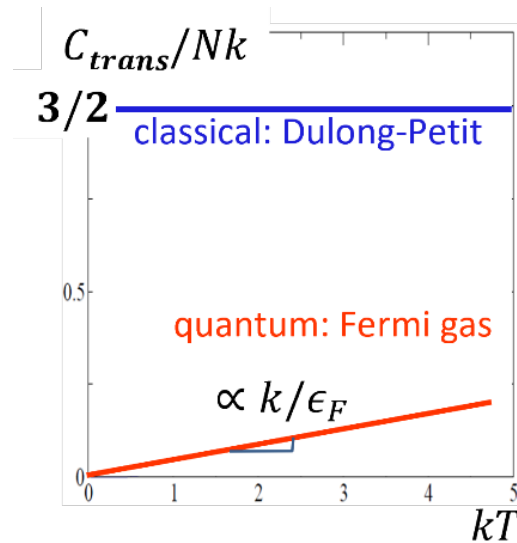


c - 4 pts Explain for all three cases the limiting behaviors at high and low temperatures and provide qualitative physical explanations for agreements and deviations of these limits between the different systems. In which of these cases does the heat capacity reflect the equipartition theorem, in which ones not? Explain why.

1. low T: exponentially vanishing; high T: algebraically vanishing (0.5 pt);
reasons: existence of energy gap at low T; saturation of entropy at high T; no higher energy levels available to populate; no equipartition possible (1 pt)
2. low T: exponentially vanishing because of energy gap (0.5 pt); high T: saturation at constant value Nk when $kT \gg hf$ because each degree of freedom is thermally fully active according to equipartition theorem (1 pt)
3. Constant $3/2Nk$ for all T. Spacing energy levels is negligible for all T. Hence, equipartition applies at all T. (1 pt)

d - 2 pts Make a new sketch comparing the heat capacity vs. temperature of the classical ideal gas (as in part b)) and an ideal Fermi gas for the same number of particles. Explain how and why the heat capacity of the Fermi gas, C_{Fermi} , is different from the classical ideal gas, C_{class} , at 'low' temperatures. Thinking of electrons in a metal: what would be a suitable reference temperature and what is its typical value? Provide an estimate for the ratio C_{Fermi}/C_{class} for this low temperature limit.

Figure (0.5 pt); linear dependence arises from the fact that only electrons near Fermi edge can absorb heat and hence contribute to the heat capacity (0.5 pt). This is approximately a fraction kT/ϵ_{Fermi} (0.5 pt) of the total amount of electrons. $T_{Fermi} \approx 10000K$ (0.5 pt). Hence, C_{Fermi}/C_{class} is in the percent range (0.5 pt).



6 Fata Morgana

ir. I.C.W.T.A. van Veldhoven
Applied Physics staff - University of Twente
10 points

The famous amusement park, *De Efteling*, has an attraction named Fata Morgana. This attraction is a tow boat ride based on the stories of 1001 Arabian nights, populated by 140 different moving puppets, called animatronics. Figure 5 shows such animatronic.

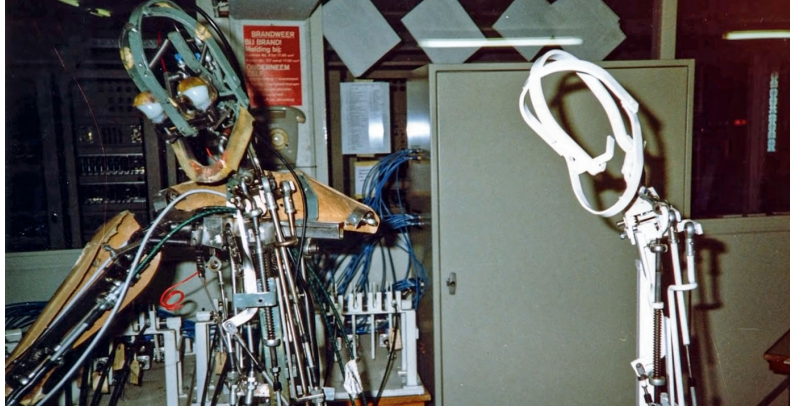


Figure 5: Animatronic

These animatronics work with pneumatic valves which are controlled by a control system. Figure 6 shows a pneumatic valve. On the left side air will flow into the system. Due to small holes in the piston, the air flow will be restricted, with a certain fluid resistance R_f . Due to this restriction a pressure difference will arise between the left and the right side, which will push the piston to the right. The pressure difference, due to the resistance, can be assumed to follow a linear relationship:

$$R_f = \frac{\Delta p}{\dot{m}} \quad (89)$$

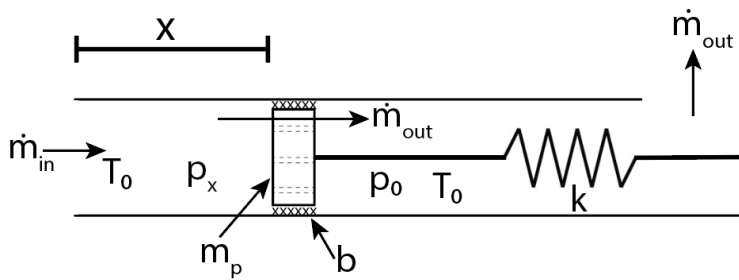


Figure 6: Pneumatic valve

The holes in the piston are so small that the volume of these holes can be neglected. The output on the right side of the valve is very large so the fluid resistance of this hole can be neglected. This means that the pressure everywhere on the right side of the piston can be assumed to be constant and equal to the ambient pressure, p_0 . The spring is assumed to be linear with spring constant k . There are three types of friction working on the piston:

1. Viscous forces, due to the fluid flowing through the channels in the piston, this is assumed to be linear with velocity, with a constant of b .
2. Static friction, due to the constant between the piston and the pipe, this friction is modelled

via this equation: $F_f = \text{sign}(v)F_{f_0}$.¹

3. Air resistance, for simplicity we assume in the calculation of this resistance that the pressure on both sides of the piston is equal to p_0 .

The cross sectional area of the piston is A . The temperature throughout the whole system, including working fluid, is constant and equal to the ambient temperature, T_0 .

a - 1 pt Determine the steady state displacement of the piston as function of a steady state input mass flow of the air and the system parameters.

(0.2pt) In steady state, all forces cancel out and are equal

(0.2pt): $F_k = F_p \Rightarrow kx = \Delta p \cdot A = R_s \dot{m}_{in} A$

(0.6pt): $x_{ss} = x_0 + \frac{R_s A}{k} \dot{m}_{in}$

b - 4 pt Derive the first order differential equations that describe (the transient behavior of) this system.

(1pt): $\frac{d}{dt} m_x = \dot{m}_{in} - \dot{m}_{out} = \dot{m}_{in} - \frac{p_x - p_0}{R_f}$

(1pt): Also: $m_x = M_{N2} n = M_{N2} \frac{p_x V_x}{RT}$.

(1pt for product rule, 0.5pt for full expression): Therefore: $\frac{d}{dt} m_x = M_{N2} \frac{A}{RT} [x \frac{dp_x}{dt} + p_x v_x] = \dot{m}_{in} - \frac{p_x - p_0}{R_f}$

$\Rightarrow \frac{M_{N2} A}{RT} x \frac{dp_x}{dt} = \dot{m}_{in} - \frac{p_x - p_0}{R_f} - \frac{M_{N2} A}{RT} p_x v_x$ (1)

(0.3pt): $m_p \frac{dv_m}{dt} = \sum_i F_i = (p_x - p_0)A - b v_m - F_h$ (2)

(0.2pt): $\frac{dF_k}{dt} = k v_m$ since $F_k = kx$ (3)

c - 3 pt Linearize all the nonlinear differential equations using a Taylor-approximation and make a state space model of this linearized system, with the mass-flow as input and the position of the piston as output.

Linearize and fill in (1): $p_x x = \bar{p}_x \hat{x} + \bar{x} \hat{p}_x \Rightarrow \frac{d}{dt} m_x = \bar{p} \frac{d\hat{x}}{dt} + \hat{x} \frac{d\bar{p}}{dt} + \bar{x} \frac{d\hat{p}}{dt} + \hat{p} \frac{d\bar{x}}{dt}$

(1) becomes $\frac{M_{N2} A}{RT} \bar{x} \frac{d\bar{p}_x}{dt} = \dot{m}_{in} - \frac{\bar{p}_x}{R_f} - \frac{M_{N2} A}{RT} \bar{p}_x \hat{v}_m$

(2) becomes $m_p \frac{d\hat{v}_m}{dt} = \hat{p}_x A - b \hat{v}_m - \hat{F}_k$

(3) becomes $\frac{d\hat{F}_k}{dt} = k \hat{v}_m$

Define state vectors $\mathbf{q} = [\hat{p}_m, \hat{v}_m, \hat{F}_k]^T$ and $\mathbf{k} = [\dot{m}_{in}]^T$ such that

$$\dot{\mathbf{q}} = \begin{bmatrix} -\frac{RT}{M_{N2} A \bar{x}} \frac{1}{R_f} & \frac{RT}{M_{N2} A \bar{p} \bar{x}} & 0 \\ \frac{A}{m_p} & -\frac{b}{m_p} & -\frac{1}{m_p} \\ 0 & k & 0 \end{bmatrix} \mathbf{q} + \begin{bmatrix} \frac{RT}{M_{N2} A \bar{x}} & 0 & 0 \end{bmatrix} \mathbf{u}$$

and

$$\mathbf{q} = \begin{bmatrix} 0 & 0 & \frac{1}{k} \end{bmatrix} \mathbf{q} + \begin{bmatrix} 0 \end{bmatrix} \mathbf{u}$$

¹Definition of the sign function: $\text{sign}(x) := \begin{cases} -1 & \text{if } x < 0, \\ 0 & \text{if } x = 0, \\ 1 & \text{if } x > 0. \end{cases}$

d - 2 pt If the piston is connected to the movement of a puppet, this can be modelled as an increase of the mass of the piston. Explain what this would change (increase, decrease or stay the same) to the response speed and final displacement.

Response speed would decrease (transient time increases), final displacement would stay the same. (1pt per reason)

7 Free-electron lasers

dr. P.J.M. van der Slot and prof. dr ir. D.A.I. Marpaung
Nonlinear Nanophotonics - University of Twente
 20 points

In a free-electron laser, electrons are accelerated to high energy and subsequently injected into an undulator where the kinetic energy of the electrons is converted into coherent radiation. Due to the acceleration process, electrons are injected in the form of short bunches. The undulator is a magnetic device that produces a spatially periodic magnetic field. A schematic of the undulator is shown in figure 7. Let the propagation direction of the electrons be the z -direction and let the magnetic field be orientated along the y -direction.

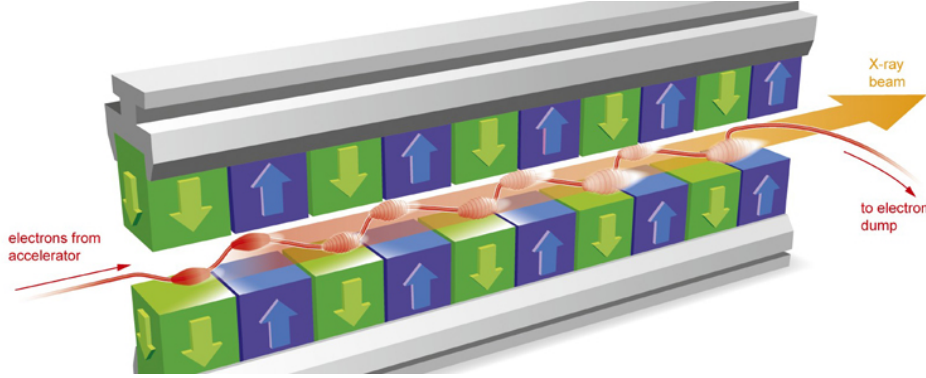


Figure 7: Schematic overview of a linearly polarized undulator showing the orientation of the permanent magnets producing a spatially alternating magnetic field. © European XFEL.

For simplicity, we ignore end-effects and close to the axis of the undulator we can write for the magnetic field

$$\mathbf{B}_u(\mathbf{r}) = B_{u0} \cos(k_u z) \hat{\mathbf{y}} \quad (90)$$

where B_{u0} is the amplitude of the magnetic field, $k_u = 2\pi/\lambda_u$ with λ_u the spatial period of the magnetic field, and $\hat{\mathbf{y}}$ is a unit vector in the y -direction.

In the following, we assume a sufficiently low number of electrons in the bunch such that space-charge forces can be neglected and that the electrons are injected into the undulator magnetic field at $z = 0$.

a - 1.0 pts Show that the magnetic field can also be described by the vector potential

$$\mathbf{A}_u = \frac{B_{u0}}{k_u} \sin(k_u z) \hat{\mathbf{x}} \quad (91)$$

where $\hat{\mathbf{x}}$ is a unit vector along the x -direction.

The relation between magnetic field and vector potential is $\mathbf{B}_u = \nabla \times \mathbf{A}_u$. As the magnetic field only has a component along the y -direction and this component only depends on z , the vector potential also only depends on z . Thus, we have $B_y = \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} = \frac{\partial A_x}{\partial z} = B_{u0} \cos(k_u z)$. Integration of this expression gives $A_x = \frac{B_{u0}}{k_u} \sin(k_u z) + C$, where C is a constant. Without loss of generality we can take $C = 0$. Thus $\mathbf{A}_u = \frac{B_{u0}}{k_u} \sin(k_u z) \hat{\mathbf{x}}$.

- (0.4 pt) $\mathbf{B}_u = \nabla \times \mathbf{A}_u$
- (0.4 pt) $\mathbf{A}_u = \frac{B_{u0}}{k_u} \sin(k_u z) \hat{\mathbf{x}}$
- (0.2 pt) integration constant C can be set to zero without loss of generality

In absence of any light, the electron equation of motion is given by

$$\frac{d\mathbf{p}}{dt} = \frac{d}{dt}(\gamma m \mathbf{v}) = -e(\mathbf{v} \times \mathbf{B}_u) \quad (92)$$

where γ is the relativistic factor $\gamma = \left(1 - \frac{v^2}{c^2}\right)^{-1/2} \equiv (1 - \beta^2)^{-1/2}$, $v = |\mathbf{v}|$, $\beta = |\boldsymbol{\beta}|$, $\boldsymbol{\beta} = \frac{\mathbf{v}}{c}$ and e is the charge of the electron. We assume that the electrons are highly relativistic, $\gamma \gg 1$.

b - 2 pt Derive an expression for the transverse velocity of the electron inside the homogeneous part of the undulator magnetic field in terms of γ and the properties of the undulator field. Assume perfect injection into the undulator field with $v_x(0) = 0$.

The magnetostatic undulator field does no work on the electron, hence its energy remains constant and $\frac{d\gamma}{dt} = 0$ (this is only true if we neglect the emission of radiation). The equation of motion becomes in this case, $\gamma m \frac{d}{dt} \mathbf{v} = -e(\mathbf{v} \times \mathbf{B}_u)$. This gives two equations for v_x and v_z , respectively.

$$\dot{v}_x = \frac{dv_x}{dt} = \frac{eB_{u0}}{\gamma m} v_z \cos(k_u z) \quad (93)$$

$$\dot{v}_z = \frac{dv_z}{dt} = -\frac{eB_{u0}}{\gamma m} v_x \cos(k_u z) \quad (94)$$

Let $\frac{dv_x}{dt} = \frac{dv_x}{dz} \frac{dz}{dt} = v_z \frac{dv_x}{dz} = \frac{eB_{u0}}{\gamma m} v_z \cos(k_u z)$. Consequently, $\frac{dv_x}{dz} = \frac{eB_{u0}}{\gamma m} \cos(k_u z)$ and direct integration gives

$$v_x(z) = \frac{eB_{u0}}{\gamma m k_u} \sin(k_u z) \equiv v_u \sin(k_u z) \quad (95)$$

where the integration constant is zero due to perfect injection of the electron into the undulator field.

- (0.5 pt) Static undulator field does no work, so magnitude of \mathbf{v} or γ is constant.
- (0.4 pt) $\gamma m \frac{d}{dt} \mathbf{v} = -e(\mathbf{v} \times \mathbf{B}_u)$
- (0.5 pt) $\frac{dv_x}{dt} = \frac{dv_x}{dz} \frac{dz}{dt} = v_z \frac{dv_x}{dz}$
- (0.6 pt) correct solution

c - 2 pt Show that the average axial electron velocity \bar{v}_z is given by

$$\bar{v}_z = c \left(1 - \frac{1}{2\gamma^2} \left(1 + \frac{K_u^2}{2} \right) \right) \equiv c\bar{\beta}_z \quad (96)$$

where $K_u \equiv \frac{eB_{u0}}{mck_u}$ is known as the undulator parameter.

As the total velocity is constant, we have γ is constant and $\frac{1}{\gamma^2} = 1 - \frac{v^2}{c^2} = 1 - \frac{v_z^2}{c^2} - \frac{v_x^2}{c^2}$. Thus, $\frac{v_z}{c} = \sqrt{1 - \frac{1}{\gamma^2} - \frac{v_x^2}{c^2}} \approx 1 - \frac{1}{2\gamma^2} - \frac{v_x^2}{2c^2}$ (Taylor expansion of square root). Thus $\bar{v}_z = c \left(1 - \frac{1}{2\gamma^2} - \frac{\bar{v}_x^2}{2c^2} \right)$. From 95 we know that v_x performs a sinusoidal motion, so the average of v_x^2 is half times the amplitude squared of the oscillation. Thus, $\bar{v}_z = c \left(1 - \frac{1}{2\gamma^2} - \frac{1}{2} \left[\frac{eB_{u0}}{\gamma m k_u} \right]^2 \frac{1}{2c^2} \right) = c \left(1 - \frac{1}{2\gamma^2} \left(1 + \frac{K_u^2}{2} \right) \right)$, with $K_u \equiv \frac{eB_{u0}}{mck_u}$, also known as the undulator parameter. Note, one could also start with $v_z = \sqrt{v^2 - v_x^2}$ and by substituting $\frac{v^2}{c^2} = 1 - \frac{1}{\gamma^2}$ leads to the same expression. Also, $v_z = \sqrt{v^2 - v_x^2} \approx v \left(1 - \frac{v_x^2}{2v^2} \right)$ leads to the same expression for highly relativistic electrons.

- (0.4 pt) $\frac{v_z}{c} = \sqrt{1 - \frac{1}{\gamma^2} - \frac{v_x^2}{c^2}}$ or $v_z = \sqrt{v^2 - v_x^2}$

- (0.4 pt) Taylor expansion
- (0.6 pt) correct calculation of \bar{v}_x^2
- (0.6 pt) correct final result

d - 1 pt Describe the motion of the electron in its rest frame in absence of any radiation.

From (b) and (c) we know that the transverse electron velocity is sinusoidal, and consequently, the transverse position is also sinusoidal with propagation distance z . As the total velocity is a constant (in absence of any radiation), the axial velocity also needs to oscillate (with twice the frequency as $v_z = \sqrt{v^2 - v_x^2}$, with $v = |v|^2$). For the velocity of the rest frame of the electron we take the average axial velocity \bar{v}_z . In the rest frame, the transverse motion remains sinusoidal, and the longitudinal motion is also sinusoidal with double the frequency. Consequently, the electron trajectory follows a figure of 8 in the rest frame of the electron, with the two lobes in the x -direction.

Although not a direct solution to the question, mentioning that the electron travels along the axis of the undulator with an average velocity superimposed with a figure of 8 oscillation in the transverse and longitudinal direction (the latter with a double frequency) is a correct description of the motion in the laboratory frame.

- (0.2 pt) sinusoidal motion in transverse plane
- (0.2 pt) sinusoidal motion in the z -direction
- (0.2 pt) sinusoidal motion in z -direction has double frequency (because of v_x^2 term)
- (0.4 pt) figure of eight motion
- Deduct 0.4 pt if description is in laboratory frame

It is well known that an oscillating electron will emit electromagnetic radiation. Therefore, the above description is only valid in the presence of weak radiation fields. To complete the description, we need to add the electromagnetic field to the equation of motion of the electron as given in eq. 92 via

$$\frac{d}{dt}(\gamma m \mathbf{v}) = e(\mathbf{E} + \mathbf{v} \times (\mathbf{B} + \mathbf{B}_u)) \quad (97)$$

where $\mathbf{E}(z, t)$ and $\mathbf{B}(z, t)$ are the electric and magnetic field components of a plane wave co-propagating with the electrons in the z -direction.

Let the radiation field be given by a vector potential

$$\mathbf{A}(z, t) = A_0(z, t) \hat{\mathbf{x}} \sin(kz - \omega t + \phi(z, t)) \quad (98)$$

where $A_0(z, t)$ and $\phi(z, t)$ are the slowly varying amplitude and phase of the radiation wave, $k = \frac{2\pi}{\lambda}$, λ is the (vacuum) wavelength and ω is the angular frequency of the radiation wave. The total potential \mathbf{A}_t experienced by the electron is then

$$\mathbf{A}_t(z, t) = \mathbf{A}(z, t) + \mathbf{A}_u(z) \quad (99)$$

e - 2 pt Derive an expression for the transverse velocity $\mathbf{v}_\perp = v_x \hat{\mathbf{x}}$ in terms of the vector potentials for the radiation and undulator fields. Assume perfect injection ($v_x(0) = 0$), and negligible initial radiation field (\mathbf{A} is a constant).

Use the correct gauge system, we have $\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}$ and $\mathbf{B} = \nabla \times \mathbf{A}$. Note, in this gauge system the space charge field is described by a scalar potential ϕ_{SC} , however this potential will be ignored as space-charge forces can be neglected. As the undulator field is not time dependent, we can also write $\mathbf{E} = -\frac{\partial \mathbf{A}_t}{\partial t}$ and $\mathbf{B} + \mathbf{B}_u = \nabla \times \mathbf{A}_t$. Note, that initially, there is only a small initial radiation field (noise, or weak co-injected field), such that the electron motion driven by the undulator is dominant. Hence, the electron oscillation inside the undulator field drives a linearly polarized radiation field with the polarization direction along the x -direction. This means that the total vector potential \mathbf{A}_t is in the x -direction and we can write for eq. 97:

$$\frac{d}{dt}(\gamma m \mathbf{v}_\perp) = \frac{d}{dt}(\gamma m v_x) \hat{\mathbf{x}} = -e \left(\frac{\partial \mathbf{A}_t}{\partial t} - (\mathbf{v} \times \nabla \times \mathbf{A}_t)_x \hat{\mathbf{x}} \right) \quad (100)$$

$$= -e \left(\frac{\partial \mathbf{A}_t}{\partial t} - (v_y (\nabla \times \mathbf{A}_t)_z - v_z (\nabla \times \mathbf{A}_t)_y) \hat{\mathbf{x}} \right) \quad (101)$$

$$= -e \left(\frac{\partial \mathbf{A}_t}{\partial t} - (-v_z (\nabla \times \mathbf{A}_t)_y) \hat{\mathbf{x}} \right) = -e \left(\frac{\partial \mathbf{A}_t}{\partial t} - \left(-v_z \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) \right) \hat{\mathbf{x}} \right) \quad (102)$$

$$= -e \left(\frac{\partial \mathbf{A}_t}{\partial t} + v_z \frac{\partial A_x}{\partial z} \hat{\mathbf{x}} \right) = -e \frac{d}{dt} \mathbf{A}_t. \quad (103)$$

Thus $\frac{d}{dt}(\gamma m \mathbf{v}_\perp) = -e \frac{d \mathbf{A}_t}{dt}$. We thus find that $\gamma m \mathbf{v}_\perp = -e \mathbf{A}_t$ for perfect injection ($\mathbf{v}_\perp(0) = 0$) and for negligible initial radiation field. Solving for the transverse velocity gives

$$\mathbf{v}_\perp = -\frac{e}{\gamma m} \mathbf{A}_t. \quad (104)$$

Note, for negligible radiation field, this equation reduces to eq. 95.

- (0.4 pt) $\frac{d}{dt}(\gamma m \mathbf{v}_\perp) = e \left(\frac{\partial \mathbf{A}_t}{\partial t} - (\mathbf{v} \times \nabla \times \mathbf{A}_t) \right)$ or for the x -component of this eq.
- (1.0 pt) to correctly derive $\frac{d}{dt}(\gamma m \mathbf{v}_\perp) = -e \frac{d \mathbf{A}_t}{dt}$
- (0.2 pt) to use perfect injection and small initial radiation field to set integration constant equal to zero
- (0.4 pt) $\mathbf{v}_\perp = -\frac{e}{\gamma m} \mathbf{A}_t$

We now continue with the derivation of an expression for the change in the energy of the electron in presence of a radiation field.

f - 2 pt Using the expression for the change in electron energy with time due to presence of the radiation field show that

$$\frac{d\gamma}{dt} = \frac{1}{2} \frac{e^2}{m^2 c^2} \frac{1}{\gamma} \frac{\partial}{\partial t} (|\mathbf{A}|^2 + 2\mathbf{A}_u \cdot \mathbf{A}) \quad (105)$$

Hint: The change in electron energy γmc^2 is given by the work done by the radiation field, which is performed by the electric field component, which gives..?

The change in electron energy γmc^2 is given by the work done by the radiation field, which is performed by the electric field component, giving

$$\frac{d}{dt}(\gamma mc^2) = e \mathbf{E} \cdot \mathbf{v}_\perp \quad (106)$$

where \mathbf{v}_\perp is the transverse electron velocity (for a plane wave, the \mathbf{E} -field is oriented perpendicular to the propagation direction and only has transverse components). Using eq. 104, we now can write $\frac{d\gamma}{dt} = \frac{e}{mc^2} \mathbf{E} \cdot \mathbf{v}_\perp = -\frac{e}{mc^2} \frac{\partial \mathbf{A}_t}{\partial t} \cdot \mathbf{v}_\perp = \frac{e}{mc^2} \frac{\partial \mathbf{A}_t}{\partial t} \cdot \left(\frac{e}{\gamma m} \mathbf{A}_t \right) = \frac{e^2}{m^2 c^2} \frac{1}{\gamma} \frac{\partial \mathbf{A}_t}{\partial t} \cdot \mathbf{A}_t = \frac{1}{2} \frac{e^2}{m^2 c^2} \frac{1}{\gamma} \frac{\partial}{\partial t} |\mathbf{A}_t|^2$. As

$|\mathbf{A}_t|^2 = (\mathbf{A} + \mathbf{A}_u) \cdot (\mathbf{A} + \mathbf{A}_u) = |\mathbf{A}|^2 + 2\mathbf{A}_u \cdot \mathbf{A} + |\mathbf{A}_u|^2$, we have $\frac{d\gamma}{dt} = \frac{1}{2} \frac{e^2}{m^2 c^2} \frac{1}{\gamma} \frac{\partial}{\partial t} (|\mathbf{A}|^2 + 2\mathbf{A}_u \cdot \mathbf{A} + |\mathbf{A}_u|^2) = \frac{1}{2} \frac{e^2}{m^2 c^2} \frac{1}{\gamma} \frac{\partial}{\partial t} (|\mathbf{A}|^2 + 2\mathbf{A}_u \cdot \mathbf{A})$. In the last step we used the fact that the undulator magnetic field is static.

- (0.6 pt) Work done on electron is $\frac{d}{dt}(\gamma m c^2) = e \mathbf{E} \cdot \mathbf{v}_\perp$
- (0.6 pt) Derive correctly $\frac{d\gamma}{dt} = \frac{1}{2} \frac{e^2}{m^2 c^2} \frac{1}{\gamma} \frac{\partial}{\partial t} |\mathbf{A}_t|^2$
- (0.8 pt) Correctly arrive at $\frac{d\gamma}{dt} = \frac{1}{2} \frac{e^2}{m^2 c^2} \frac{1}{\gamma} \frac{\partial}{\partial t} (|\mathbf{A}|^2 + 2\mathbf{A}_u \cdot \mathbf{A})$

To find the change in electron energy with propagation through the undulator, we assume highly relativistic electrons and use $v_x \ll v_z$ (paraxial approximation) to write $\frac{d}{dt} \approx v_z \frac{d}{dz} \approx c \frac{d}{dz}$ in eq. 105 to obtain

$$\frac{d\gamma}{dz} = \frac{1}{2} \frac{e^2}{m^2 c^3} \frac{1}{\gamma} \frac{\partial}{\partial t} (|\mathbf{A}|^2 + 2\mathbf{A}_u \cdot \mathbf{A}) \quad (107)$$

It turns out that up to close to saturation of the laser, we have that $|\mathbf{A}_u| \gg |\mathbf{A}|$ and the second term is the dominant term on the RHS. So, we now consider

$$\frac{d\gamma}{dz} = \frac{e^2}{m^2 c^3} \frac{1}{\gamma} \mathbf{A}_u \cdot \frac{\partial}{\partial t} \mathbf{A}. \quad (108)$$

Substituting eqs. 91 and 98 into eq. 108 gives

$$\frac{d\gamma}{dz} = \frac{e^2}{m^2 c^3} \frac{\omega}{\gamma} \frac{B_{u0}}{k_u} A_0(z, t) \sin(k_u z) \cos(kz - \omega t + \phi(z, t)) \quad (109)$$

where we have neglected the terms proportional to the derivatives $\frac{\partial A_0}{\partial t}$ and $\frac{\partial \phi}{\partial t}$ in order to obtain a basic understanding of how a free-electron laser amplifies light and can generate a coherent radiation field. Using goniometric relations, eq. 109 can be written as

$$\frac{d\gamma}{dz} = \frac{e^2}{m^2 c^3} \frac{\omega}{\gamma} K_u A_0 \frac{1}{2} \left(\sin((k_u + k)z - \omega t + \phi) + \sin((k_u - k)z + \omega t - \phi) \right). \quad (110)$$

The expression $\theta = (k + k_u)z - \omega t$ that appears in the argument of the first sine function is known as the pondermotive phase.

g - 2 pt Show that there is a specific radiation wavelength that causes the pondermotive phase to be approximately constant along the propagation direction. Derive an expression for this wavelength in terms of the undulator parameters and the electron energy γ . Assume the case of highly relativistic electrons.

For a constant pondermotive phase, we need $\frac{d\theta}{dt} = 0$. now, $\frac{d\theta}{dt} = (k + k_u) \frac{dz}{dt} - \omega = 0$. For the axial velocity $v_z = \frac{dz}{dt}$ we take the average velocity \bar{v}_z given by eq. 97, and using $\omega = ck$, we get $(k + k_u)\bar{v}_z - ck = 0$. Solving for $k = \frac{2\pi}{\lambda}$ gives $k = k_u \frac{\bar{\beta}_z}{1 - \bar{\beta}_z}$ or $\lambda = \lambda_u \frac{1 - \bar{\beta}_z}{\bar{\beta}_z}$. For highly relativistic electrons, $\bar{\beta}_z \approx 1$ and we can approximate the latter expression as $\lambda = \lambda_u (1 - \bar{\beta}_z) = \frac{\lambda_u}{2\gamma^2} \left(1 + \frac{K_u^2}{2} \right)$, where eq. 97 is used in the last step. Note, a similar argument leading to the same result can be obtained by setting $\frac{d\theta}{dz} = 0$ instead of $\frac{d\theta}{dt} = 0$.

- (0.6 pt) Conclude that either $\frac{d\theta}{dt} = 0$ or $\frac{d\theta}{dz} = 0$ is required
- (0.4 pt) Use average velocity \bar{v}_z given by eq. 97
- (0.4 pt) Approximate $\frac{1 - \bar{\beta}_z}{\bar{\beta}_z}$ by $1 - \bar{\beta}_z$ for highly relativistic electrons.
- (0.6 pt) for correct final answer.

This specific wavelength is called the resonant wavelength of the free-electron laser. For the second sine function in eq. 110, there is no specific wavelength that produces a constant phase and therefore this term is fast oscillating and on average becomes zero.

h - 1 pts Explain in words the physical significance of having a resonant wavelength for which the ponderomotive phase is approximately constant when propagating through the undulator.

Having an approximately constant ponderomotive phase when the electron propagates through the undulator means that $\frac{d\gamma}{dz}$ is approximately constant and there can be an energy transfer from the electron to the co-propagating radiation field (or vice-versa) over a large, i.e., macroscopic, distance. The energy gained or lost by the electron is lost or gained by the radiation field. The value of the ponderomotive phase determines the direction of the energy flow.

- (0.4 pt) $\frac{d\gamma}{dz}$ is constant (or $\frac{d\gamma}{dt}$ is constant)
- (0.6 pt) constant energy flow from electron to radiation field (or from radiation field to electron) when electron propagates through undulator (with copropagating radiation field), i.e., constant energy flow over macroscopic distance.

i - 2 pt The resonant wavelength scale as $\frac{1}{\gamma^2}$ with the electron energy. Provide in words a physical explanation for this scaling.

The origin of the scaling can be found as a double Doppler shift. The electrons are performing an oscillation in the transverse plane while moving approximately with a constant speed along the axis of the undulator. One way to determine the emission wavelength is to perform a Lorentz transformation to the rest frame of the electrons. The static undulator field in the lab frame is seen as a (pseudo) radiation field travelling towards the stationary electron in the rest frame (first Doppler shift). The frequency of this radiation field is proportional to γ . This radiation field brings the electrons in oscillation (in the transverse plane) and the electrons will emit dipole radiation with the same frequency. This dipole radiation field needs to be transformed back to the laboratory frame and this Lorentz transformation adds another factor of γ to the radiation frequency as observed in the laboratory frame (second Doppler shift). So, the frequency scales with γ^2 and the radiation wavelength with $\frac{1}{\gamma^2}$.

- (0.4 pt) Interaction can be seen as a physical process requiring a double Doppler shift
- (0.4 pt) One Doppler shift due to Lorentz transform from lab to rest frame for static undulator field
- (0.4 pt) In rest frame, undulator field causes the electron to emit dipole radiation with same frequency
- (0.4 pt) Observation of dipole radiation in lab frame requires a second Doppler shift
- (0.4 pt) Each Doppler shift changes the frequency by a factor γ

In a free-electron laser the electrons are typically accelerated in the form of a bunch containing many electrons. The longitudinal size, i.e., the length of the electron bunch in the propagation direction, is much longer than the radiation wavelength that is resonant. For simplicity assume that the bunch has a top-hat profile, meaning a constant charge density within the bunch.

j - 5 pt Explain in words how the free-electron laser can generate or amplify coherent radiation having the resonant wavelength. Assume highly relativistic electrons.

The large (compared to the resonant radiation wavelength) size of the electron bunch and the more-or-less uniform distribution of electrons within the bunch, means that when the electrons are entering the undulator field, together with a co-propagating radiation field (having the resonant wavelength), the pondermotive phases of the electrons are more or less uniformly distributed (with a small random variation due to shot-noise in the electron bunch). This means that electrons with $\pi < \theta_i < 2\pi$ will be decelerated, (energy flow towards the radiation field) and electrons with $0 < \theta_i < \pi$, will be accelerated (energy flow from radiation field to electrons). Similar for other ranges of θ_i as the phase is determined up to an integer multiple of 2π . So, initially, there is no net energy exchange between electrons and radiation field. Upon propagation through the undulator, the faster moving electrons will catch up with the slower moving electrons and the electron distribution becomes non-uniform. The location of increased electron density is around pondermotive phases $\theta = \pi + 2n\pi$, with n an integer. This process is called micro-bunching. The spatial separation of these maxima in electron micro-bunching is $\lambda_p = \frac{2\pi}{k+k_u}$. For highly relativistic electrons we have that $k \gg k_u$ (see 105 and 108) and therefore, $\lambda_p \approx \lambda$. This means that the micro-bunches within the electron bunch are approximately one radiation wavelength apart. Now all the electrons within the micro-bunches will emit in phase and a coherent radiation field is generated. The total radiation field scales with the number of electrons in the micro-bunches and the corresponding intensity with the number of electrons squared. The amplified radiation field enhances the micro-bunching thus providing positive feedback that leads to exponential growth of a coherent radiation field.

- (1 pt) Radiation generates velocity modulation within electron bunch with periodicity λ_p
 - (1 pt) Initially no net energy exchange
 - (1 pt) Upon propagation through undulator, velocity modulation is transformed into density modulation (micro-bunching) with the same periodicity.
 - (1 pt) Micro-bunching ensures electrons (or at least the majority) are emitting in phase, generating or amplifying a coherent radiation field
 - (1 pt) A stronger radiation field enhances the micro-bunching.
-

8 Polymer coatings exposed to vapors

dr. ir. S.J.A. de Beer and L.A. Smook MSc
Functional Polymer Surfaces - University of Twente
10 points

Smells consist of a combination of molecular vapors with a specific compositions. These smells can originated from many sources, ranging from a bakery that gives off the aroma of fresh bread to a local farm that gives off the stench of manure. Similarly, some diseases can be characterized by a specific smell or biomarkers. Therefore, if we can ‘smell’ these biomarkers, we can potentially speed up the diagnosis for these diseases. However, devices that ‘smell’ these scents are often bulky and costly (think of a mass spectrometer) or not sensitive enough. One promising way to create sensitive sensors for these biomarkers is by coating existing sensor technologies with polymer materials to enhance the signal of these sensors.

In this exercise, we consider two types of polymer coatings to achieve this goal: a thin film and a brush. Thin films consists of a spin-coated film of a polymer material onto the sensor surface, and brushes consist of polymers that are grafted to the sensor by one of their chain ends. This grafting creates a stronger adhesion between the polymer layer an the sensor, but it also changes the physics of these coatings and their interaction with vapors.

The physical behavior of these polymer layers can be described rather accurately using an adapted Flory-Huggins lattice model. This model describes the free energy of a mixture based on an energetic contribution related to the interaction energy between different molecules in the system and entropic contribution related to mixing and the physics of polymers in the canonical ensemble.

a - 1.5 pts Consider a binary mixture of molecule A and molecule B with identical molecular volumes. Derive a expression for the entropy of mixing of this solution. Normalize your expression based on thermal energy ($k_B T$) and the volume of the system (V). Express your answer as a function of the volume fraction of both components (ϕ_A and ϕ_B).

Hint: Use the multiplicity of the system in your derivation and assume that the number of molecules is large so Stirling’s approximation ($\ln(x!) = x \ln x - x$) is valid.

Mixing without change in volume and temperature so canonical (NVT) ensemble N_A molecules of type A , N_B molecules of type B , N molecules in total.

$$\Omega = \frac{N!}{N_A! N_B!} = \frac{(N_A + N_B)!}{N_A! N_B!} \quad (111)$$

$$\Delta S = k \ln \Omega = (N_A + N_B) \ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B \quad (112)$$

Collecting the terms yields:

$$\Delta S = k[N_A \ln(1/\phi_A) + N_B \ln(1/\phi_B)] = -k[N_A \ln(\phi_A) + N_B \ln(\phi_B)] \quad (113)$$

Normalizing by V ultimately gives $\Delta S = -k[\phi_A \ln(\phi_A) + \phi_B \ln(\phi_B)]$

b - 0.5 pts Molecule A can be polymerized. Suppose molecule A polymerize into perfectly monodisperse polymers consisting of N monomers. How should your expression be adjusted to reflect this change in the system?

Hint: What happens to the number of molecules in the system?

When a monomer polymerizes, the number of molecules of type A decreases from N_A to N_A/N . So $\Delta S = -k[(\phi_A/N) \ln(\phi_A) + \phi_B \ln(\phi_B)]$

In the following questions, we consider a polymer containing N segments of length b . The segments form a linear chain that follows along a line that can follow along a line. The polymer is free to cross the same line segment multiple times.

c - 1 pt Derive an expression for the entropy of this polymer.

Each segment can move along the line in backward or forward direction, so each segment has 2 options. This gives $2N$ accessible states (Ω). So $S = k \ln \Omega = kN \ln 2$

d - 1 pt Now imagine two “finite beings” that each hold the polymer by a different terminal monomer. The beings are at the whims of the gods of thermodynamics. Show that the probability of finding the beings at a distance x apart for a chain of N segments can be given by the following expression:

$$P_{1d}(N, x) = -N \ln 2 + \ln(N!) - 2 \ln \left(\frac{N}{2}! \right) - \sum_{s=1}^{x/2} \ln \left(\frac{(N/2) + s}{(N/2) + 1 - s} \right) \quad (114)$$

When end-to-end distance is R and we consider R in units of unit chain length, we can set the following expressions:

$$R = N_u - N_d \quad (115)$$

$$N = N_u + N_d \quad (116)$$

Combining these expressions, we can find that $N_u = (N + R)/2$ and $N_d = (N - R)/2$. Probability is given by the ratio between all (equiprobable) states ($\Omega_{all} = 2N$), see previous question) and all (equiprobable) states with end-to-end distance R (Ω_R)

$$\Omega_R = \frac{(N_u + N_d)!}{((N + R)/2)!((N - R)/2)!} \quad (117)$$

$$P_{1d}(N, x) = \ln \frac{\Omega_R}{\Omega_{all}} = \ln \left(\frac{N!}{((N + R)/2)!((N - R)/2)!} \right) - \ln 2^N \quad (118)$$

Here, we can express $\ln((N + R)/2)!$ and $\ln((N - R)/2)!$ as a sum of logarithms.

$$\ln((N + R)/2)! = \ln \left(\left(\frac{N}{2} \right)! \left(\frac{N}{2} + 1 \right)! \left(\frac{N}{2} + 2 \right)! \dots \left(\frac{N}{2} + \frac{R}{2} \right)! \right) = \ln \left(\frac{N}{2} \right)! + \sum_{s=1}^{R/2} \ln(N/2 + s) \quad (119)$$

Analogously:

$$\ln((N - R)/2)! = \ln \left(\frac{N}{2} \right)! - \sum_{s=1}^{R/2} \ln(N/2 - s + 1) \quad (120)$$

Combining the above expressions:

$$\ln(P_{1d}(N, R)) = -N \ln 2 + \ln(N!) - 2 \ln \left(\frac{N}{2} \right)! - \sum_{s=1}^{R/2} \ln \left(\frac{(N/2) + s}{(N/2) + 1 - s} \right) \quad (121)$$

e - 1 pt Show that the expression above can be approximated as a Gaussian distribution function and express this distribution in terms of end-to-end distance (x) and the mean-squared end-to-end distance ($\langle x^2 \rangle$).

Hint: Stirling's approximation can also be written as $x! = \sqrt{2\pi x} \left(\frac{x}{e} \right)^x$

The first three terms are independent of R . The summation can be expanded for $s \ll \frac{N}{2}$ such that $\ln(1 + y) \approx y$ for $|y| \ll 1$.

$$\ln \left(\frac{(N/2) + s}{(N/2) + 1 - s} \right) = \ln \left(\frac{1 + \frac{2s}{N}}{1 + \frac{2}{N} - \frac{2s}{N}} \right) = \ln \left(1 + \frac{2s}{N} \right) - \ln \left(1 + \frac{2}{N} - \frac{2s}{N} \right) = \frac{4s}{N} - \frac{2}{N}$$

We can use this in the full expression:

$$\begin{aligned}
\ln(P_{1d}(N, x)) &= -N \ln 2 + \ln(N!) - 2 \ln \left(\left(\frac{N}{2} \right)! \right) - \sum_{s=1}^{R/2} \left(\frac{4s}{N} - \frac{2}{N} \right) \\
&= -N \ln 2 + \ln(N!) - 2 \ln \left(\left(\frac{N}{2} \right)! \right) - \frac{4}{N} \sum_{s=1}^{R/2} s + \frac{2}{N} \sum_{s=1}^{R/2} 1 \\
&= -N \ln 2 + \ln(N!) - 2 \ln \left(\left(\frac{N}{2} \right)! \right) - \frac{4}{N} \cdot \frac{(R/2 + 1)(R/2)}{2} + \frac{R}{N} \\
&= -N \ln 2 + \ln(N!) - 2 \ln \left(\left(\frac{N}{2} \right)! \right) - \frac{4}{N} \left(\frac{(R/2)(R/2)}{2} + \frac{R/2}{2} \right) + \frac{R}{N} \\
&= -N \ln 2 + \ln(N!) - 2 \ln \left(\left(\frac{N}{2} \right)! \right) - \frac{R^2}{2N}
\end{aligned}$$

Thus, the result is:

$$P_{1d}(N, x) = \frac{N!}{\left(\frac{N}{2} \right)! \left(\frac{N}{2} \right)! 2^N} \exp \left(-\frac{R^2}{2N} \right)$$

Now apply Stirling's approximation such that:

$$\frac{N!}{\left(\frac{N}{2} \right)! \left(\frac{N}{2} \right)! 2^N} = \sqrt{\frac{2}{\pi N}}$$

and find:

$$P_{1d}(N, R) = \sqrt{\frac{2}{\pi N}} \exp \left(-\frac{R^2}{2N} \right)$$

Note that R and N are discrete, and $P_{1d}(N, R)$ is non-zero only for odd (or even) values, depending on whether N is odd or even. This means that the final (continuous) probability function differs by a factor of 2 from the previous expression:

$$P_{1d}(N, R) = \frac{1}{\sqrt{2\pi N}} \exp \left(-\frac{R^2}{2N} \right)$$

f - 1 pt Now the “beings” start to play tug of war with the polymer. They start the game at the same location but at a certain point in the game, the beings are a distance R apart. How did the entropy of the polymer change compared to the starting state where $R = 0$?

The entropy is given by $S = k \ln \Omega(N, R)$, where $\Omega(N, R)$ is the number of configurations where the end-to-end distance is between R and $R + dR$. This is equivalent to the probability of finding this end-to-end distance times the full multiplicity of the system ($\Omega(N, R)dR$) such that

$$\Omega(N, R) = P_{1d}(N, R) \int \Omega(N, R) dR$$

The entropy $S(N, R)$ is then

$$S(N, R) = k \ln P_{1d}(N, R) + k \ln \left(\int \Omega(N, R) dR \right)$$

Substituting $P_{1d}(N, R) = \frac{1}{\sqrt{2\pi N}} \exp \left(-\frac{R^2}{2N} \right)$, we get:

$$\begin{aligned}
 S(N, R) &= k \ln \left(\frac{1}{\sqrt{2\pi N}} \exp \left(-\frac{R^2}{2N} \right) \right) + k \ln \left(\int \Omega(N, R) dR \right) \\
 &= -k \frac{R^2}{2N} + k \ln \left(\frac{1}{\sqrt{2\pi N}} \right) + k \ln \left(\int \Omega(N, R) dR \right) \\
 &= -k \frac{R^2}{2N} + S(N, 0)
 \end{aligned}$$

The change in entropy can therefore be expressed as:

$$\Delta S(R) = S(N, R) - S(N, 0) = -k \frac{R^2}{2N} + S(N, 0) - S(N, 0) = -k \frac{R^2}{2N}$$

Thus, the entropy decreases quadratically with extension, with a prefactor of $-\frac{k}{2N}$.

A polymer material with perfectly monodisperse chain lengths is deposited onto a sensor surface as a thin film. This thin film is exposed to a molecular vapor. Assume that the interaction energy between the vapor and the polymer is negligible.

g - 1 pt Manipulate the expression you derived in question (a) and provide an expression that relates the layer thickness to the chemical potential of the molecular vapor.

From question 1, we know the entropy of mixing is (note we need the system entropy here):

$$\Delta S = -kV \left[\frac{\phi_A}{N} \ln \phi_A + \phi_B \ln \phi_B \right]$$

Using $\phi_A = 1 - \phi_B$, we get:

$$\Delta S = -kV \left[\frac{(1 - \phi_B)}{N} \ln(1 - \phi_B) + \phi_B \ln \phi_B \right]$$

The free energy is given by $\Delta F = \Delta U - T\Delta S$, where $\Delta U \equiv 0$ since the interaction energy is negligible. The chemical potential can be found via:

$$\mu = \frac{\partial \Delta F}{\partial N_B}$$

Applying the chain rule, we find that:

$$\mu = \frac{\partial \Delta F}{\partial \phi_B} \cdot \frac{\partial \phi_B}{\partial N_B}$$

Since $\frac{\partial \phi_B}{\partial N_B} = \frac{1}{V}$, we get:

$$\mu = \frac{1}{V} \frac{\partial \Delta F}{\partial \phi_B} = \frac{\partial}{\partial \phi_B} (-T\Delta S)$$

Substituting for ΔS , we have:

$$\mu = kTV \frac{\partial}{\partial \phi_B} \left[(1 - \phi_B) \ln(1 - \phi_B) + \phi_B \ln \phi_B \right]$$

This simplifies to:

$$\mu = kTV \left[\left(-\frac{\ln(1 - \phi_B)}{N} - \frac{1}{N} \right) + (\ln \phi_B + 1) \right]$$

Combining the terms, the chemical potential can be expressed as:

$$\mu = kT \left[\left(-\frac{\ln(1 - \phi_B)}{N} - \frac{1}{N} \right) + (\ln \phi_B + 1) \right]$$

Now consider a polymer brush where the polymers are anchored to the surface with a grafting density ρ . In this configuration, one end of the polymer is confined to the grafting plane and we assume that the other chain end is confined at the top of the brush.

h - 1.5 pt Provide an expression that relates the brush height to the chemical potential of the vapor.

We can start from the expression of question 1, but we have to make adjustments. Polymers lose entropic freedom, so the term $(1 - \phi_B) \ln(1 - \phi_B)$ can be removed. Additionally, the chains now also lose entropy by stretching, which is equivalent to $\frac{3kT}{2N} H^2$. Since the chains are grafted, H , V , and ρ are related via:

$$H = V\rho = \frac{V_0\rho}{1 - \phi_B}$$

The free energy expression for the system then reads:

$$\Delta F = kTV\phi_B \ln \phi_B + \frac{3kT}{2N} \left(\frac{V_0\rho}{1 - \phi_B} \right)^2$$

Again, we use $\mu = \frac{\partial \Delta F}{\partial N_B}$. Applying the chain rule, we have:

$$\mu = \frac{\partial \Delta F}{\partial \phi_B} \cdot \frac{\partial \phi_B}{\partial N_B} = \frac{1}{V} \frac{\partial \Delta F}{\partial \phi_B}$$

Thus, we compute:

$$\mu = kTV \frac{\partial}{\partial \phi_B} \left(\phi_B \ln \phi_B + \frac{3kT}{2N} \left(\frac{V_0\rho}{1 - \phi_B} \right)^2 \right)$$

Taking the derivatives, we get:

$$\mu = kTV(\ln \phi_B + 1) + \frac{3kT}{2N} \cdot 2 \frac{(V_0\rho)^2}{(1 - \phi_B)^3}$$

So, we find:

$$\mu = kT(\ln \phi_B + 1) + \frac{3kT}{2NV} \cdot \frac{2(V_0\rho)^2}{(1 - \phi_B)^3}$$

where $V = \frac{V_0}{1 - \phi_B}$, so the chemical potential becomes:

$$\mu = kT(\ln \phi_B + 1) + \frac{3kT}{N} \cdot \frac{V_0\rho^2}{(1 - \phi_B)^2}$$

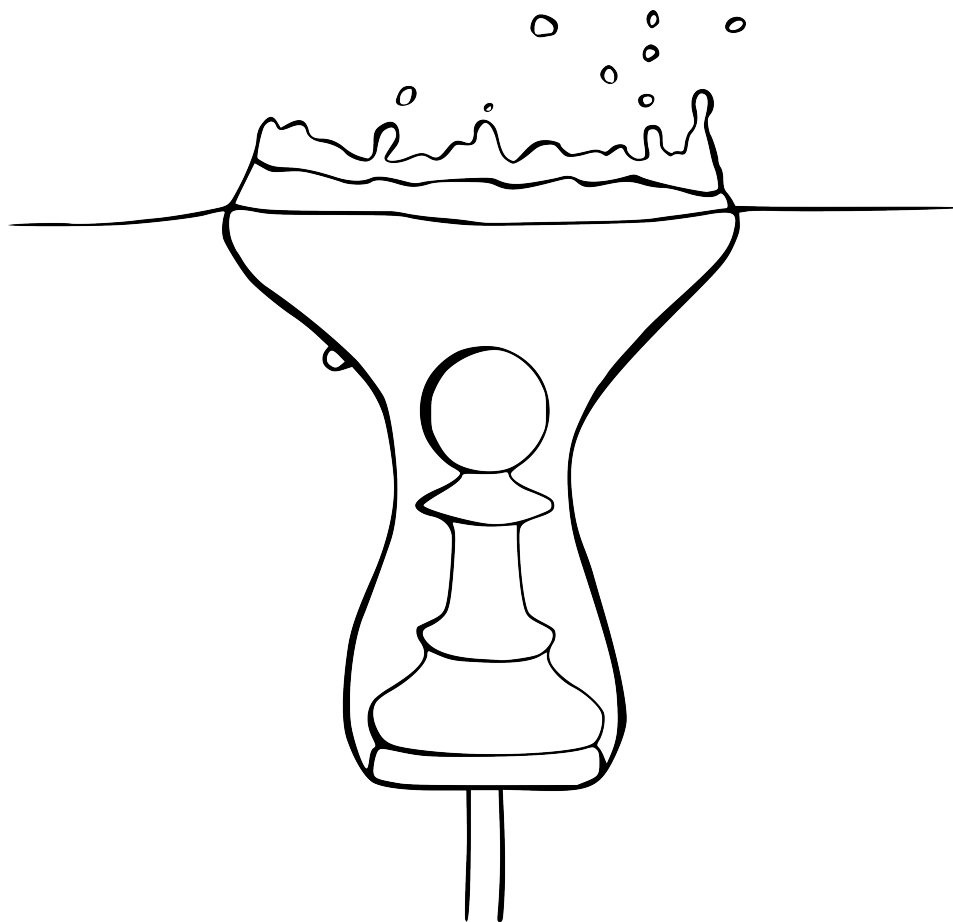
j - 0.5 pts Comment on the validity of this expression if the mixing of the polymer and the liquid is highly exothermic.

If the mixing is exothermic, this means that there is an interaction between the solvent and the polymer. This will lead to stronger swelling of the brush. If the brush swells too much, the Gaussian assumption in the entropy of stretching of a free chain will no longer hold.

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PION2024



Thank you for participating!