

Problem 1. Manipulating Taylor Series

You are expected to know the following Taylor series in addition to $\sin(x)$ and $\cos(x)$:

$$e^x = 1 + x + \frac{1}{2!}x^2 + \mathcal{O}(x^3) \quad (1)$$

$$\log(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \mathcal{O}(x^4) \quad (2)$$

$$(1+x)^\alpha = 1 + \alpha x + \frac{\alpha(\alpha-1)}{2!}x^2 + \frac{\alpha(\alpha-1)(\alpha-2)}{3!}x^3 + \mathcal{O}(x^4) \quad (3)$$

$$\frac{1}{1+x} = 1 - x + x^2 + \mathcal{O}(x^3) \quad (4)$$

These get me through life. Here x is considered to be a small, dimensionless, number. The $\mathcal{O}(x^3)$ etc shows an estimate for the size of the terms that have been dropped. Some Taylor expansions will be needed in the next problem and throughout the course. These are to be found by combining the Taylor series above. The function we will study in detail is wildly important:

$$\frac{1}{e^x - 1}. \quad (5)$$

It determines the average number of vibrational quanta in a quantum harmonic oscillator at temperature T .

- (a) (Optional) Show that Eq. (2) follows from Eq. (4) by integration.
- (b) (Optional) Show that the Taylor series $(1+x)^\alpha$ gives the exact result for $\alpha = 2$.
- (c) Consider large x , i.e. $x \gg 1$. Then e^{-x} is very small, i.e. $e^{-x} \ll 1$. Show that

$$\frac{1}{e^x - 1} \simeq e^{-x} (1 + e^{-x} + e^{-2x} + \mathcal{O}(e^{-3x})) \quad (6)$$

The first two terms are compared to the full function in Fig. 1

- (d) By combining the expansion of $1/(1+x)$ and e^x derive the following expansion for $x \ll 1$:

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} - \frac{1}{2} + \frac{1}{12}x + \mathcal{O}(x^2) \quad (7)$$

The first two terms are compared to the full function in Fig. 1

Hint: First expand e^x to second order inclusive (i.e. the error is $\mathcal{O}(x^3)$). Substitute this in Eq. (7) and pull out a factor of $\frac{1}{x}$. You should find that the resulting expression takes

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} \left(\frac{1}{1+u} \right) \quad (8)$$

where $u \simeq \frac{1}{2}x + \frac{1}{6}x^2$. Then expand further:

$$\frac{1}{1+u} \simeq 1 - u + u^2 + \mathcal{O}(u^3) \quad (9)$$

When evaluating u^2 to an accuracy of $\mathcal{O}(x^3)$ you can (and should!) keep only the first term of $u(x) \simeq \frac{1}{2}x$:

$$u^2 + \mathcal{O}(x^3) = \left(\frac{1}{2}x + \frac{1}{6}x^2\right)^2 + \mathcal{O}(x^3) \simeq \left(\frac{1}{2}x\right)^2 + \mathcal{O}(x^3) \quad (10)$$

This is better (and less work) than evaluating the “exact” result:

$$u^2 + \mathcal{O}(x^3) = \left(\frac{1}{2}x + \frac{1}{6}x^2\right)^2 + \mathcal{O}(x^3) = \frac{1}{4}x^2 + \frac{1}{6}x^3 + \frac{1}{36}x^4 + \mathcal{O}(x^3), \quad (11)$$

which is mathematically inconsistent, since other terms of order $\mathcal{O}(x^3)$ have already been discarded. Indeed, there is no reason to keep the terms $\frac{1}{6}x^3$ and $\frac{1}{36}x^4$ after other terms of order $\mathcal{O}(x^3)$ and $\mathcal{O}(x^4)$ have been discarded.

- (e) Following the methodology of (c), determine an approximate series for

$$\frac{1}{e^{-x} + 1} \quad (12)$$

for $x \gg 1$. This is useful in describing the thermodynamics of metals.

- (f) Following the methodology of part (d), combine Taylor series to show that

$$\log(1 - e^{-x}) \simeq \log(x) - \frac{1}{2}x + \frac{x^2}{24} + \mathcal{O}(x^3) \quad (13)$$

for $x \ll 1$. This is useful in entropy of ideal gas of photons.

- (g) (Optional) A clever student will notice that Eq. (13) follows from Eq. (7) via integration as in part(a). Give the details of this clever thought process.

Manipulating Taylor Series

$$a) \quad \frac{1}{1+x} = 1 - x + x^2 - x^3 + \dots$$

This follows from the geometric series
 $1/(1-u) = 1 + u + u^2 + \dots$ with $u = -x$

Integrating

$$\int_0^x \frac{dx'}{1+x'} = \log(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

b)

c) For x large we have $e^{-x} \ll 1$

$$\frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}}$$

call $u = e^{-x} \ll 1$

$$\frac{1}{e^x - 1} = \frac{u}{(1-u)} = u (1 + u + u^2 + \dots)$$

$$\boxed{\frac{1}{e^x - 1} = e^{-x} (1 + e^{-x} + e^{-2x} + O(e^{-3x}))}$$

$$d) \frac{1}{e^x - 1}$$

$$\text{we expand } e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{6}$$

$$\frac{1}{e^x - 1} \approx \frac{1}{x + x^2/2 + x^3/6} = \frac{1}{x} \frac{1}{(1 + x/2 + x^2/6 + O(x^3))}$$

$$\text{calling, } u = x/2 + x^2/6, \text{ we have}$$

$$\frac{1}{e^x - 1} \approx \frac{1}{x} \left(\frac{1}{1+u} + O(x^3) \right)$$

$$\approx \frac{1}{x} (1 - u + u^2 + O(x^3))$$

$$\approx \frac{1}{x} \left(1 - \left(\frac{x}{2} + \frac{x^2}{6} \right) + \left(\frac{x^2}{4} \right) + O(x^3) \right)$$

$$\frac{1}{e^x - 1} \approx \frac{1}{x} \left(1 - \frac{x}{2} + \frac{x^2}{12} \right) + O(x^2)$$

$$e) \frac{1}{e^{-x} + 1} \approx 1 - e^{-x} + e^{-2x} \quad \text{set } u = e^{-x}$$

$$f) \log(1 - e^{-x}) \approx \log\left(1 - \left(1 - x + \frac{x^2}{2} - \frac{x^3}{6}\right)\right)$$

$$\approx \log x \left(1 - \frac{x}{2} + \frac{x^2}{6}\right) = \log x + \log\left(1 - \frac{x}{2} + \frac{x^2}{6}\right)$$

So

$$\log(1 - e^{-x}) = \log(x) + \log\left(1 - \overbrace{\frac{x}{2} + \frac{x^2}{6}}^{\text{call it } u}\right) + O(x^3)$$

Setting $u = -\frac{x}{2} + \frac{x^2}{6}$ we have

$$\log(1 + u) = u - \frac{u^2}{2} + O(u^3) \quad \text{with } x \text{ of order } u$$

So

$$\log(1 - e^{-x}) \approx \log(x) + \left(-\frac{x}{2} + \frac{x^2}{6}\right) - \frac{1}{2}\left(-\frac{x}{2}\right)^2 + O(x^3)$$

$$\log(1 - e^{-x}) \approx \log x - \frac{x}{2} + \frac{x^2}{24} + O(x^3)$$

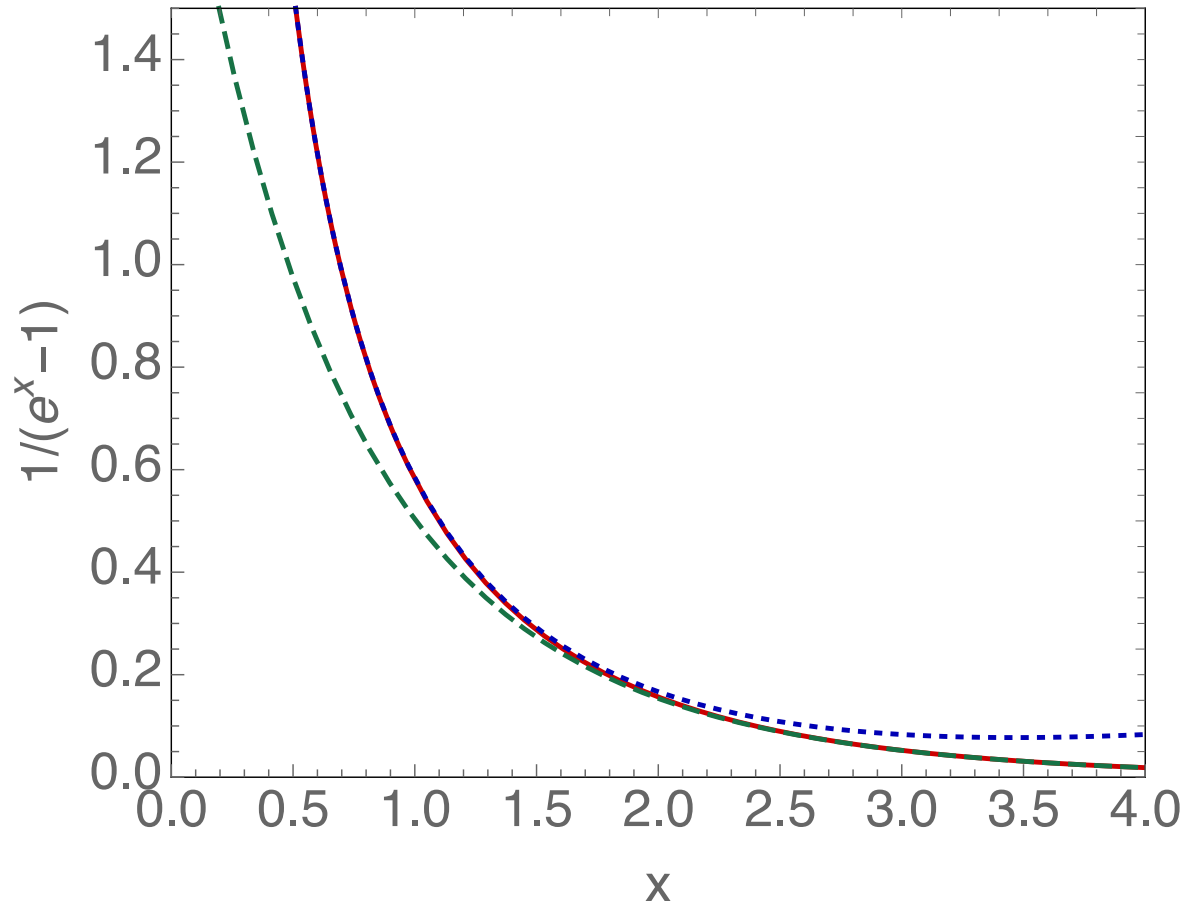


Figure 1: The function $1/(e^x - 1)$ (red) and our approximations to it. At small x the function is well approximated by $\frac{1}{x} - \frac{1}{2}$ (blue dotted line). At large x the function is well approximated by $e^{-x} + e^{-2x}$, green dashed line.

Problem 2. Energy of the quantum harmonic oscillator

Recall from previous homework that the mean energy of a single classical harmonic oscillator interacting with the thermal environment is

$$\langle \epsilon \rangle = kT \quad (14)$$

Now we will compare this classical result to the quantum version of the harmonic oscillator. This builds on the previous which worked out the partition function.

Recall that the energy levels of the oscillator are $\epsilon_n = n\hbar\omega_0$, where we have shifted what we call zero energy to be ground state energy $n = 0$, while higher vibrational states have $n = 1, 2, \dots$

- (a) Determine the average energy $\langle \epsilon \rangle$ of the quantum harmonic oscillator at temperature T or $\beta = 1/kT$, using the partition function from a previous homework. Express your result using β and $\hbar\omega_0$. You can check your result using the next item.
- (b) How is the mean vibrational quantum number $\langle n \rangle$ related to $\langle \epsilon \rangle$? Plot the mean number of vibrational quanta $\langle n \rangle$ versus $kT/\hbar\omega_0$ for $kT/\hbar\omega_0 = 0 \dots 4$. Determine (from your graph) the temperature in units of $\hbar\omega_0$ where $\langle n \rangle = 1$. I find $T = 1.4427 \hbar\omega_0/k_B$. You may wish to compare your exact number 1.4427 to your estimate of Problem 3 of Homework 3.

- (c) Plot

$$\frac{\langle \epsilon \rangle}{kT} \quad (15)$$

versus $kT/\hbar\omega_0$ for $kT/\hbar\omega_0 = 0 \dots 4$.

- (d) You will now use the Taylor expansions of problem 2. Show that at low temperatures $T \ll \hbar\omega_0$ we have

$$\langle \epsilon \rangle \simeq \hbar\omega_0 e^{-\hbar\omega_0/kT} \quad (16)$$

or more generally

$$\langle \epsilon \rangle \simeq \hbar\omega_0 e^{-\beta\hbar\omega_0} (1 + e^{-\beta\hbar\omega_0} + \dots) \quad (17)$$

Show that at high temperatures $T \gg \hbar\omega_0$ we have

$$\langle \epsilon \rangle \simeq kT \quad (18)$$

or more generally

$$\langle \epsilon \rangle \simeq kT \left(1 - \frac{\hbar\omega_0}{2kT} + \dots \right) \quad (19)$$

A plot of the two approximations to the full function is shown in Fig. 2.

- (e) The high temperature limit $T \gg \hbar\omega_0$ is

$$\lim_{T \rightarrow \infty} \langle \epsilon \rangle \simeq kT \quad (20)$$

Explain why at high temperatures the $\langle \epsilon \rangle$ of the quantum oscillator agrees with the classical one by discussing the significance of the graph in (b) in the high temperature limit.

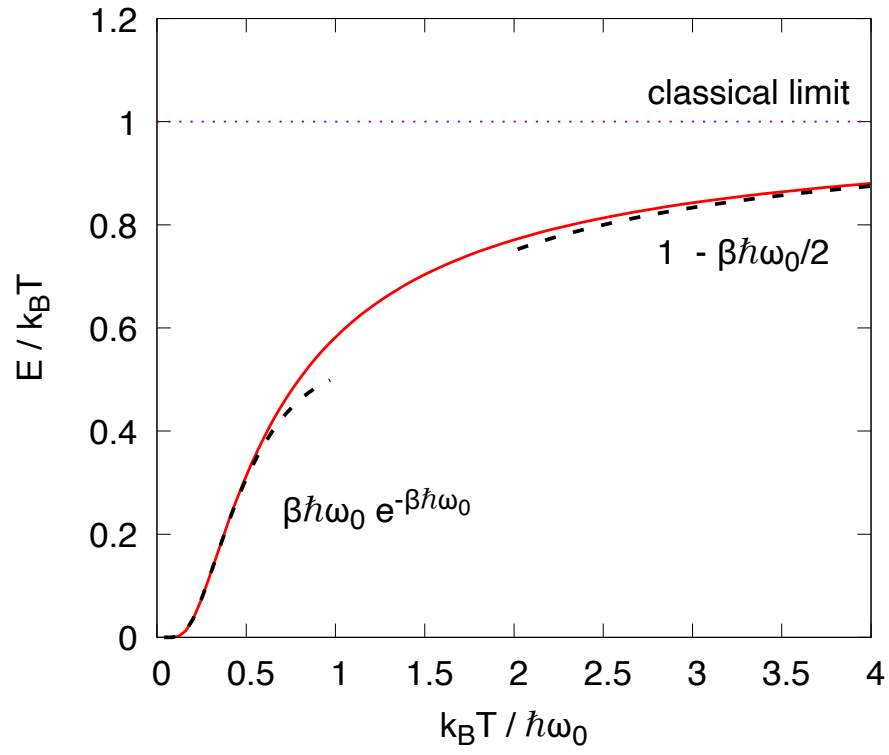


Figure 2: The energy $\langle \epsilon \rangle / kT$. Together with the expansions developed at large and small temperatures

- (f) Consider a diatomic ideal gas. Recall that the mean energy of each molecule consists of a classical contribution from translational degrees of freedom $\frac{3}{2}kT$, plus a classical contribution from the rotational degrees of freedom $\frac{2}{2}kT$. Now, a quantum mechanical contribution from the vibrations can be added. The energy computed in part (a) is the contribution of the vibrational motion, and was computed quantum mechanically. As discussed in class, the total energy for an ideal gas takes the form

$$U = Ne_0(T) \quad (21)$$

and is independent of the volume.

- (i) What is $e_0(T)$? (Hint: just read the question!)
- (ii) What are C_V and C_p ? You should find that the specific heat C_p is

$$C_p = Nk_B \left[\frac{7}{2} + \frac{(\beta\hbar\omega_0)^2 e^{-\beta\hbar\omega_0}}{(1 - e^{-\beta\hbar\omega_0})^2} \right] \quad (22)$$

and that the specific heat per mole

$$C_p^{1\text{ml}} = R \left[\frac{7}{2} + \frac{(\beta\hbar\omega_0)^2 e^{-\beta\hbar\omega_0}}{(1 - e^{-\beta\hbar\omega_0})^2} \right] \quad (23)$$

- (iii) Recall that for diatomic hydrogen the first vibrational frequency is $\hbar\omega_0 \simeq 0.54 \text{ eV}$. Using this number together with $k_B = 0.025 \text{ eV}/300^\circ\text{K}$, I made a graph of Eq. (23) that is shown below. Compare the result to the experimental data. What qualitatively does the (simple-minded) calculation get right and wrong? Explain.

Energy of SHO

a) We have

$$Z = \frac{1}{1 - e^{-\beta \hbar \omega_0}}$$

Then

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \log Z = + \frac{\partial}{\partial \beta} \log (1 - e^{-\beta \hbar \omega_0})$$

$$= \frac{1}{1 - e^{-\beta \hbar \omega_0}} e^{-\beta \hbar \omega_0} \hbar \omega_0$$

$$\boxed{\langle E \rangle = \frac{\hbar \omega_0}{e^{\beta \hbar \omega_0} - 1}}$$

b) Then

$$\frac{\langle E \rangle}{\hbar \omega_0} = \frac{1}{e^{\hbar \omega_0 / kT} - 1} = \langle n \rangle$$

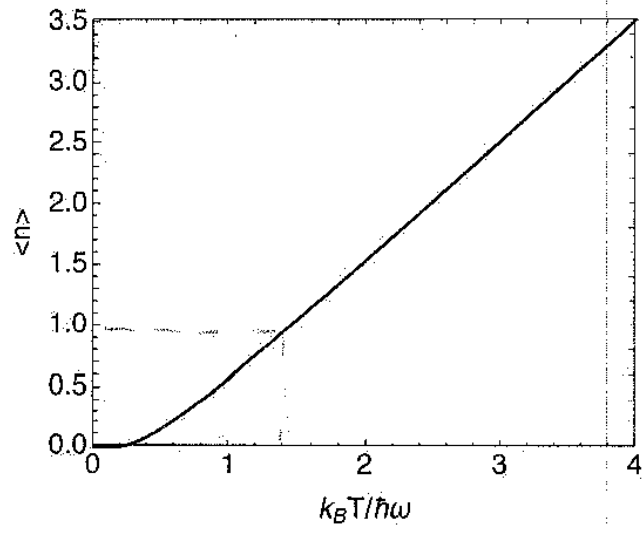
Then



Then from graph

$$\langle n \rangle = 1 \quad \text{when}$$

$$k_B T / \hbar \omega_0 = 1.45$$



or

$$k_B T = 1.45 \hbar \omega_0$$

(c) Then a nice plot of $\langle E \rangle$ is given in the problem statement.

(d) Using the series of problem 1

with $x \equiv \hbar \omega_0 / k_B T$

at low temperature $k_B T \ll \hbar \omega_0$ then $x \gg 1$,
and

$$\frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}} \approx e^{-x} (1 + e^{-x} + \dots)$$

And

$$\langle E \rangle = \hbar \omega_0 e^{-\beta \hbar \omega_0} (1 + e^{-\beta \hbar \omega_0} + \dots)$$

At high temperature $x \ll 1$

$$\frac{1}{e^x - 1} \approx \frac{1}{x} - \frac{1}{2}$$

$$\langle E \rangle = \hbar \omega_0 \left(\frac{k_B T}{\hbar \omega_0} - \frac{1}{2} \right) \approx k_B T \left(1 - \frac{\hbar \omega_0}{2 k_B T} \right)$$

e) At high temperature the number of quanta $\langle n \rangle$ is very large. In this regime $\langle n \rangle \gg 1$, quantum mechanics becomes continuous, $\frac{\Delta E}{E} \ll 1$, and it approaches classical mechanics.

This is the Bohr correspondence principle

f) We have

$$i) \quad U = N \left[\frac{5}{2} kT + \frac{\hbar \omega_0}{e^{\beta \hbar \omega_0} - 1} \right]$$

this is $f_0(T)$

Then

$$ii) \quad C_V = \left(\frac{dU}{dT} \right)_V = N \left[\frac{5}{2} k + \frac{-\hbar \omega_0 e^{\beta \hbar \omega_0}}{(e^{\beta \hbar \omega_0} - 1)^2} \hbar \omega_0 \frac{2}{\partial T} \frac{1}{kT} \right]$$

$$= N \left[\frac{5}{2} k + \frac{(\beta \hbar \omega_0)^2 e^{\beta \hbar \omega_0}}{(e^{\beta \hbar \omega_0} - 1)^2} k \right]$$

$$C_V = Nk \left[\frac{5}{2} + \frac{(\beta \hbar \omega_0)^2 e^{\beta \hbar \omega_0}}{(e^{\beta \hbar \omega_0} - 1)^2} \right]$$

So

$$C_p = C_v + Nk_B$$

$$C_p = Nk_B \left[\frac{7}{2} + \frac{(\beta \hbar \omega_0)^2}{(e^{\beta \hbar \omega_0} - 1)^2} \right]$$

iii) So we see that the model nicely captures the transition from $C_p = \frac{7}{2} = 3.5$ to $\frac{9}{2} = 4.5$

but misses the transition to $\frac{5}{2}$ at low temperatures

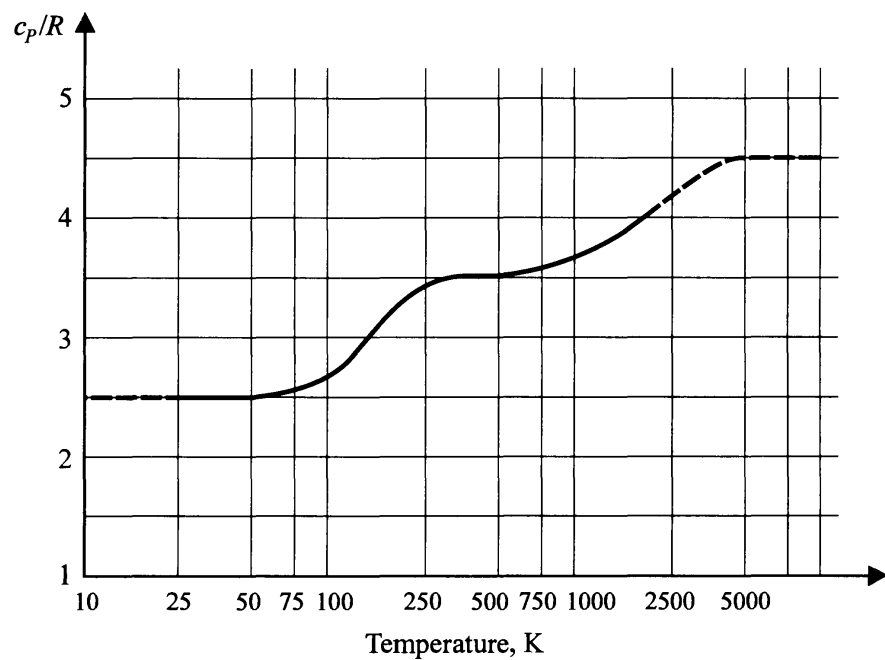
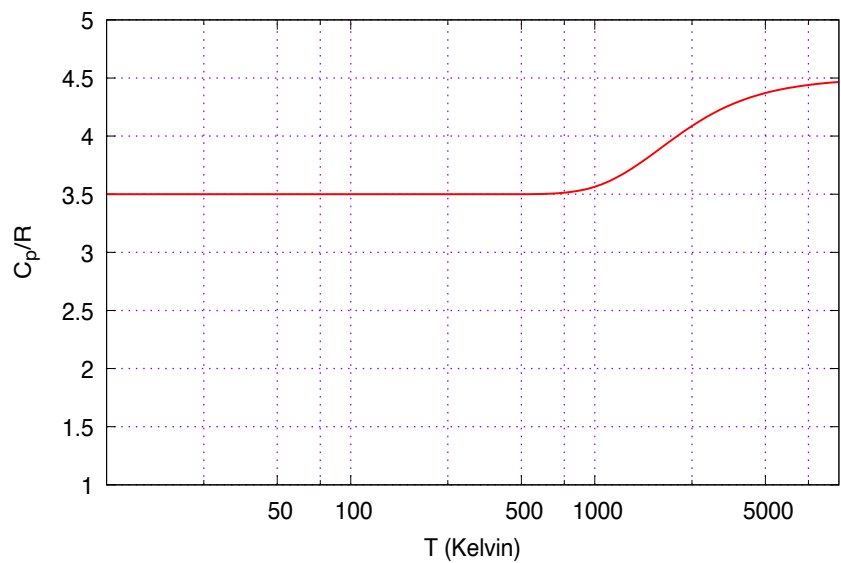


Figure 3: Top: a calculation of the specific heat per mole of diatomic hydrogen in units of R . Bottom: experimental data on C_p per mole in units of R

Problem 3. Phase Space and Entropy of a MAIG

The phase space volume is a measure of the total number of possible ways for N of particles to *share* (or partition) the total energy and volume. For instance one particle could have almost all the available energy and the remaining $N - 1$ particles could have very little. Such configurations are unlikely since they occupy only a small portion of the available phase space volume.

Consider a single particle in three dimensions in a box

$$0 < x, y, z < L \quad (24)$$

The three momenta components are sharing (or partitioning) the total energy which lies between E and $E + \delta E$, i.e.

$$E < \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} < E + \delta E, \quad (25)$$

The particle is free to move around in phase space but the energy must lie in this range. $\delta E/E$ is the precision in the energy and should be considered small, say 10^{-4} . You should realize that this means that the momentum is confined to a spherical shell between $p \equiv \sqrt{2mE}$ and $p_{\max} = \sqrt{2m(E + \delta E)}$.

(a) Show that the accessible phase space volume is

$$V_{\text{ps}} = \int_{[E, E+\delta E]} d^3\mathbf{r} d^3\mathbf{p} = V \left[4\pi (2mE)^{3/2} \frac{\delta E}{2E} \right] \quad (26)$$

Hint: Show that the thickness of the shell in momentum space is

$$\delta p \equiv p_{\max} - p \simeq p \frac{\delta E}{2E} \quad (27)$$

To count the number of configurations, divide up the phase space volume into cells of (arbitrary) small size $h = \Delta x \Delta p_x$, or in three dimensions cells of size¹

$$h^3 = (\Delta x \Delta y \Delta z) (\Delta p_x \Delta p_y \Delta p_z) \quad (28)$$

The “number of ways” for p_x, p_y, p_z and to share (or partition) the available energy is denoted by $\Omega(E, V)$ and it is phase space volume divided by the cell size

$$\Omega(E, V) = \frac{1}{h^3} \int_{[E, E+\delta E]} d^3\mathbf{r} d^3\mathbf{p} \quad (29)$$

$$= V \left(\frac{2mE}{h^2} \right)^{3/2} 4\pi \frac{\delta E}{2E} \quad (30)$$

¹Classically this cell size was arbitrary. With the advent of quantum mechanics, it was realized that a natural choice for the cell size is Planck's constant h . But here let's understand it from a classical perspective first, choosing the cell size to be h somewhat arbitrarily.

$\Omega(E, V)$ is the number of accessible states for a single particle with energy between E and $E + \delta E$.

The number of accessible configurations for two particles sharing the available energy between E and $E + \delta E$ is

$$\Omega(E, V) = \frac{1}{2!} \int_{[E, E+\delta E]} \frac{d^3 \mathbf{r}_1 d^3 \mathbf{p}_1}{h^3} \frac{d^3 \mathbf{r}_2 d^3 \mathbf{p}_2}{h^3}. \quad (31)$$

The $2!$ is inserted because if I simply exchange what I call particle 1 and particle 2, that is not to be considered a new configuration.

- (b) Show that for two particles in three dimensions the number of accessible configurations is

$$\Omega(E, V) = V^2 \left(\frac{2mE}{h^2} \right)^3 \pi^3 \frac{\delta E}{4E}. \quad (32)$$

Hint: It is helpful to recall that the area of a sphere in d dimensions is given by a general formula

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1}. \quad (33)$$

In class we showed that for N particles with total energy E and volume V , the total the number of configurations and corresponding entropy of the system are given by

$$\Omega(E, V) = C(N) V^N E^{3N/2} \quad (34)$$

$$S(E, V) = k_B \ln \Omega = \frac{3}{2} N k_B \log E + N k_B \log V + \text{const}. \quad (35)$$

In the remainder of the exercise we will keep track of the constant $C(N)$.

- (c) Show that the total number of ways for N particles to share the energy E (i.e. total number of accessible configurations with energy between E and $E + \delta E$) is

$$\Omega(E, V) = \frac{1}{N!} \int \frac{d^3 \mathbf{r}_1 d^3 \mathbf{p}_1}{h^3} \dots \frac{d^3 \mathbf{r}_N d^3 \mathbf{p}_N}{h^3}, \quad (36)$$

$$= \frac{1}{N!} V^N \left(\frac{2\pi m E}{h^2} \right)^{3N/2} \frac{1}{\Gamma(3N/2)} \frac{\delta E}{E}. \quad (37)$$

N is large and is of order Avogadro's number.

- (d) Use the Stirling approximation to show that²

$$\Omega(E, V) \simeq e^{5N/2} \left(\frac{V}{N} \right)^N \left(\frac{4\pi m}{3h^2} \frac{E}{N} \right)^{3N/2}, \quad (39)$$

$$(40)$$

²For large n

$$\Gamma(n) \equiv (n-1)! \simeq n! \simeq (n/e)^n \quad (38)$$

Note the Stirling approximation works for n not integer, if $n!$ is understood as $\Gamma(n+1)$.

and that the entropy is

$$S(E, V) = Nk_B \log \left[\left(\frac{V}{N} \right) \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} Nk_B, \quad (41)$$

$$= Nk_B \left[\log \left(\frac{v_N}{\lambda_{\text{th}}^3} \right) + \frac{5}{2} \right]. \quad (42)$$

Here $v_N = V/N$ is the volume per particle and

$$\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{4\pi m E/(3N)}}, \quad (43)$$

is the typical de Broglie wavelength at temperature T . The temperature is determined by the energy per particle for a monoatomic gas, $E/N = \frac{3}{2}k_B T$.

Hint: The $\delta E/E$ term is not exponentially large in contrast to the other terms. Thus $\delta E/E$ can be set to one via the following approximation:

$$e^{5N/2} \left(\frac{\delta E}{E} \right) = e^{5N/2 + \log(\delta E/E)} \simeq e^{5N/2}. \quad (44)$$

Convince yourself of this step by taking $\delta E/E = 10^{-6}$ (or whatever you like). How big is $\log(\delta E/E)$ compared to $5N/2$? Something is exponentially large if its logarithm is of order Avogadro's number.

Discussion: The result for S in Eq. (42) is known as the Sackur Tetrode equation and is fundamental. The Sackur-Tetrode equation says that the entropy per particle S/Nk_B is of order the logarithm of the accessible phase space per particle in units of h^3 . Roughly speaking each particle has volume $v_N = V/N$. The *typical* momentum of a particle is of order $p_{\text{typ}} \sim \sqrt{m k_B T}$. The phase space per particle is the coordinate space volume v_N times the momentum space volume $\sim p_{\text{typ}}^3$ and is of order

$$V_{\text{ps}} \sim v_N p_{\text{typ}}^3. \quad (45)$$

The entropy per particle (divided k_B) is the logarithm of this phase space in units of h^3 and is of order

$$\frac{S}{Nk_B} \sim \log \left(\frac{v_N p_{\text{typ}}^3}{h^3} \right) \sim \log \left(\frac{v_N}{\lambda_{\text{th}}^3} \right). \quad (46)$$

This logarithm is never very large (at most 10), and in practice the entropy per particle is an order one number.

Phase Space

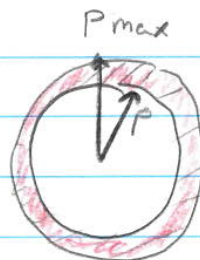
$$\begin{aligned} \text{a)} \quad V_{ps} &= \int_{[E, E+\delta E]} d^3r d^3p = V \int_{\text{shell with energy in range } [E, E+\delta E]} d^3p \\ &= V 4\pi p^2 \delta p \end{aligned}$$

Then

$$p = \sqrt{2mE}$$

See
lecture!

$$p_{\max} = \sqrt{2m(E+\delta E)}$$



$$\begin{aligned} \delta p &= p_{\max} - p = \sqrt{2mE} (1 + \delta E/E)^{1/2} - \sqrt{2mE} \\ &\approx \sqrt{2mE} \left(1 + \frac{1}{2} \frac{\delta E}{E} \right) - \sqrt{2mE} \end{aligned}$$

$$\delta p = p \frac{\delta E}{2E} \quad \text{i.e.} \quad \frac{\delta p}{p} = \frac{\delta E}{2E}$$

So

$$V_{ps} = V 4\pi p^3 \frac{\delta E}{2E} = V [4\pi (2mE)^{3/2} \frac{\delta E}{2E}]$$

b) Then

$$\begin{aligned}\Omega(E, V) &= \frac{1}{2!} \int \frac{d^3 r_1 d^3 p_1}{h^3} \frac{d^3 r_2 d^3 p_2}{h^3} \\ &= \frac{V^2}{2!} \int \frac{d^3 p_1 d^3 p_2}{h^6} \\ &\quad \underbrace{[E, E+\delta E]}_{\text{shell volume}/h^6}\end{aligned}$$

The momentum integral is a spherical shell in 6 dimensions
The momentum space volume is :

$$\frac{\text{Shell volume}}{h^6} = \frac{2 \pi^{6/2}}{\Gamma(6/2)} p^5 \frac{\delta p}{h^6}$$

As before

$$\delta p = p \frac{\delta E}{2E}$$

So

$$p = \sqrt{2mE}$$

$$\Omega(E, V) = \frac{V^2}{2!} \frac{2 \pi^3}{2!} \left(\frac{p}{h} \right)^6 \frac{\delta E}{2E}$$

$$\Omega(E, V) = V^2 \pi^3 \left(\frac{2mE}{h^2} \right)^3 \frac{\delta E}{4E}$$

c) Now the general case

$$\Omega(E, V) = \frac{1}{N!} \int \frac{d^3 r_1 d^3 p_1}{h^3} \dots \frac{d^3 r_N d^3 p_N}{h^3}$$

$$= \left(\frac{V^N}{N!} \right) \int_{[E, E+\delta E]} (d^3 p_1 \dots d^3 p_N) / h^{3N}$$

↑ coordinate space ← momentum space
shell volume / h^{3N}

So this is again a shell of dimension $3N$

$$\frac{\text{Shell volume}}{h^{3N}} = \frac{2 \pi^{3N/2}}{\Gamma(3N/2)} \left(\frac{p}{h} \right)^{3N} \frac{\delta E}{E}$$

Using $\frac{p}{h} = \left(\frac{2mE}{h^2} \right)^{1/2}$ we get:

$$\Omega(E, V) = \left(\frac{V^N}{N!} \right) \left(\frac{1}{\Gamma(3N/2)} \left(\frac{2\pi m E}{h^2} \right)^{3N/2} \right) \frac{\delta E}{E}$$

↑ coordinate space ← momentum space

d) Writing

$$N! = \left(\frac{N}{e} \right)^N, \quad \Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2e} \right)^{3N/2}$$

We have

$$\Omega(E, V) = \left[e^N \left(\frac{V}{N} \right)^N \right] \left[e^{3N/2} \left(\frac{4\pi m E}{3N h^2} \right)^{3N/2} \right]$$

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Taking the log of this expression, and dropping the $\delta E/E$ term, we have

$$S = k \ln \Omega$$

$$S = k \left[\frac{5N}{2} + N \ln \frac{V}{N} + N \ln \left(\frac{4\pi m E}{3N h^2} \right)^{3/2} \right]$$

The term: $\left(\frac{4\pi m E}{3N h^2} \right)^{3/2} = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} = \left(\frac{1}{\lambda_{th}^2} \right)^{3/2} = \frac{1}{\lambda_{th}^3}$

where we used $\frac{E}{N} = \frac{3}{2} kT$

So finally

$$S = Nk \left[\ln \left(\frac{V}{N \lambda_{th}^3} \right) + \frac{5}{2} \right]$$

↑ we will derive this in other ways as the course progresses. Here we have derived it from the microcanonical ensemble. Later we will derive it from the canonical ensemble.

Problem 4. A reminder on Jacobians

Recall that if I have a probability distribution

$$d\mathcal{P}_x = P(x)dx, \quad (47)$$

and I want to change variables to a new variable $u(x)$, then the probability distribution for u is

$$d\mathcal{P}_u = P(x(u)) \left| \frac{dx}{du} \right| du. \quad (48)$$

So the probability densities are related by

$$P(u) = P(x(u)) \left| \frac{dx}{du} \right|. \quad (49)$$

We had (or will have) physical examples of this in prior homework.

The change of variables generalizes to two and higher dimensions. Suppose we have a probability density in x, y describing a particle's position:

$$d\mathcal{P}_{x,y} = P(x, y) dx dy, \quad (50)$$

and definiteness consider the Gaussian

$$d\mathcal{P}_{x,y} = \frac{1}{2\pi\sigma^2} \exp\left(-\frac{x^2}{2\sigma^2} - \frac{y^2}{2\sigma^2}\right) dx dy, \quad (51)$$

shown in Fig. ?? . It seems more natural here to use polar coordinates, defining $x = r \cos \theta$ and $y = r \sin \theta$ with $r \in [0, \infty]$ and $\theta \in [0, 2\pi]$ shown in the figure.

In analogy with the 1D case, for a change of variables $x(r, \theta)$ and $y(r, \theta)$, the probability of finding a particle with radius between r and $r + dr$ and angle θ between θ and $\theta + d\theta$ is

$$d\mathcal{P}_{r,\theta} = P(x(r, \theta), y(r, \theta)) \left\| \frac{\partial(x, y)}{\partial(r, \theta)} \right\| dr d\theta. \quad (52)$$

The double bars mean determinant and then absolute value of the Jacobian matrix, which is defined as a matrix with the derivatives of the map $(r, \theta) \rightarrow (x, y)$:³

$$\frac{\partial(x, y)}{\partial(r, \theta)} \equiv \begin{pmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} \end{pmatrix}. \quad (53)$$

So the densities are related by

$$P(r, \theta) = P(x, y) \left\| \frac{\partial(x, y)}{\partial(r, \theta)} \right\|, \quad (54)$$

where it is understood that $x = r \cos \theta$ and $y = r \sin \theta$.

³Sometimes people use $\partial(v_x, v_y)/\partial(v, \theta)$ to mean the determinant of the Jacobian matrix, rather than just the matrix itself. Our book uses this notation, as is described in appendix C.

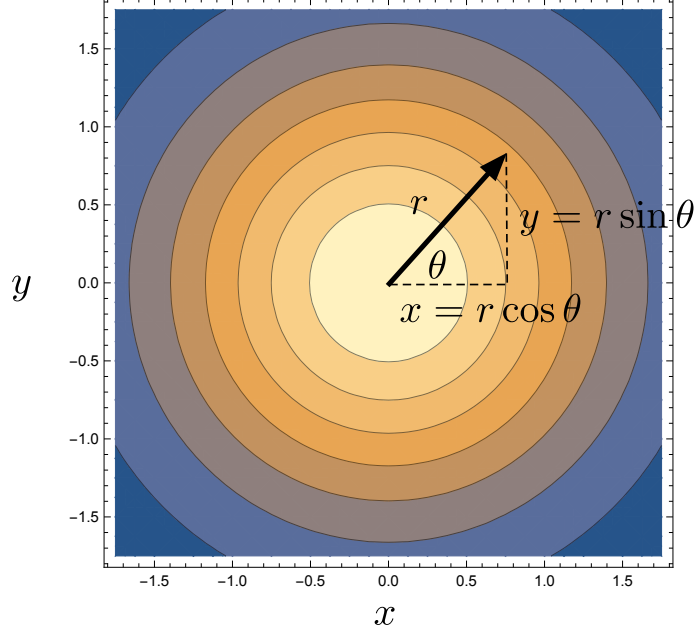


Figure 4: A probability distribution which has no dependence on θ .

We say that the “volume elements” are related by the Jacobian determinant:

$$dx dy = \left\| \frac{\partial(x, y)}{\partial(r, \theta)} \right\| dr d\theta = r dr d\theta \quad (55)$$

It is understood that these expressions are meant to be integrated over.

- (a) Compute the Jacobian matrix and find its determinant. Explicitly determine $d\mathcal{P}_{r,\theta} = P(r, \theta) dr d\theta$ for the probability distribution in Eq. (51). By integrating over the unobserved coordinate, determine $d\mathcal{P}_r = P(r) dr$ and $d\mathcal{P}_\theta = P(\theta) d\theta$, that is to say the probability distribution for r (without regards to θ) and the probability distribution for θ (without regards to r) ?
- (b) Let's understand the Jacobian. The columns of the Jacobian form vectors

$$\mathbf{e}_r \equiv \frac{\partial x}{\partial r} \hat{\mathbf{i}} + \frac{\partial y}{\partial r} \hat{\mathbf{j}} = \frac{\partial \mathbf{R}}{\partial r}, \quad (56)$$

$$\mathbf{e}_\theta \equiv \frac{\partial x}{\partial \theta} \hat{\mathbf{i}} + \frac{\partial y}{\partial \theta} \hat{\mathbf{j}} = \frac{\partial \mathbf{R}}{\partial \theta}, \quad (57)$$

where $\mathbf{R} = x\hat{\mathbf{i}} + y\hat{\mathbf{j}}$ is the position vector of the particle. The determinant of two vectors is the area of the parallelogram spanned by the two vectors⁴. Compute the vectors⁵ $\mathbf{e}_r dr$ and $\mathbf{e}_\theta d\theta$, and the norms of these vectors $|\mathbf{e}_r dr|$ and $|\mathbf{e}_\theta d\theta|$ and show

⁴See for instance [The Kahn video](#).

⁵I am asking for the vector \mathbf{e}_r times an (arbitrary) small increment in radial coordinate dr . Weighting \mathbf{e}_r and \mathbf{e}_θ by the corresponding coordinate increments dr and $d\theta$ gives these vectors a simple geometric meaning, which I hope you will begin to understand.

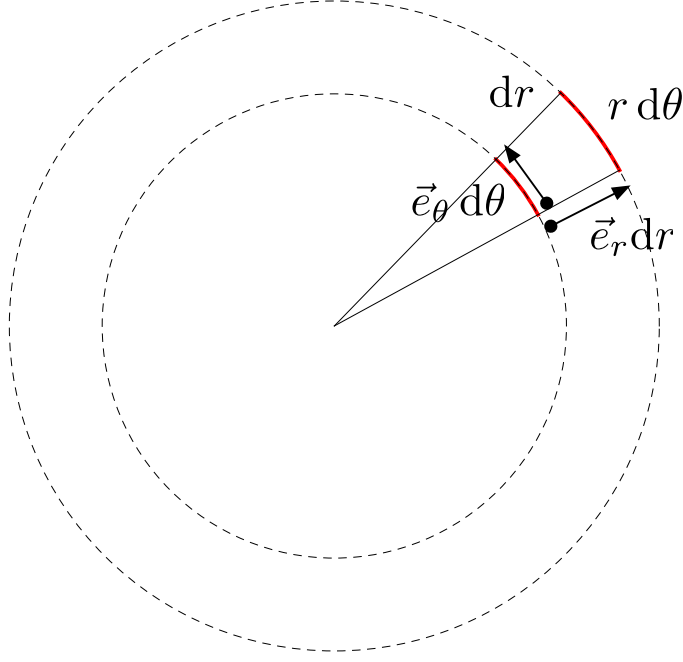


Figure 5: Cylindrical coordinates in two dimensions.

that the vectors are orthogonal in this case. Interpret the displacement vectors $\mathbf{e}_r dr$ and $\mathbf{e}_\theta d\theta$ and their lengths by referring to Fig. 5. Note that the volume element is $|\mathbf{e}_r dr| |\mathbf{e}_\theta d\theta|$ since the vectors are orthogonal.

Consider the probability distribution

$$d\mathcal{P}_{x,y} = \frac{1}{6\pi} e^{(-5x^2 + 2xy - 2y^2)/18} dx dy \quad (58)$$

A contour plot of this probability distribution is shown in Fig. 6(a). Consider the change of variables

$$x = (u + v) \quad (59)$$

$$y = (-u + 2v) \quad (60)$$

The u, v coordinates are better adapted to the probability distribution and are shown in Fig. 6(a).

(c) Compute the Jacobian of the map and compute the probability distribution

$$d\mathcal{P}_{u,v} = P(u, v) du dv \quad (61)$$

Your result should be qualitatively consistent with the contour plot of the result shown in Fig. 6(b).

Show that the probability of finding u in an interval between u and $u + du$ is

$$d\mathcal{P}_u = P(u) du \quad \text{with} \quad P(u) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}u^2}. \quad (62)$$

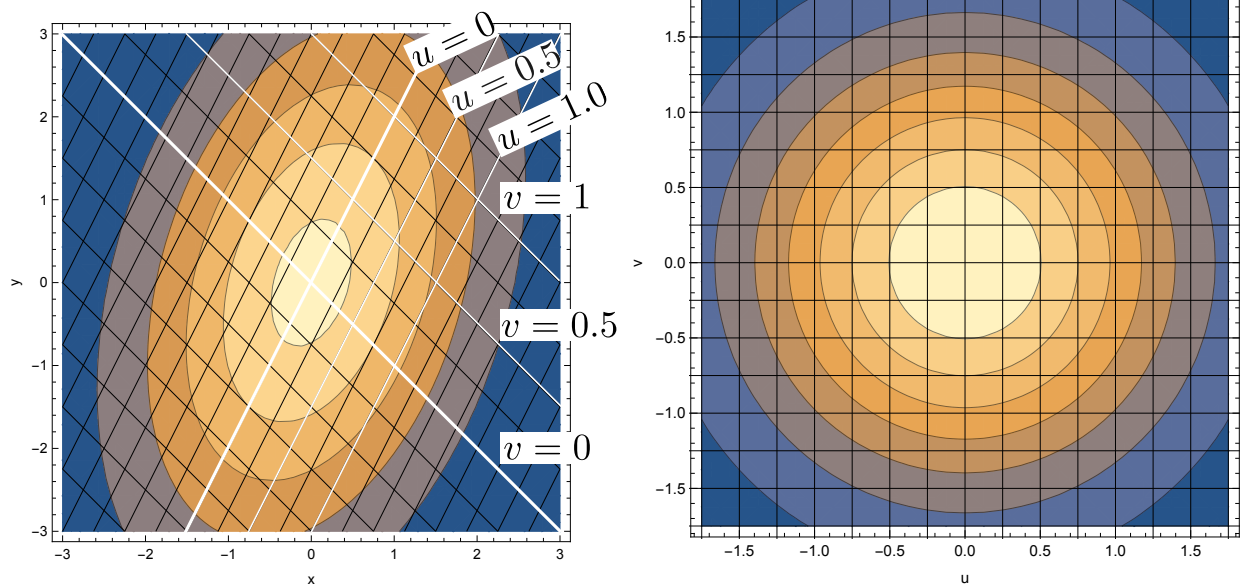


Figure 6: (a) A contour plot of the probability distribution $P(x, y)$ with lines of constant u and v indicated. Specific lines of constant u and v are indicated by the white lines. (b) a contour plot $P(u, v)$ with corresponding lines of constant u and v . The distribution becomes circular for this change of variables.

- (d) Find the column vectors, \mathbf{e}_u and \mathbf{e}_v , of the Jacobian of the map $(u, v) \mapsto (x, y)$.

Now interpret these vectors: Sketch a unit coordinate displacement, $du = 1$ and $dv = 1$ in Fig. 6(b) and sketch the displacement vectors $\mathbf{e}_u du$ for $du = 1$ and $\mathbf{e}_v dv$ for $dv = 1$ in Fig. 6(a).

Jacobians

$$a) \quad x = r \cos \theta \quad y = r \sin \theta$$

$$\begin{bmatrix} \partial x / \partial r & \partial x / \partial \theta \\ \partial y / \partial r & \partial y / \partial \theta \end{bmatrix} = \begin{pmatrix} \cos \theta & -r \sin \theta \\ \sin \theta & r \cos \theta \end{pmatrix}$$

So the determinant is

$$J = \cos^2 \theta \cdot r + (\sin^2 \theta) r = r$$

So

$$d\mathcal{P}(r, \theta) = \frac{1}{2\pi\sigma^2} e^{-r^2/2\sigma^2} r dr d\theta$$

Integrating over θ :

$$d\mathcal{P}(r) = \int_{\text{over } \theta} d\mathcal{P}(r, \theta) = \frac{1}{2\pi\sigma^2} e^{-r^2/2\sigma^2} r dr \cdot 2\pi$$

$$d\mathcal{P}_r = \frac{1}{\sigma^2} e^{-r^2/2\sigma^2} r dr$$

Similarly integrating over r

$$d\mathcal{P}_\theta = \int_{\text{over } r} d\mathcal{P}_{r, \theta} = d\theta \int_0^\infty \frac{1}{2\pi\sigma^2} e^{-r^2/2\sigma^2} r dr = \frac{d\theta}{2\pi}$$

b) So

$$\underbrace{\vec{e}_r}_{\text{this vector points in the direction of increasing } r} = \frac{\partial \vec{R}}{\partial r} = \cos\theta \hat{i} + \sin\theta \hat{j}$$

this vector points in the direction of increasing r
 $\vec{e}_r dr$ is the change in position \vec{R} with a small change in radius

$$\vec{e}_\theta = \frac{\partial \vec{R}}{\partial \theta} = -r \sin\theta \hat{i} + r \cos\theta \hat{j}$$

So $\vec{e}_\theta d\theta$ is the change in position \vec{R} with an increase in angle θ

Note:

- $|\vec{e}_r dr| = (\cos^2\theta + \sin^2\theta)^{1/2} dr = dr \leftarrow \text{this is the length of } |\vec{e}_r dr|$
- $|\vec{e}_\theta d\theta| = (r^2 \sin^2\theta + r^2 \cos^2\theta)^{1/2} d\theta = r d\theta$
- Then they are orthogonal

$$\vec{e}_r \cdot \vec{e}_\theta = -r \cos\theta \sin\theta + r \cos\theta \sin\theta = 0$$

- Clearly since $\vec{e}_\theta d\theta$ is the displacement due to a change of by $d\theta$, the magnitude of this displacement is by geometry $r d\theta$, which is confirmed by the math $|\vec{e}_\theta d\theta| = r d\theta$
- Since the vectors are orthogonal the volume element is

$$dV = |\vec{e}_r dr| |\vec{e}_\theta d\theta| = dr (r d\theta) = r dr d\theta$$

c) We have

$$J = \begin{vmatrix} \partial x / \partial u & \partial x / \partial v \\ \partial y / \partial u & \partial y / \partial v \end{vmatrix} = \begin{vmatrix} 1 & 1 \\ -1 & 2 \end{vmatrix} = 3$$

So the argument of the exponent is

$$\begin{aligned} -5x^2 + 2xy - 2y^2 &= -5(u+v)^2 + 2(u+v)(-u+2v) \\ &\quad + 2(-u+2v)(-u+2v) \\ &= -9u^2 - 9v^2 \end{aligned}$$

So

$$d\mathcal{P}_{u,v} = \frac{1}{6\pi} \exp((-9u^2 - 9v^2)/18) \cdot 3 du dv = \frac{1}{2\pi} \exp\left(-\frac{u^2}{2} - \frac{v^2}{2}\right) du dv$$

If we don't care about v we integrate over it (aka we "marginalize" over v), So

$$\begin{aligned} d\mathcal{P}_u &= \int_{\text{over } v} d\mathcal{P}_{u,v} = \frac{e^{-u^2/2}}{2\pi} du \cdot \int_{-\infty}^{\infty} e^{-v^2/2} dv \\ &= \frac{e^{-u^2/2}}{2\pi} du \sqrt{2\pi} = \frac{e^{-u^2/2}}{\sqrt{2\pi}} \end{aligned}$$

The vectors are

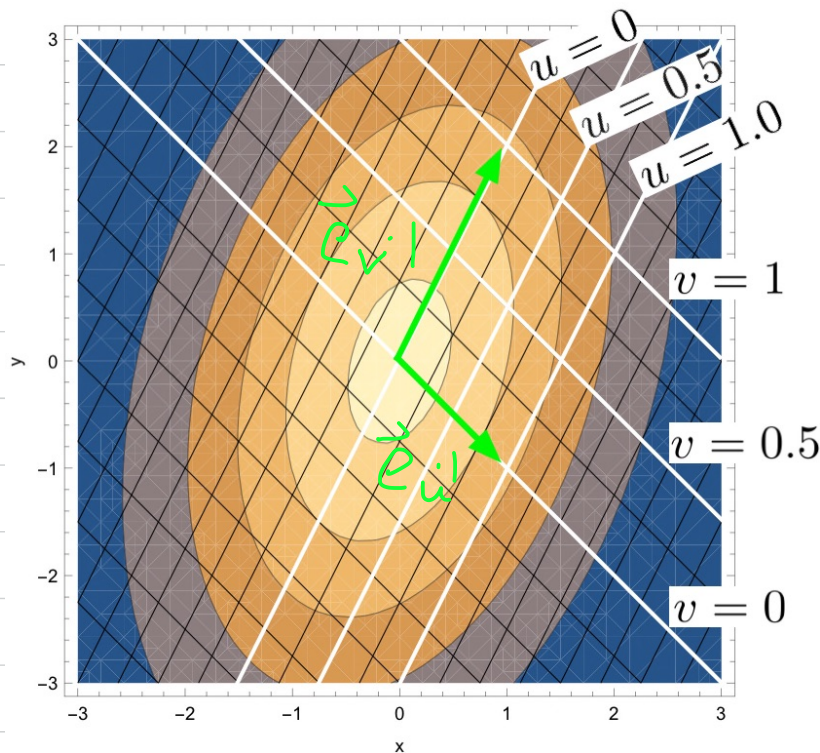
$$\vec{e}_u = \frac{\partial \vec{R}}{\partial u} = \hat{i} - \hat{j}$$

$$\vec{e}_v = \frac{\partial \vec{R}}{\partial v} = \hat{i} + 2\hat{j}$$

$\vec{e}_u du$ is the displacement for given du , at given u, v

$\vec{e}_v dv$ is the displacement for given dv , at given u, v

Then at the origin and $du=1$ $dv=1$



Problem 5. (Fall 2023) 2D World of a classical gas

Consider a mono-atomic ideal gas in a two dimensional world, so the velocities are labeled by $\mathbf{v} = (v_x, v_y)$.

- (a) Write down the normalized Maxwell velocity distribution, $d\mathcal{P}(v_x, v_y) = P(v_x, v_y)dv_x dv_y$. Change variables to speed v and velocity angle θ , $v_x = v \cos \theta$ and $v_y = v \sin \theta$ and determine

$$d\mathcal{P}(v, \theta) = P(v, \theta)dv d\theta \quad (63)$$

Then determine the normalized speed distribution by integrating over θ

$$d\mathcal{P}(v) = P(v)dv, \quad (64)$$

Describe in plain speak and a simple picture (like Fig. 5) what we are doing with the whole “Jacobian + integral over θ ” steps.

You should find that all factors of π have canceled in your final expression for $P(v)$ in two dimensions. You can check your result by doing the next item.

- (b) Compute $\langle \frac{1}{2}mv^2 \rangle$ using the speed distribution. You should find kT . Is your result consistent with the equipartition theorem? Explain.

Solution

(a) We have

$$d\mathcal{P}_{v_x v_y} = \left(\frac{m}{2\pi kT} \right)^{2/2} e^{-\frac{1}{2}m(v_x^2 + v_y^2)/kT} dv_x dv_y, \quad (65)$$

After a change of variables $v = \sqrt{v_x^2 + v_y^2}$ and $\theta = \tan^{-1}(v_y/v_x)$ we find

$$d\mathcal{P}_{v,\theta} = \left(\frac{m}{2\pi kT} \right) e^{-\frac{1}{2}mv^2/kT} v dv d\theta. \quad (66)$$

This is the probability to have speed between v and $v + dv$ and angle between θ and $\theta + d\theta$. If we don't care what is θ , then we “marginalize” over this variable, meaning that we integrate over it to find the total probability to have speed between v and $v + dv$, regardless of the value of θ , i.e.

$$d\mathcal{P}_v = \int_{\text{over } \theta} d\mathcal{P}_{v,\theta} = \left(\frac{m}{2\pi kT} \right) e^{-\frac{1}{2}mv^2/kT} 2\pi v dv. \quad (67)$$

Clearly this is just saying we want to find the probability to be in a ring of radius between v and $v + dv$ (see figure) .

(b) We have

$$\langle \frac{1}{2}mv^2 \rangle = \int_0^\infty P(v) dv \left[\frac{1}{2}mv^2 \right] = \int_0^\infty \frac{m}{kT} e^{-mv^2/2kT} v dv \left[\frac{1}{2}mv^2 \right]. \quad (68)$$

Changing variables to a dimensionless velocity

$$u = \frac{v}{(kT/m)^{1/2}}, \quad (69)$$

as suggested by the $\exp(-mv^2/2kT)$ factor, we have

$$\langle \frac{1}{2}mv^2 \rangle = kT \underbrace{\int_0^\infty e^{-u^2/2} u du \left[\frac{1}{2}u^2 \right]}_{\text{This is an order one number}} \equiv kT I. \quad (70)$$

This is an order one number

where I is an integral to be evaluated

This integral is essentially the Γ function. We write

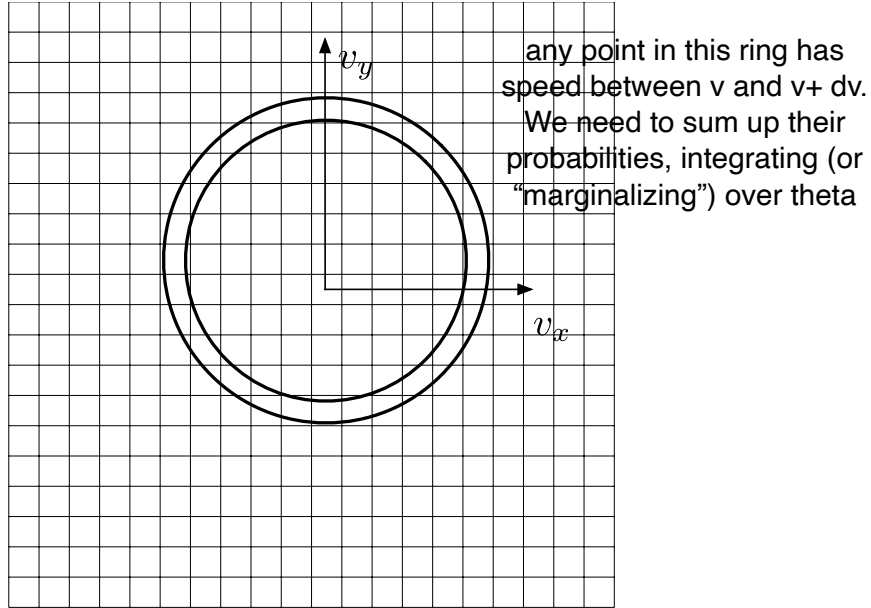
$$y = \frac{u^2}{2} \quad dy = u du \quad (71)$$

Then

$$I = \int_0^\infty e^{-y} dy y = \Gamma(2) = 1! = 1 \quad (72)$$

So

$$\langle \frac{1}{2}mv^2 \rangle = kT \quad (73)$$



This is consistent with the equipartition theorem. The classical Hamiltonian (or the energy as a function of \mathbf{r} and \mathbf{p}) is purely kinetic

$$\mathcal{H}(\mathbf{r}, \mathbf{p}) = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} \quad (74)$$

Thus there are two quadratic forms (“degrees of freedom”) in the classical Hamiltonian one for p_x and one for p_y . So we have by the equipartition theorem

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \left\langle \frac{p_y^2}{2m} \right\rangle = \frac{1}{2}kT \quad (75)$$

And the average energy is

$$\langle \mathcal{H} \rangle = 2 \times \frac{1}{2}kT = kT. \quad (76)$$