Lecture Notes for Phys 641 "Statistical Mechanics"

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April 28, 2011

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Part I

Introduction

Chapter 1

Overview

There are several closely related disciplines which study properties of macroscopic bodies. Each has a somewhat different emphases and its own advantages/disadvantages. Here is a non-rigorous classification.

- **Thermodynamics**. Establishes the most general relations without a detailed study of the molecular structure of the bodies involved. (In fact, most of the thermodynamic relations were derived in "pre-molecular" times). In the heart of thermodynamics are the 1st Law (energy conservation when heat is involved), and especially the 2d Law:

  $$\frac{dS}{dt} \geq 0 \tag{1.1}$$

  for a closed system, S being the entropy. Can be traced back to Joule and Clausius, respectively. The thermodynamic relations are valid regardless of the state of the bodies involved, or if their microscopic parts obey classical or quantum laws. However, the thermodynamics cannot predict the equation of state, even the simplest one for an ideal gas

  $$p = nk_BT \tag{1.2}$$

  with p being pressure, and n the density of molecules (although, once such an equation is introduced, thermodynamics can do a lot...).

- **Statistical Physics**. Attempts a better understanding of thermodynamic laws and fluctuations from the fact that bodies are macroscopic and thus can be considered as very large number of smaller parts (each still large on a molecular scale). At the heart of Statistical Physics is the Gibbs distribution for a system in a "thermostat" with a fixed temperature T:

$$w_n = \frac{1}{Z} \exp\left(-\frac{E_n}{k_B T}\right) \tag{1.3}$$

Here w_n is the probability to find the system in the nth state, E_n is the energy and Z follows from the normalization condition, $\sum w_n = 1$. The 2d Law is not questioned, and it is considered that the correctness of the Gibbs distribution is manifested by the correct prediction of thermodynamic relations.

- **Statistical Mechanics**. Attempts to provide a microscopic justification for thermodynamics, starting from individual molecules. The most significant contribution is by Boltzmann. The problem of a strict microscopic justification of the 2d Law is in no way closed; occasionally one can hear from respected member of Statistical Mechanics community about possible "violations of the 2d Law" - people outside of their immediate surrounding usually attribute this to a wrong definition of entropy. There is less reverence towards thermodynamics, and one sometimes hears that "thermodynamics is the limit of Statistical Mechanics when N, the number of particles, tends to infinity". [This is of course a noble goal but very hard to realize in practice. In reality, there are many problems which can be treated thermodynamically, but not starting from statistical mechanics]. Generally, the Statistical Mechanics path is hard, and often significant contributions come from mathematical community. Another aspect of Statistical Mechanics is the study of model systems for which the above Gibbs distribution is postulated, and the thermodynamic properties are derived from that. For non-trivial models the methods employed are usually extremely involved, but results can be extremely instructive. The best example is the Ising model. Verification of the ergodicity hypothesis (which leads to Gibbs distribution) for simple mechanical systems is also part of Statistical Mechanics and is also very hard.

- Kinetic theory. Can be considered as a precursor of Stat. Mech., and can be traced to the times when most people, except for the few best ones, did not believe in molecules. Derived equations for simple gases, as eq. (1.2), but the real challenge was the explanation of the 2d Law, the main puzzle being the reversibility of the equations of mechanics which seems to contradict the irreversibility of the entropy change. (Boltzmann provided here the most up to date explanation). Today, when talking about kinetic theory one puts a somewhat stronger emphasis on transport properties (heat conductivity, etc.). Boltzmann equation is the central one when describing kinetics, at least for molecules which obey classical mechanics. This equation -we might discuss it closer to the end of the course if there is time- describes the evolution of the distribution of molecules due to binary collisions. From there macroscopic transport coefficient, such as viscosity, coefficient of heat conductivity, etc. can be extracted, although that is not easy.

The approach of our course will be the closest to Statistical Physics...

Chapter 2

Math

2.1 Integrals and asymptotic relations

2.1.1 Gauss integral

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \tag{2.1}$$

For $\alpha \to \infty$ the integrand $\to$ δ-function:

$$\delta(x) = \lim_{\alpha\to\infty} \sqrt{\frac{\alpha}{\pi}} e^{-\alpha x^2} \tag{2.2}$$

with

$$\int_{-\epsilon}^{\epsilon} \delta(x)\, dx = 1 \ , \quad \int_{-\infty}^{\infty} \delta(x) f(x)\, dx = f(0) \tag{2.3}$$

for any finite $\epsilon > 0$ and smooth $f(x)$.

HW: *Consider an integral*

$$\int_0^{\infty} x^n e^{-ax^2}\, dx \ , \quad a > 0$$

calculate for $n = 1, 2, 4$*, and try general* n

2.1.2 The Stirling formula

Consider

$$N! = \int_0^\infty x^N e^{-x} dx = N^{N+1} \int_0^\infty e^{-N\phi(z)} dz$$

with $\phi(z) = z - \ln z$

HW: *check this*

For $N \to \infty$ very sharp maximum near $z = z_* = 1$. Thus,

$$\phi(z) \approx \phi(z_*) + \frac{1}{2}\phi''(z_*)(z - z_*)^2$$

Using Gauss integral,

$$N! \simeq N^{N+1} \sqrt{\frac{2\pi}{N\phi''(z_*)}} e^{-N\phi(z_*)}$$

Or,

$$N! \simeq \sqrt{2\pi N} \left(\frac{N}{e}\right)^N \tag{2.4}$$

HW: *Include the cubic correction to $\phi(z)$ near $z = 1$. Show that its contribution is small for $N \to \infty$ or, better, find the correction explicitly for large but finite N. Hint: expand the exponential of the cubic correction using $e^\epsilon \simeq 1 + \epsilon + \epsilon^2/2$, $\epsilon \ll 1$. Think if quartic corrections will have a comparable contribution.*

2.2 Functions of 2 and more variables

2.2.1 Exact and nonexact differentials

Let us construct

$$dF = X(x, y)dx + Y(x, y)dy \tag{2.5}$$

The integral along a path (I)

$$\int_{(I)} dF$$

can depend on the entire path, or only on the initial and final points. In the latter case, one calls dF an *exact* differential.

For an exact differential,

$$\frac{\partial X}{\partial y} = \frac{\partial Y}{\partial x} \tag{2.6}$$

Theorem (no proof) In 2D there always exists an integrating factor $g(x, y)$ so that gdF becomes an exact differential, even if dF is not.

Future examples:

Nonexact differentials: dQ (heat), dW (work). Exact: dS (entropy), dE (energy), etc. One of the many versions of the 2d Law is that $1/T$ is an integrating factor for dQ (i.e. that $dQ/T = dS$ is an exact differential).

HW: *Let* $dF = -y\,dx + x\,dy$. *(a) check for exactness; (b) integrate along a path* $(x_1\,,\,y_1) \;\rightarrow\; (x_1\,,\,y_2) \;\rightarrow\; (x_2\,,\,y_2)$*; (c) integrate along a path* $(x_1\,,\,y_1) \;\rightarrow\; (x_2\,,\,y_1) \;\rightarrow\; (x_2\,,\,y_2)$*; (d) find an integrating factor for* dF*. [Hint: look for something simple, like* x^α*].*

2.2.2 Legendre transformations

Given a function of two variables

$$df = \frac{\partial f}{\partial x}\,dx + \frac{\partial f}{\partial y}\,dy \equiv u\,dx + v\,dy \tag{2.7}$$

change the differentials from dx and dy to du and dy with the transformation

$$g \equiv f - ux \tag{2.8}$$

$$dg = df - u\,dx - x\,du = u\,dx + v\,dy - u\,dx - x\,du = v\,dy - x\,du$$

Now,

$$x \equiv -\frac{\partial g}{\partial u}\;,\quad v \equiv \frac{\partial g}{\partial y}$$

HW: *Let* $L(x, v) = mv^2/2 - U(x)$*. Using Legendre transformations construct* $-H(x, p)$ *with* $p = \partial L/\partial v$*. (A "-" here is just a convention).*

HW: *Let* $dE(S, V) = TdS - pdV$*. Construct* $F(T, V)$ *with*

$$dF = -SdT - pdV$$

2.2.3 Homogeneous functions

Homogeneous function of the order n:

$$f\left(\lambda x_1\ ,\ \lambda x_2\ , \ldots\ , \lambda x_N\right) = \lambda^n f\left(x_1\ ,\ x_2\ , \ldots\ , x_N\right) \tag{2.9}$$

$$\sum_i^N x_i \frac{\partial f}{\partial x_i} = nf \tag{2.10}$$

("Euler theorem")

HW: *Proove this. Hint: use $\lambda = 1 + \epsilon$ with $\lambda^n \simeq 1 + n\epsilon$.*

Preview. Why important in physics?

in mechanics: kinetic energy K is a homogeneous function of velocities with $n = 2$ (even in generalized, non-Cartesian coordinates!); important when conservation of energy is introduced

in motion of charged particles (or planets): potential energy U is a homogeneous function of coordinates with $n = -1$; this leads, e.g., to $\bar{K} = -\frac{1}{2}\bar{U}$, an important consequence of the virial theorem

in thermodynamics: extensive variables $n = 1$ (energy, etc.) and intensive $n = 0$ (T or p). Important in many cases, e.g. for solutions one has homogeneous functions of $N_1\ ,\ N_2\ , \ldots$, the numbers of molecules, and the Euler theorem leads to famous Gibbs-Duhem equations, though better known to chemists.

2.3 Variational principles

2.3.1 The Euler equation

Consider

$$J = \int_{x_1}^{x_2} f\left(y, y', x\right)\, dx \tag{2.11}$$

$y(x)$ - unknown(!); $J = \min$ (or, max).

Suppose, we know $y(x)$. Let us perturb it a bit:

$$y(x, \alpha = 0) = y(x)\ ,\quad y(x, \alpha) = y(x, 0) + \alpha\eta(x)$$

Now

$$J = J(\alpha)$$

Since $\eta(x)$ is arbitrary, to ensure a $J(\alpha) = \min$, one needs:

$$\frac{d}{dx}\frac{\partial f}{\partial y'} - \frac{\partial f}{\partial y} = 0 \tag{2.12}$$

These are Euler equations (Lagrange in mechanics - see below). Three major simplifications:

- no y-dependence

  $$\frac{\partial f}{\partial y'} = const \tag{2.13}$$

  ("momentum conservation")

- no explicit x-dependence:

  $$f - y'\frac{\partial f}{\partial y'} = const \tag{2.14}$$

  related to energy conservation in mechanics

- no y'-dependence

  $$\frac{\partial f}{\partial y} = 0 \tag{2.15}$$

  (thermodynamics).

Examples: minimal surfaces

2.3.2 Generalizations: several variables

several dependent variables $y_1\ ,\ y_2\ ,\ldots$
A separate Euler equation for each variable, often written in vector form:

$$\frac{d}{dx}\frac{\partial f}{\partial \vec{y}\,'} - \frac{\partial f}{\partial \vec{y}} = 0 \tag{2.16}$$

(with prime, as before, indicating the derivative with respect to the independent variable, x).

several independent variables $x_1\ ,\ x_2\ ,\ldots$

$$\sum_j \frac{\partial}{\partial x_j}\frac{\partial f}{\partial y'_{x_j}} - \frac{\partial f}{\partial y} = 0 \tag{2.17}$$

Example: Laplace equation

2.3.3 "undetermined" Lagrange multipliers

Suppose we want to find a maximum of J with an additional constraint

$$\int \phi\left(y, y', x\right) dx = 0$$

Then, construct

$$g = f + \lambda\phi$$

and get regular Euler equations for g, which will contain however a yet unknown λ. Those equations can be solved together with the constraint equation. If necessary, λ also can be determined.

HW: *Consider a line $y(x)$ with $y(\pm 1) = 0$, with a fixed area $\pi/2$ and min length (semicircle). (a) Write down the Euler equations. (b) (optional) solve them.*

2.4 Elements of probability theory and stochastic processes

2.4.1 Probability and probability density

Let x - discrete random variable, with possible values x_1, x_2, etc. Then

$$\sum_m P\left(x_m\right) = 1$$

$$\bar{f} \equiv \langle f\rangle = \sum_m f\left(x_m\right) P\left(x_m\right)$$

$$\sigma^2 \equiv \left\langle x^2\right\rangle - \bar{x}^2$$

which is the second central moment.
HW: show that

$$\left\langle (x-\bar{x})^2\right\rangle = \left\langle x^2\right\rangle - \bar{x}^2$$

Examples: Bernoulli, Poisson (below) and Binomial (later)
Poisson distribution, $0 \le m < \infty$:

$$P(m, a) = \frac{1}{m!} e^{-a} a^m \tag{2.18}$$

HW: *check normalization*

$$\bar{m} = a, \langle m^2 \rangle = a^2 + a$$

thus $\sigma^2 = a$ **HW**: *check this*

Let x - continuous random variable,

$$\int p(x)dx = 1$$

$$\bar{f} = \int f(x)p(x)dx$$

Examples:

- uniform:

$$p(x) = 1 \ , \quad 0 < x < 1 \tag{2.19}$$

  and $p(x) = 0$ otherwise. (computer random number generators are done like that).

- Gaussian

$$p_G\left(x, a, \sigma\right) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-a)^2}{2\sigma^2}\right] \tag{2.20}$$

  HW: *show that for Gaussian*

$$\bar{x} = a$$

and

$$\left\langle (x-\bar{x})^{2n} \right\rangle = \frac{1}{\sqrt{\pi}} \left(2\sigma^2\right)^n \Gamma(n+1/2)$$

2.4.2 Transformation of variables

$$x \to y \ , \quad p(x) \to P(y) = p(x)\frac{dx}{dy}$$

$$\int P(y)dy = 1$$

HW: *write Gauss distribution for $y = (x-a)/\sigma$* **HW**: *consider a one-dimensional distribution $p(v) \sim \exp\left(-mv^2/(2kT)\right)$ ("Maxwell distribution"). (a) Calculate the proportionality factor; (b) write the distribution $P(\epsilon)$ in terms of energy $\epsilon = mv^2/2$.*

2.4.3 Several random variables and statistical independence

Consider $p\,(x_1\,, x_2)$ with

$$\int\int p\,(x_1\,, x_2)\; dx_1\, dx_2 = 1$$

Two random variables are statistically independent if

$$p\,(x_1\,, x_2) = p_1\,(x_1)\, p_2\,(x_2)$$

Then,

$$\langle x_1^m x_2^n \rangle = \langle x_1^m \rangle \, \langle x_2^n \rangle$$

2.4.4 Binomial distribution

Consider a "loaded" coin with unequal probabilities of heads and tails, p and $q = 1 - p$. Then, probability to get m heads is

$$P_m^{bin} = C_n^m p^m q^{n-m} \tag{2.21}$$

see Fig. 2.1.

HW: *(a) verify normalization*

$$\sum_{m=0}^{n} P_m^{bin} = 1$$

(b) show that

$$\bar{m} \equiv \sum_{m=0}^{n} m P_m^{bin} = pn \tag{2.22}$$

2.4.5 Limits of the binomial distribution

2.4.6 Poisson

Consider $n \to \infty$, $p \to 0$ with fixed $\bar{m} = pn$. Then,

$$P_m^{bin} \approx \frac{n!}{(n-m)!\, n^m} \frac{\bar{m}^m}{m!} \left(1 - \frac{\bar{m}}{n}\right)^n = \frac{\bar{m}^m}{m!} e^{-\bar{m}} \tag{2.23}$$

which is the Poisson distribution, P_m. See Fig. 2.2.

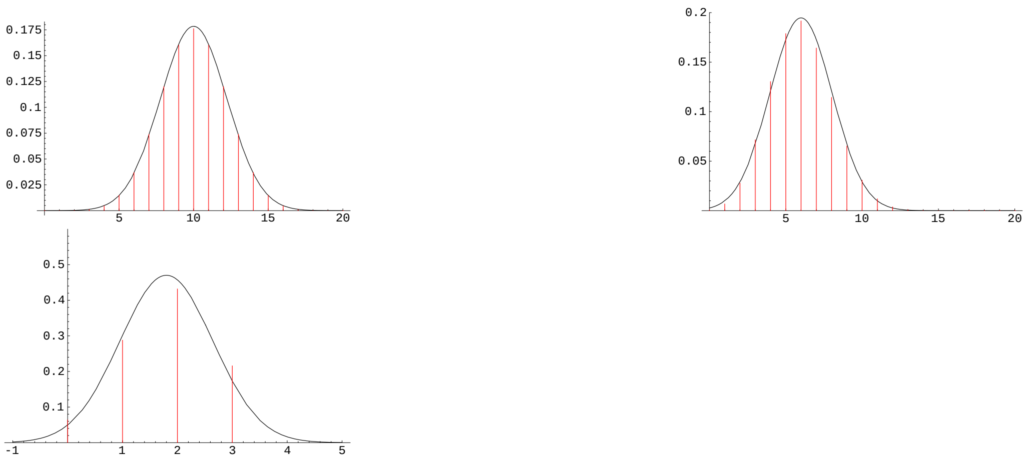

Figure 2.1: Binomial probability function and approximation of the results by a gaussian curve for $n = 20\,, p = 1/2$ (left, unbiased), $n = 20\,, p = 0.3$ (middle, biased) and $n = 3\,, p = 0.6$ (right). The approximation becomes exact for $n \to \infty$ ("Limit theorem of de Moivre and Laplace") but in practice is good starting from very modest n.

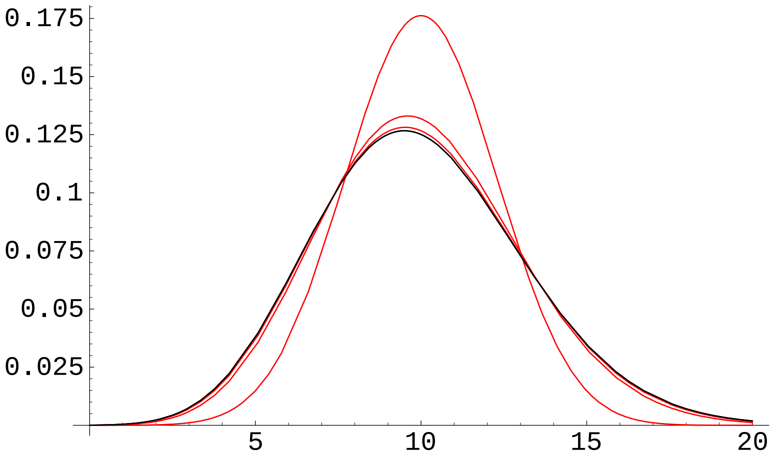

Figure 2.2: Poisson distribution P_m (black) for $\bar{m} = 10$ and binomial distributions P_m^{bin} (red) with different n and $p = \bar{m}/n$. From top to bottom: $n = 20$, $n = 100$ and $n = 400$ (which practically blends with the Poisson curve)

2.4.7 Normal

Alternatively, let m be close to the average $n/2$ for $p = q = 1/2$. We will use

$$x = 2m - n$$

and further switch to scaled

$$y = x/\sqrt{n} \sim 1$$

(with this the distribution is multiplied by $\sqrt{n}$ to ensure normalization). This leads to Gaussian. Major steps:

- use Stirling approximation

$$n! \simeq \sqrt{2\pi n}\,(n/e)^n \ , \quad n \gg 1 \tag{2.24}$$

  for *both* $n!$ and $(n-m)!$

- replace m by $(n + y\sqrt{n})/2$ (and multiply by $\sqrt{n}/2$ to ensure normalization).

- Take the limit $n \to \infty$

-

$$P^{gauss}(y) = \frac{1}{\sqrt{2\pi}} e^{-y^2/2} \tag{2.25}$$

HW: *(a) reproduce in detail every step of the derivation; (b) derive normal distribution from Poisson when $\bar{m} \gg 1$; (c) (optional) derive normal distribution for $p \neq q \neq 1/2$*

2.4.8 Non-trivial example: fluctuation of number of particles in an ideal gas

Consider a large number n of non-interacting particles in a large (blue) box, as in Fig. 2.4. Particles are randomly distributed. The average number of particles, $\bar{m}$, in a selected small (red) counting box is

$$\bar{m} = n/k$$

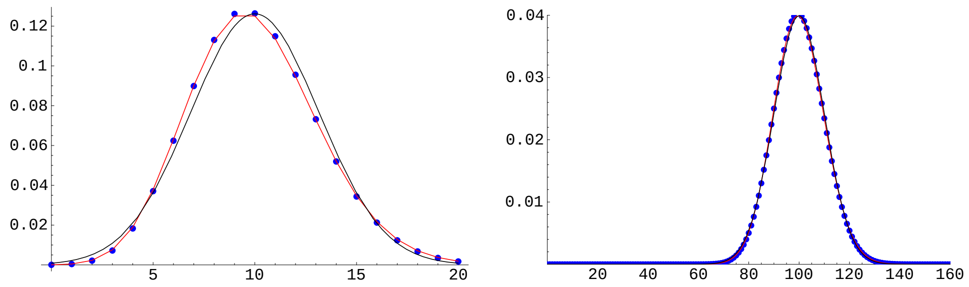

Figure 2.3: Exact binomial distribution with $p = 1/50$ for $\bar{m} = 10$ (left, $n = 500$) and $\bar{m} = 100$ (right, $n = 5000$) shown by symbols. Red line - Poisson distribution (works for any $\bar{m}$); black line - Gauss distribution, which is accurate for large $\bar{m}$. Note that for larger $\bar{m}$ the distribution broadens, but becomes narrow on a relative scale $m/\bar{m}$, approaching a δ-function for $\bar{m} \to \infty$.

where k is the number of red boxes. Unlike n, the value of $\bar{m}$ does not have to be large or integer. However, the actual number of particles can be different from $\bar{m}$. What is the probability to get exactly m particles in a red box?

If the total (blue) volume is V and the "red" volume is v, the probability for a selected particle to get into the box is

$$p = v/V = \bar{m}/n$$

For m particles the probability for each to get inside is p^m, and the exact expression is

$$p_m = C_n^m p^m (1-p)^{n-m}$$

i.e. the binomial distribution. This depends, on the blue box, but intuitively if this box is large, it should not matter. Indeed, for $n, V \to \infty$ (with n/V fixed) one gets a Poisson distribution

$$p_m \simeq \frac{1}{m!} e^{-\bar{m}} \bar{m}^m$$

This is rather accurate - see Figs. 2.3. Further, for $\bar{m} \gg 1$ the gaussian is approached with

$$\sigma^2 = \bar{m}$$

HW: *under normal conditions there are about* $2.7 \cdot 10^{19}$ *molecules in 1* cm^3 *of a gas. ("Loshmidt number"). Consider a tiny volume of, say* $1\,mm^3$. *(a) find*

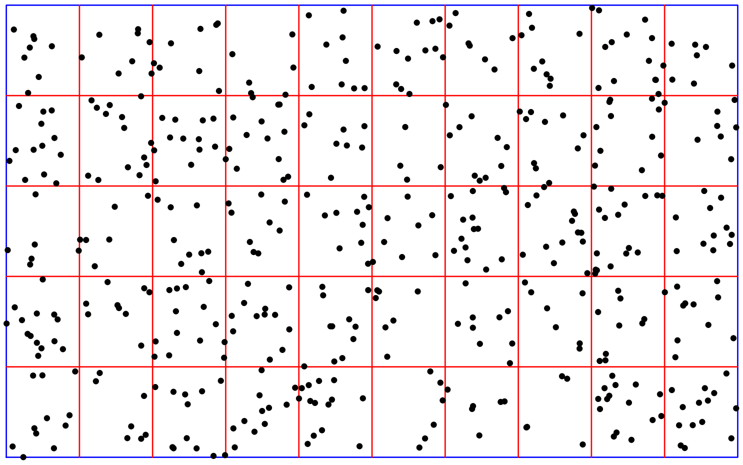

Figure 2.4: 500 non-interacting particles randomly distributed in a large (blue) box. Probability to find exactly m particles in a selected red box is given by a binomial distribution. If the outer blue box becomes very large (while density of particles remains the same) a Poisonnian distribution is approached which depends only on $\bar{m}$, the average number of particles in a red box. For $\bar{m} \gg 1$ the distribution is Gaussian, narrowly peaked around the average value. (see the homework example).

the average number of molecules (b) what is the probability to get $10,000$ *more molecules than the average? (c) what is the probability to get* 0.01% *more than the average number? (d) repeat for a smaller volume of* $1\,\mu m^3$.

HW: *consider* $k = 2$, *the blue box is divided in just two red boxes but* n *is large. Consider the difference in the number of particles in the two boxes. The Poisson distribution will not work here, but the Gauss will work if this difference is much smaller than* n. *Find the Gaussian, compare with exact.*

2.4.9 Random walk and evolution equations

Consider a random walk

$$x_{n+1} = x_n + \zeta$$

with $\zeta = \pm 1$ being a random variable.

The evolution equation Consider a very large number N of statistically identical ensembles. Then, at a given "time" t (number of random walk steps) one can talk about the "distribution function" $f_k(t)$, with f_k/N corresponding to probability. One has

$$\begin{aligned} f_k(t+1) &= f_k(t) + \frac{1}{2} f_{k-1}(t) + \frac{1}{2} f_{k+1}(t) - f_k = \\ &= f_k(t) + D\left[f_{k-1}(t) + f_{k+1}(t) - 2f_k(t)\right]\ ,\quad D = 1/2 \end{aligned} \tag{2.26}$$

Since this equation is linear, an identical equation will hold for the probability $p_k(t)$ to occupy a given position k. The equation of this kind is known as the "evolution" or 'master" equation. It is exact, but we re-arranged it to simplify the following transition.

Considering $f_k(t)$ as a smooth function of both t and k, one has (with k replaced by x)

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2} \tag{2.27}$$

The solution ("Greens function") is given by

$$G(x,t) = \frac{1}{2\sqrt{\pi D t}} \exp\left\{-\frac{x^2}{4Dt}\right\} \tag{2.28}$$

which is a Gaussian with zero average and with

$$\sigma = \sqrt{Dt}$$

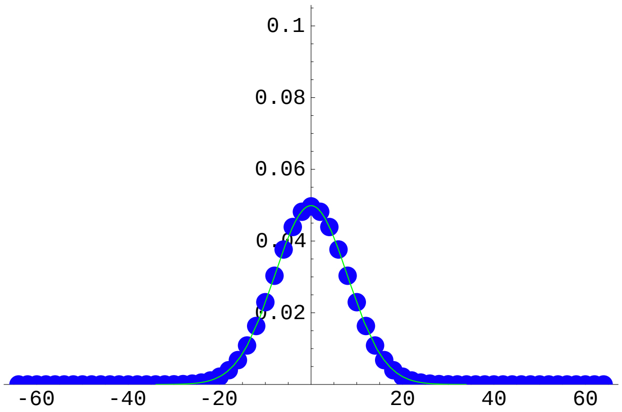

Figure 2.5: Non-biased random walk (points) and the diffusion approximation

HW: consider proper physical units, i.e. random walk with step a and $t = \tau n$. Re-write the results.

Exact description

For this specific problem an exact description is possible, so that the diffusion approximation can be verified. Consider a total of n steps with equal probabilities of 1/2 to go right or left. If there were m steps to the right (and $n-m$ steps left) there will be a total displacement of $m-(n-m) = 2m-n$ steps. Since the steps are taken in any order, there will be

$$C_n^m = \frac{n!}{m!(n-m)!}$$

possibilities to do that (again a binomial distribution!). All in all, there will be 2^n outcomes of n steps, so that

$$\frac{1}{2^n} C_n^m$$

will give the exact probability of going $2m-n$ to the right from origin.

Correspondence of the diffusion approximation with the exact solution is excellent - see Fig. 2.5 (however, a log plot would reveal that tails are not described that accurately. Why?)

Thus, the diffusion equation is a good approximation for random walk. More generally, it is an example of a continuous time evolution equation,

2.4.10 Information entropy

Consider a system which can be in one of the Γ states with $\Gamma \gg 1$. The probability to be in state i is p_i. Then,

$$S = -k \sum_{i=1}^{\Gamma} p_i \ln p_i \tag{2.29}$$

with

$$k \equiv k_B = 1.38 \cdot 10^{-23} J/{}^o K$$

Note that this is just a formal mathematical definition. It turns out, however, that this information entropy is extremely close to the one used in thermodynamics.

Maximization of entropy with constrains
We use Lagrange multipliers α, β, etc.

- "microcanonical"

$$\sum_{i=1}^{\Gamma} p_i = 1$$

and

$$-\sum_{i=1}^{\Gamma} [p_i \ln p_i - \alpha p_i] = \max$$

Thus,

$$\ln p_i + 1 - \alpha = 0$$

or

$$p_i = const = 1/\Gamma \ , \quad S_{\max} = k \ln \Gamma$$

- "canonical"

$$\sum_{i=1}^{\Gamma} p_i = 1 \ , \quad \bar{x} \equiv \sum_{i=1}^{\Gamma} x_i p_i = x_0$$

Now,

$$-\sum_{i=1}^{\Gamma} [p_i \ln p_i - \alpha p_i + \beta p_i x_i] = \max$$

Thus,

$$\ln p_i + 1 - \alpha + \beta x_i = 0$$

or

$$p_i = \frac{1}{Z(x)} \exp\left(-\beta x_i\right)$$

with

$$Z(x) = \sum_i \exp\left(-\beta x_i\right)\ , \quad S_{\max} = k \ln Z + k\beta x_0$$

So far, we leave the Lagrangian multipliers undetermined. In physics, if x_i are energy levels, with $\beta = 1/kT$ we get the Gibbs distribution.

HW: *show that*

$$x_0 = -\frac{\partial \ln Z}{\partial \beta}$$

Continuous variable:

$$S = -k \int p(x) \ln p(x)\, dx \tag{2.30}$$

Note: the units for $p(x)$ in eq. (2.30) are 1/over units of x. Thus, S will get a constant when we switch to new units. Usually this does not matter since the change of entropy is of interest, but should be kept in mind. *Preview: In physics, x is multidimensional, with dx corresponding to the product of $d\vec{r}_i d\vec{p}_i$. To make things dimensionless, $\hbar^N$ has to be introduced, even if otherwise the problem is classical.*

HW: Calculate S for the Gauss distribution

HW: using the constrains

$$\int_{-\infty}^{\infty} p(x)\, dx = 1\ , \quad \int_{-\infty}^{\infty} x^2 p(x)\, dx = \sigma^2$$

find the distribution which leads to maximum of S (it is very similar to the discrete case, but you need to actually evaluate the Lagrange multipliers.

Growth of entropy

$$\frac{dS}{dt} \geq 0 \tag{2.31}$$

HW: consider the evolution with time of the random walk entropy in the diffusion approximation (with $p(x,t)$ given by the Green's function)

What would it mean if eq.(2.31) would be violated? Either the definition of entropy or the evolution equations would be bad. Let us show that the diffusion evolution equation is "good":

$$\frac{1}{k}\frac{dS}{dt} = -\int \frac{d}{dt}\left(p\ln p\right)\,dx = -\int \dot{p}\left(\ln p + 1\right)\,dx = \tag{2.32}$$
$$-\int \dot{p}\ln p\,dx = -D\int \frac{\partial^2 p}{\partial x^2}\ln p\,dx = D\int \left(\frac{\partial p}{\partial x}\right)^2 \frac{1}{p} \geq 0$$

Note in open space diffusion always leads to increase of entropy. In a closed "volume" - length L in 1-dimensional, entropy is maximum for $p(x) = const = 1/L$, achieved as $t \to \infty$.

2.4.11 Relation to physical entropy

There is nothing wrong with the formal definition of the information entropy, but the examples do not emphasise the fact that the number of states Γ in the definition is incredibly large and rapidly increases with the size of the system. [we know from thermodynamics that entropy linearly increases with size, while in the examples dependence appears logarithmic(?)].

In reality Γ is not the number of particles N, but the number of states, which is much larger, of the order of $N!$. Let us estimate Γ for the familiar "physical" problem - n particles in a box partitioned into m chapters. Naturally, we expect $n \gg m \gg 1$. The number of states can be approximated using the Stirling formula

$$\Gamma = \frac{(n+m)!}{m!n!} \sim (1+m/n)^{m+n}\left(\frac{n}{m}\right)^m \tag{2.33}$$

HW: *Show that. Neglect all non-exponential factors, such as $\sqrt{2\pi n}$. Show that this is a large number whether n is larger or smaller than m.*

Now from the "microcanonical" example

$$S/k = \ln\Gamma = (m+n)\ln\left(1+m/n\right) + m\ln\frac{n}{m}$$

If the big box will be doubled in size, with the same density of particles and the same size of partitions, S will double as well - exactly what we need from entropy!

Chapter 3

Mechanics

3.1 Newton's equations

$$m_i \ddot{\vec{r}}_i = \vec{F}_i \left(\vec{r}_1 \,, \vec{r}_2 \,, \dots \,, \vec{r}_N \,,\ \dot{\vec{r}}_1 \,, \dot{\vec{r}}_2 \,, \dots \,, \dot{\vec{r}}_N \,, t \right) \tag{3.1}$$

Conservation laws (closed system):

$$K + U = const \,, \quad \vec{P} = const \,, \quad \vec{L} = const \tag{3.2}$$

Center of mass

$$\vec{R} = \frac{1}{M} \sum_{i=1}^{N} m_i \vec{r}_i \,, \quad M = \sum_{i=1}^{N} m_i \tag{3.3}$$

Momentum:

$$\vec{P} = \sum_{i=1}^{N} m_i \vec{v}_i = M \dot{\vec{R}} \equiv M \vec{V} \tag{3.4}$$

Kinetic energy:

$$K = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 = \frac{1}{2} M V^2 + \sum_{i=1}^{N} \frac{1}{2} m_i \left(\vec{v}_i - \vec{V} \right)^2 \tag{3.5}$$

HW: show this

Note an important difference: $\vec{P}$ is *only* the CM motion, while energy also includes motion relative to the CM. Thus, in a collision of solid bodies $(N \to \infty)$ $\vec{P}$ is conserved, but energy can be re-distributed over a large amount of microscopic motions, and thus "lost" from a macroscopic point of view. (i.e., formally energy is there, but it cannot be used to get any work, just leading to heating of the two bodies involved in an inelastic collision).

3.2 Lagrange equation

$$\mathcal{L}\left(\vec{q},\ \dot{\vec{q}},\ t\right) = K - U \tag{3.6}$$

$$\text{action} = \int_{t_1}^{t_2} \mathcal{L} d\, t \tag{3.7}$$

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_i} = \frac{\partial \mathcal{L}}{\partial q_i} \tag{3.8}$$

Compared to Newton's equations:

- (advantage) deal with scalars ($\mathcal{L}$), not vectors ($\vec{F}$), thus easy to change coordinates
- (advantage) in problems with constrains forces which do not work also do not enter into the equations (e.g., pendulum)
- (advantage) conservation laws - "automatic". If q_i does not enter $\mathcal{L}$ then the component of a "generalized momentum"

  $$p_i \equiv \frac{\partial \mathcal{L}}{\partial \dot{q}_i} = const \tag{3.9}$$

  If no explicit time in $\mathcal{L}$, then

  $$\sum_i \dot{q}_i \frac{\partial \mathcal{L}}{\partial \dot{q}_i} - \mathcal{L} = const \tag{3.10}$$

  (if quadratic dependence of K on $\dot{q}_i$ and U does not depend on $\dot{q}_i$ then regular energy conservation $K + U = const$)

- (advantage) can be generalized beyond classical mechanics (relativistic and quantum); the variational formulation especially convenient
- (disadvantage) hard to deal with empirical forces (e.g. friction) which do not comply with energy conservation

HW: *First application of Euler's homogeneous function: show that eq.(3.10) indeed corresponds to regular energy conservation if K is a quadratic function of $\dot{q}_i$ and U is independent of $\dot{q}_i$*

Example: Physical pendulum

1st method:

$$\mathcal{L} = \frac{1}{2} m l^2 \dot{\theta}^2 + mgl \cos\theta$$

Thus,

$$ml^2 \ddot{\theta} + mgl \sin\theta = 0$$

2d method ("undetermined" Lagrange multipliers):

$$\mathcal{L} = \frac{1}{2} m \left(\dot{r}^2 + r^2 \dot{\theta}^2 \right) + mgr \cos\theta + \lambda (l - r)$$

Thus (3 equations),

$$r^2 \ddot{\theta} + mgr \sin\theta = 0$$

$$\ddot{r} + \lambda - mg \cos\theta - mr\dot{\theta}^2 = 0$$

$$l - r = 0$$

Thus, same equation for θ and $\lambda = mg\cos\theta + mr\dot{\theta}^2$ (force!)

3.2.1 Vibration of molecules

Index-free notations Familiar:

$$\vec{a} \cdot \vec{b} = \sum_i a_i b_i \tag{3.11}$$

Thus can construct more complex expressions with every one $\cdot$ corresponding to summation (convolution) with respect to one dummy index. E.g., if $\hat{M}$ is a matrix ("tensor of the 2d rank"), then $\hat{M} \cdot \vec{a}$ is a vector ("tensor of the 1st rank") with components

$$\left(\hat{M} \cdot \vec{a} \right)_k = \sum_i M_{ki} a_i$$

or (not the same thing!)

$$\left(\vec{a}\cdot\hat{M}\right)_k = \sum_i a_i M_{ik}$$

I.e. a dot $\cdot$ reduces the rank of a tensor by 1. Double summation is also possible leading to a scalar ("tensor of the 0th rank"):

$$\vec{a}\cdot\hat{M}\cdot\vec{b} = \sum_{i,k} a_i M_{ik} b_k \tag{3.12}$$

Instead of "inner product" given by $\cdot$ (which reduces the rank of a tensor) one also can get an "outer product" which increases the rank. E.g., out of two vectors $\vec{a}$ and $\vec{b}$ can construct a matrix $C_{ik} = a_i b_k$, or

$$\hat{C} = \vec{a}\otimes\vec{b} \equiv \vec{a}\,\vec{b}$$

(we will use the latter notation, with no symbol between two side-by side vectors for the outer product; other options, e.g. $\wedge$ are also used in mathematical papers). Note that gradient of a scalar function Φ

$$\frac{\partial}{\partial\vec{u}}\Phi$$

is also a vector. Thus,

$$\frac{\partial}{\partial\vec{u}}\frac{\partial}{\partial\vec{u}}\Phi$$

will represent a matrix of the second derivatives or "Hessian".

Molecules

Let a set of 3D vectors $\vec{r}_n(t)$ $(n = 1,\ldots,N)$ determine the positions of atoms in a molecule, with r_n^0 being the equilibrium positions. We define a multidimensional vector

$$\vec{u}(t) = \left(\vec{r}_1 - \vec{r}_1^{\,0}\,,\ \ldots\ ,\vec{r}_N - \vec{r}_N^{\,0}\right) \tag{3.13}$$

With small deviations from equilibrium, both kinetic and potential energies are expected to be quadratic forms of $\dot{\vec{u}}$ and $\vec{u}$:

$$K = \frac{1}{2}\dot{\vec{u}}\cdot\hat{M}\cdot\dot{\vec{u}} > 0 \tag{3.14}$$

$$U = \frac{1}{2}\vec{u}\cdot\hat{k}\cdot\vec{u} \geq 0 \tag{3.15}$$

With $\hat{M}$ and $\hat{k}$ being the "inertial" and "elastic" matrix respectively:

$$\hat{M} = \frac{\partial}{\partial \dot{\vec{u}}} \frac{\partial}{\partial \dot{\vec{u}}} \mathcal{L} \tag{3.16}$$

$$\hat{k} = -\frac{\partial}{\partial \vec{u}} \frac{\partial}{\partial \vec{u}} \mathcal{L} \tag{3.17}$$

The Lagrange equations will have the form:

$$\hat{M} \cdot \ddot{\vec{u}} + \hat{k} \cdot \vec{u} = 0 \tag{3.18}$$

We look for a solution

$$\vec{u}(t) = \vec{u}_0 \exp{(i\omega t)} \tag{3.19}$$

which leads to

$$-\omega^2 \hat{M} \cdot \vec{u}_0 + \hat{k} \cdot \vec{u}_0 = 0 \tag{3.20}$$

Using the fact $\hat{M} > 0$ one can write

$$\hat{M}^{-1} \cdot \hat{k} \cdot \vec{u}_0 = \omega^2 \vec{u}_0 \tag{3.21}$$

so that ω^2 are eigenvalues of a matrix $\hat{M}^{-1} \cdot \hat{k}$ ("secular matrix"). Note that $\omega^2 \geq 0$, with zero values corresponding to non-vibrational motion (translation and rotation).

Normal coordinates

Once the secular equation is solved, one can find $3N$ generalized coordinates Q_α which are linear combinations of all $3N$ initial coordinates, so that

$$\mathcal{L} = \frac{1}{2} \sum_\alpha \left(\dot{Q}_\alpha^2 - \omega_\alpha^2 Q^2 \right) \tag{3.22}$$

We will not need much explicit Q_α, except for in examples - they determine shapes of characteristic vibrations - but rather the very fact that the above representation is possible. (*Preview:* we will need this in the equipartition theorem and when studying phonons)

HW: write explicit equations for $\ddot{Q}_\alpha$. Show that indeed you get oscillations with frequencies ω_α. What happens for $\omega_\alpha = 0$?

Example: diatomic molecule

$$\mathcal{L} = \frac{1}{2}\left(m_1\dot{x}_1^2 + m_2\dot{x}_2^2\right) - \frac{1}{2}k_1\left(x_2 - x_1\right)^2$$

A human way to solve the problem is to reduce the number of independent variables by fixing the center of mass:

$$x_2 = -\frac{m_1 x_1}{m_2}\ , \quad X = x_2 - x_1$$

Now

$$\mathcal{L} = \frac{1}{2}\mu\dot{X}^2 - \frac{1}{2}k_1 X^2$$

with

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{3.23}$$

with

$$\omega = \sqrt{\frac{k_1}{m}}$$

HW: *(a) solve the same problem using the matrix technique*
HW: *consider a hypothetical molecule with one atom of mass 1 amu (hydrogen) and the other 20 amu. The spring constant is $1000N/m$ and the equilibrium distance is $1\AA$*
a) find the frequency b) (optional) estimating the vibrational energy as $k_B T$, with T being the room temperature, find the amplitude of vibrations. Compare this to equilibrium distance - must be small in order to treat vibrations as harmonic.

Additional reading: Goldstein. Classical mechanics. A very good description of the matrix approach to molecular vibrations, without computer assistance (for that reason, also a bit too detailed for our purposes).

3.2.2 Rotation

A solid is characterized by a single angular velocity $\vec{\Omega}$ and

$$\vec{v} = \vec{\Omega} \times \vec{r}$$

Thus kinetic energy can be written as

$$K = \frac{1}{2}\int \rho\left(\vec{r}\right) v^2\left(\vec{r}\right) dV \tag{3.24}$$

with

$$\left(\vec{\Omega} \times \vec{r}\right)^2 = \Omega^2 r^2 - \left(\vec{\Omega} \cdot \vec{r}\right)^2$$

one gets

$$K = \frac{1}{2}\vec{\Omega} \cdot \hat{I} \cdot \vec{\Omega} \tag{3.25}$$

with

$$I_{ik} = \int \rho \left(r^2 \delta_{ik} - r_i r_k\right) dV \tag{3.26}$$

being the tensor of rotational inertia.
HW: *write a discrete analog of the above expression assuming nuclei of negligible size located at positions* $\vec{r}_\alpha$. *Note: in the above integral* r_i , r_k *correspond to* x, y, z *components, so be careful with notations*

Angular momentum:

$$\vec{L} = \hat{I} \cdot \vec{\Omega} \tag{3.27}$$

HW: *Show this. Hint:* $d\vec{L} = \rho \, dV \vec{r} \times \vec{v}$

Principal axes of rotation:

$$\hat{I} = \text{diag}\left\{I_1 \ , \ I_2 \ , \ I_3\right\} \tag{3.28}$$

$$K = \frac{1}{2}\left(\frac{L_x^2}{I_1} + \frac{L_y^2}{I_2} + \frac{L_z^2}{I_3}\right) \tag{3.29}$$

HW. Show that for a diatomic molecule with r being the separation between atoms

$$I = \mu r^2 \tag{3.30}$$

with μ being the reduced mass.
HW Consider HCl with $r \sim 1\mathring{A}$ (you can use a more accurate value). (a) find I; (b) estimating the rotational energy as $1/2 k_B T$, find Ω at room temperature. (c) Alternatively, use $L \sim \hbar \sim 10^{-34} J \cdot s$; find Ω.

HW: *Fill out the Table 3.1. Calculate the spring constants for* H_2, O_2 *and* NO

Molecule	$\hbar\omega/k_b$	$\hbar^2/(2k_bI)$
H_2		
O_2		
N_2		
HCl		
NO		

Table 3.1: Parameters of some diatomic molecules

3.2.3 Virial theorem

Consider n particles performing finite motion with potential energy being homogeneous function of the order α (e.g., $\alpha = 2$ for harmonic motion and $\alpha = -1$ for Coulomb/gravitational interactions). Since K is homogeneous function of $\vec{v}_a$ of the order 2 one has from Euler theorem

$$2K = \sum_{a=1}^{n} \vec{v}_a \cdot \frac{\partial}{\partial \vec{v}_a} K = \sum_{a=1}^{n} \vec{v}_a \cdot \vec{p}_a = \frac{d}{dt} \sum_{a=1}^{n} \vec{r}_a \cdot \vec{p}_a - \sum_{a=1}^{n} \vec{r}_a \cdot \dot{\vec{p}}_a \tag{3.31}$$

Now take the average with respect to time. Time derivative will give zero due to finite motion. With the Newtons equations

$$\dot{\vec{p}}_a = -\frac{\partial}{\partial \vec{r}_a} U$$

one has

$$2\langle K \rangle = \left\langle \sum_a \vec{r}_a \cdot \frac{\partial}{\partial \vec{r}_a} U \right\rangle = \alpha \langle U \rangle \tag{3.32}$$

(again, Euler theorem was used).

HW: *Express both average kinetic and potential energies through total energy* $E = K + U$

3.3 Hamilton's approach

The first example of Legendre transformations:

$$\mathcal{L}\left(\vec{q}, \dot{\vec{q}}, t\right) \rightarrow H\left(\vec{q}, \vec{p}, t\right) \tag{3.33}$$

with

$$\vec{p} = \frac{\partial}{\partial \dot{\vec{q}}} \mathcal{L} \tag{3.34}$$

Then,

$$H = \vec{p} \cdot \vec{q} - L \tag{3.35}$$

Now,

$$\dot{\vec{q}} = \frac{\partial}{\partial \vec{p}} H \ , \ \ \dot{\vec{p}} = -\frac{\partial}{\partial \vec{q}} H \tag{3.36}$$

3.3.1 Liouville's theorem

Preview: incompressible liquid

Consider a liquid with density ρ and velocity field $\vec{v}$, then the continuity equation is

$$\frac{\partial}{\partial t}\rho + \frac{\partial}{\partial \vec{r}} \cdot (\vec{v}\rho) = 0 \tag{3.37}$$

Now the the full derivative (together with the flow) is given by

$$\frac{D}{D\,t} = \frac{\partial}{\partial t} + \vec{v} \cdot \frac{\partial}{\partial \vec{r}} \tag{3.38}$$

The condition

$$\mathrm{div}\vec{v} \equiv \frac{\partial}{\partial \vec{r}} \cdot \vec{v} = 0 \tag{3.39}$$

is equivalent to

$$\frac{D\,\rho}{D\,t} = 0 \tag{3.40}$$

i.e. incompressible fluid.

The Theorem: *"Phase fluid" is incompressible.*

Indeed, consider a density

$$\rho\,(\vec{q},\ \vec{p})$$

Points move in the 6N-dimensional phase space with "velocities"

$$\vec{V} = (\dot{q}_1\ , \ldots\ , \dot{q}_{3N}\ , \dot{p}_1\ , \ldots\ , \dot{p}_{3N}) \equiv \left(\dot{\vec{q}},\ \dot{\vec{p}}\right) \tag{3.41}$$

From Hamilton's equations:

$$\mathrm{div}\vec{V} \equiv \frac{\partial}{\partial \vec{q}} \cdot \dot{\vec{q}} + \frac{\partial}{\partial \vec{p}} \cdot \dot{\vec{p}} = \frac{\partial}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} H - \frac{\partial}{\partial \vec{p}} \cdot \frac{\partial}{\partial \vec{q}} H = 0 \tag{3.42}$$

which is equivalent to incompressible fluid, i.e.

$$\rho\left(\vec{q}(t),\ \vec{p}(t)\right) = const \tag{3.43}$$

along the phase trajectory.

3.3.2 Numerical illustrations

See Figs. 3.1 and 3.2. The phase volume remains constant with time, but the shape gets more and more complicated, with mixing of phase points after a long time. At that point one has an urge to switch to statistical description.

3.4 Relativistic

$$H_{rel} = \sqrt{p^2c^2 + m^2c^4} + U \tag{3.44}$$

Limits :
slow

$$H_{rel} \rightarrow mc^2 + \frac{p^2}{2m} + U \tag{3.45}$$

fast

$$H_{rel} \rightarrow cp + U \tag{3.46}$$

HW: *estimate temperatures when the thermal enrgy kT is comparable to $2m_ec^2$ (creation of electron-positron pairs)*

HW: *(optional) consider a relativistic harmonic oscillator with $U(x) = 1/2m\omega^2x^2$. Plot a few representative phase trajectories for small and large values of kinetic energy $H_{rel} - mc^2$*

3.5 Limitations of classical mechanics in Statistics

Maxwell's demon and the Gibbs paradox
will be discussed in class

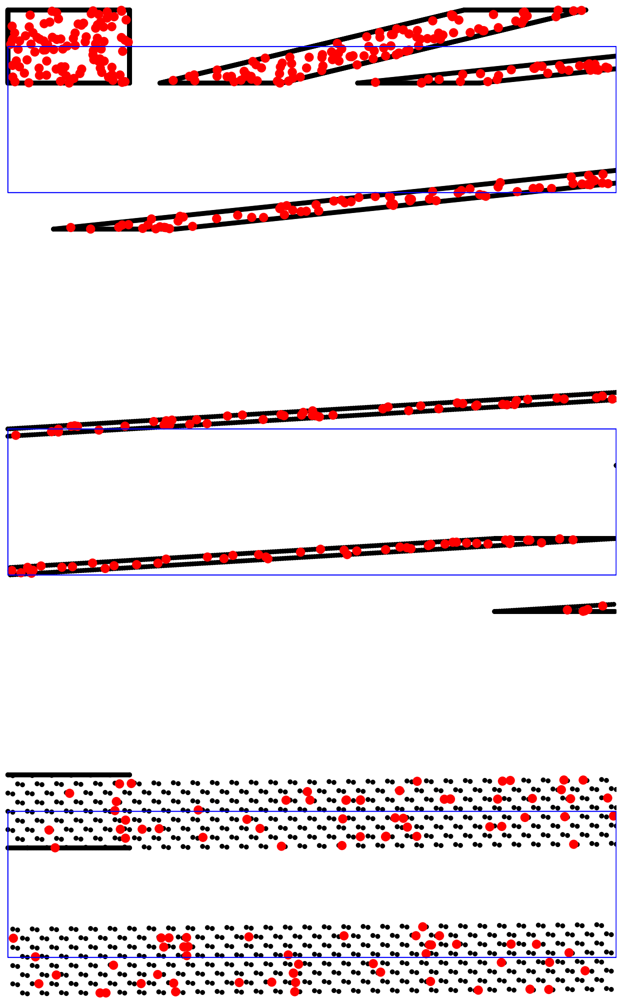

Figure 3.1: A one-dimensional particle between two mirrors ("billiard"). Length is 1, mass is 1 and momenta are distributed between 0, 25 and 0.75 (initial coordinates are between 0 and 0.2) (see *liouville.nb*). The blue line is a phase trajectory with $p(0) = 0.5$. Black particles are on the boundaries of the phase volume, and red particles are inside. Upper figure - evolution of the phase volume from $t = 0$ to $t = 2.4$. Middle figure - a snapshot at $t = 4$, and lower figure - a snapshot at $t = 32$. Note: in upper and lower figures (a) preservation of phase volume and (b) particles do not cross boundaries (thus density is *const* - Liouville's theorem); in the lower figure there is good mixing. Liouville's theorem is valid but is hard to track due to very fine boundary. [case (c) is extremely important for statistics]

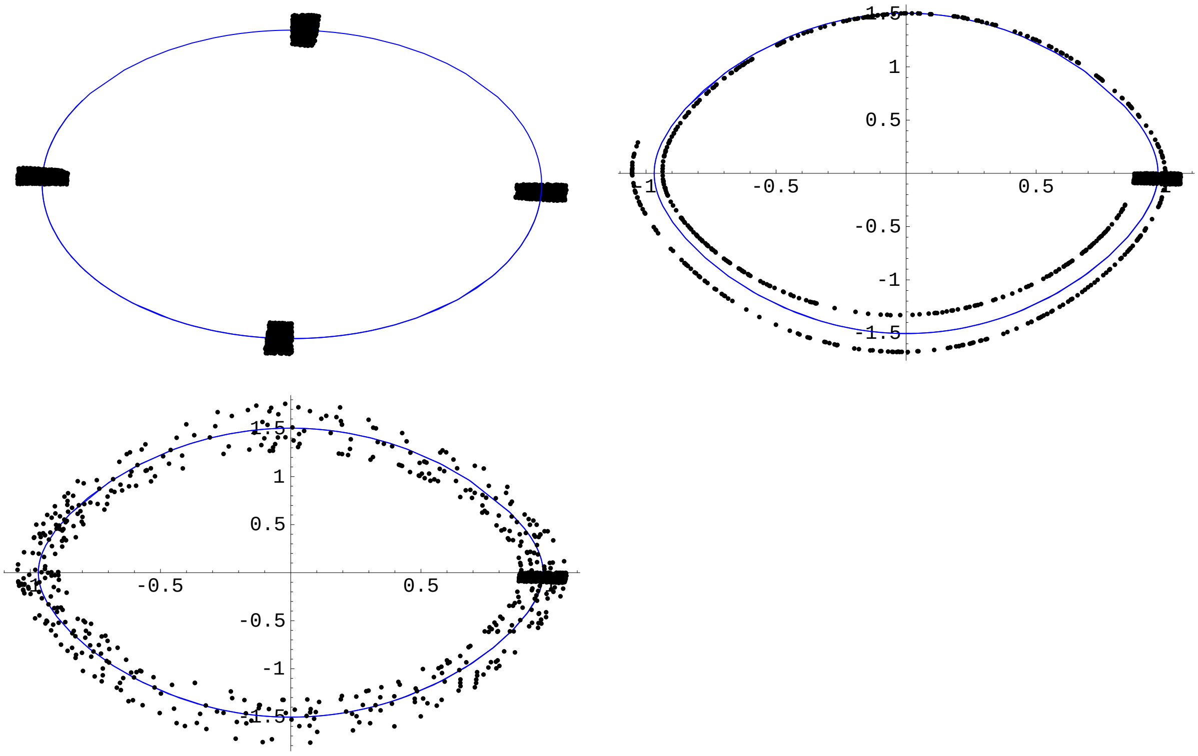

Figure 3.2: Harmonic oscillator (top) and anharmonic oscillator after about 10 (middle) and about 100 (lower figure) periods; the blue line is a phase trajectory of a selected point. See the *liouville.nb* with the description of parameters. The Liouville's theorem is always valid, but the non-spreading of phase points is an artifact of a harmonic oscillator. Otherwise, note good mixing of the phase space at long times.

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Chapter 4

Quantum Mechanics

4.1 Overview

We consider only quantum properties with immediate relevance to our goals. In most cases the key is the discrete spectrum. Note the following:

- discrete spectrum of electromagnetic radiation will be required for a correct description of its thermal equilibrium (Planck's formula)
- discrete spectrum of molecular vibrations and rotations is required when calculating statistical properties of non-monatomic gases
- The discrete spectrum of translational motion of molecules in macroscopic bodies is mostly an artificial construction - levels are so dense that there is absolutely no way to resolve them. Nevertheless even if only conceptual, consideration of such levels is crucial for a proper definition of entropy

Another essentially quantum aspect is the indistinguishable nature of particles, leading to Bose-Einstein or Fermi-Dirac statistics, depending on the spin.

Myth. The uncertainty principle, the absence of a particle trajectory and probability aspects of quantum mechanics explain statistical nature of matter. In reality, according to the Shrödinger equation, evolution of the wave function is fully deterministic; probability appears only when one interprets or predicts the results of measurements. If a state of a system can be described by wave function, it is purely mechanical, with zero entropy which remains as such upon further evolution.

4.2 Quantum properties of light (and other waves)

Energy

$$E_{ph} = h\nu = \hbar\omega \tag{4.1}$$

$$\hbar \simeq 1.055 \cdot 10^{-34} \; J \cdot s$$

$h = 2\pi\hbar$ This is also valid for other waves (phonons!)

Momentum:

$$\vec{p} = \hbar\vec{k}$$

or

$$p = h/\lambda$$

Note:

$$E_{ph} = cp \tag{4.2}$$

as classical. Similar for acoustic wave, with c being speed of sound.

Note: in many aspects waves behave like particles (with a different dispersion law), but there is an important difference for statistical mechanics: the number of such "particles" is not conserved. This will correspond to a zero chemical potential, as we discuss later.

4.3 Quasiclassical quantization

4.3.1 General

$$\oint p_i dx_i = 2\pi\hbar\,(n + \gamma_i) \;\;,\;\; 0 \leq \gamma_i < 1 \;,\;\; n = (0), 1, 2, \ldots \tag{4.3}$$

Strictly speaking, valid for $n \gg 1$, but often works for small n as well. See Fig. 4.1.

HW: use the quantization rules with $\gamma = 1/2$ to find levels of a harmonic oscillator

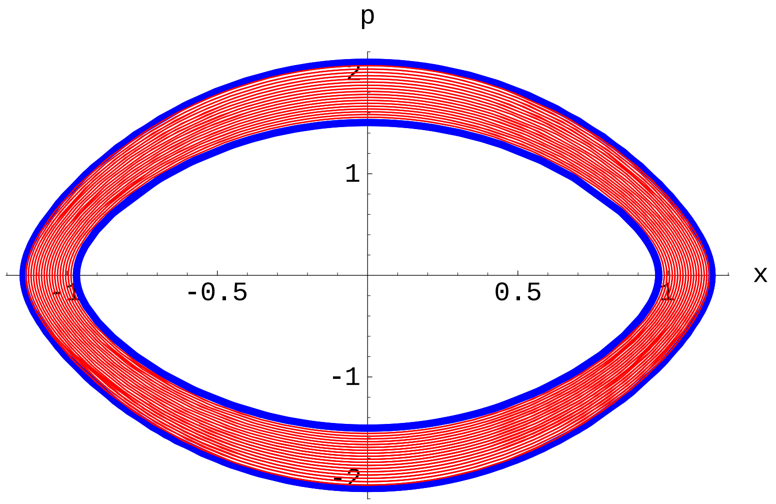

Figure 4.1: Quasiclassical quantization. Blue phase trajectories correspond to stationary energy levels. The red area between two close levels corresponds to $2\pi\hbar$.

4.3.2 Rotation

Start with Lagrangian (kinetic energy)

$$\mathcal{L} = \frac{1}{2} I \left(\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta \right)$$

Construct generalized momenta

$$p_\theta = I\dot{\theta} \; , \quad p_\phi = I\dot{\phi} \sin^2 \theta$$

Now construct a Hamiltonian

$$H = p_\theta \dot{\theta} + p_\phi \dot{\phi} - \mathcal{L} = \frac{1}{2I} \left(p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right)$$

HW: *Show this*

Since there is no ϕ-dependence $p_\phi = const$ or

$$\oint p_\phi \, d\phi = 2\pi p_\phi = \text{quasiclassical quantization} = 2\pi\hbar m$$

or

$$p_\phi = \hbar m \; , \quad m = 0, \pm 1, \ldots$$

For quantization of energy $E = H = const$ we use

$$p_\theta = \left(2EI - \frac{m^2\hbar^2}{\sin^2\theta}\right)^{1/2}$$

Now quantization looks like

$$2\pi\hbar n = 2\int_{-\theta_0}^{\theta_0} p_\theta \, d\theta$$

where θ_0 is the angle where $p_\theta = 0$. Switching to $w = \cos\theta$ the integral is reduced to

$$2\sqrt{2EI}\int_{-a}^{a} \frac{dw}{1-w^2}\left(a^2 - w^2\right)^{1/2} \;, \quad a^2 \equiv 1 - m^2\hbar^2/(2EI)$$

which gives

$$2\sqrt{2EI}\pi\left(1 - \frac{m\hbar}{\sqrt{2EI}}\right) = 2\pi\hbar n$$

introducing a new number $l = m + n$ one has

$$\sqrt{2EI} = l\hbar \;, \;\; \text{i.e.} \;\; E = \frac{\hbar^2}{2I} l^2$$

This is almost the correct value of $l(l+1)$. The values of m do not enter (degeneracy!) and their number is $2l+1$:

$$|m| \leq l$$

4.4 de Broglie wave

$$\lambda = \frac{h}{p} \;\; \text{or} \;\; \vec{k} = \vec{p}/\hbar \tag{4.4}$$

HW: find λ for an (a) $1eV$ electron, (b) a $1eV$ neutron, (c) a 0.1 mg dust particle with a speed 1 m/s.

Note: ANY p, including relativistic (!). Relation to energy: from

$$E_{rel} = \sqrt{c^2p^2 + m^2c^4}$$

Non-relativistic ($E = E_{rel} - mc^2$):

$$\lambda = \frac{h}{\sqrt{2mE}} \tag{4.5}$$

Relativistic: $m \to 0$, $p \to E/c$ and

$$\lambda = \frac{hc}{E} \tag{4.6}$$

This is exactly as for a photon:

$$E = h\nu \tag{4.7}$$

and

$$\lambda = c/\nu \tag{4.8}$$

Myth: for a good understanding of QM you always need the Shrödinger equation. No! In very many cases the de Broglie picture is sufficient, and allows for a deep analogy with optics.

4.4.1 Standing waves

Example (non-relativistic) Particle in a cubic box
in every direction

$$n\lambda/2 = a \ , \ \ n = 1, 2, \ldots \tag{4.9}$$

Thus,

$$E = \frac{\pi^2 \hbar^2}{2ma^2} \left(n_x^2 + n_y^2 + n_z^2\right) \ , \ \ n_x \ , \ n_y \ n_z = 1, 2, \ldots \tag{4.10}$$

Example (ultra-relativistic, or any wave). Wave in a cubic box
Same eq. (4.9), which is now just a classical wave equation (we consider a single polarization). Thus,

$$E = cp = \frac{2\pi c\hbar}{\lambda} = \frac{\pi c\hbar}{a} \cdot (n_x + n_y + n_z) \ , \ \ n_x \ , \ n_y \ , \ n_z = 1, 2, \ldots \tag{4.11}$$

Note degeneration of levels for $D > 1$.

HW: *Write a general relation for enrgy levels in a cubic box for a relativistic particle (not assuming limits)*

HW: *For a non-relativistic particle write enrgy levels for a rectangular box with sides A, B, C. Note: degeneracy is removed for $A \neq B \neq C$.*

4.5 The Shrödinger equation (SE)

4.5.1 What is Ψ?

M. Born:

$$|\Psi|^2$$

proportional to probability density. Two situations:

- infinite motion. In classics - $E > U(x)$ for all accessible x. Experimental - scattering problem.

$$\int |\Psi(x)|^2 \, dx = \infty$$

- finite motion. In classics - $E \geq U(x)$ only for a finite interval of x. Experimental - discrete energy levels.

$$\int |\Psi(x)|^2 \, dx = 1 \tag{4.12}$$

Note: in Statistics we will mostly discuss the 2d, discrete option. (Scattering is important, e.g. in non-ideal bose gas, but will not be considered in this part of the course.) Even for practically unlimited motion we will consider an artificial bounding "box" to make the spectrum discrete, and only then tend the size of the box to infinity, if necessary.

4.5.2 How to construct a SE?

The Hamilton operator

$$H = \frac{p^2}{2m} + U(x) \rightarrow \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x) \tag{4.13}$$

$$\hat{H}\Psi = i\hbar\frac{\partial \Psi}{\partial t} \tag{4.14}$$

Steady-state: fixed E

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{4.15}$$

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + [E - U(x)]\,\psi = 0 \tag{4.16}$$

Free particle: $U = 0$.

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + E\psi = 0$$

$$\psi(x) \propto e^{\pm ikx} \tag{4.17}$$

with $k = \sqrt{2mE}$. And

$$\Psi(x,t) \propto e^{\pm ikx - i\omega t}$$

with $\omega = E/\hbar$. Note: k, ω - very large(!)

Example. Discrete spectrum: $U(x) = 0$ for $0 < x < a$ and $U(x) = +\infty$ otherwise. (same as de Broglie waves).

4.5.3 Harmonic oscillator and molecular vibrations

$$U(x) = \frac{1}{2}m\omega^2x^2 \tag{4.18}$$

SE:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}m\omega^2x^2\right)\psi = 0 \tag{4.19}$$

or with $\zeta = x\sqrt{m\omega/\hbar}$,

$$\psi'' + \left(\frac{2E}{\hbar\omega} - \zeta^2\right)\psi = 0$$

here E must be discrete to satisfy

$$\int_{-\infty}^{\infty}\psi^2(x)dx < \infty$$

One has

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \tag{4.20}$$

Wave functions:

$$\psi_n \propto e^{-\zeta^2/2} H_n(\zeta) \tag{4.21}$$

with

$$\psi_0 \propto e^{-\zeta^2/2} \tag{4.22}$$

corresponding to the lowest energy state. Otherwise,

$$H_n(\zeta) = (-1)^n e^{\zeta^2} \frac{d^n e^{-\zeta^2}}{d\zeta^n}$$

HW: plot several ψ_n.

Molecular vibrations: almost classical - same set of ω_α. Some new features - degeneration due to symmetry in polyatomic molecules (will not need much) and tunneling in anharmonic vibrations, e.g. NH_3. [see E. Merzbacher, *Quantum Mechanics* for additional reading.]

4.6 Schrödinger equation in 3D: Quantization of angular momentum

4.6.1 The SE and separation of variables

The Hamilton operator

$$H = \frac{p^2}{2m} + U(\vec{r}) \to \hat{H} = -\frac{\hbar^2}{2m}\hat{\Delta} + U(\vec{r}) \tag{4.23}$$

$$\hat{\Delta} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\ , \quad \text{i.e.} \quad \hat{\Delta}\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \tag{4.24}$$

Look for a steady-state solution:

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}) \tag{4.25}$$

In spherical coordinates one has

$$\hat{\Delta} = \hat{\Delta}_r - \frac{1}{r^2}\hat{l}^2 \tag{4.26}$$

with $\hat{l}^2$ given by

$$\hat{l}^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{4.27}$$

$$\hat{\Delta}_r = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} \tag{4.28}$$

(although specific form of these operators mostly will not be required...)

First we use just spherical symmetry (but not specific $U(r)$). Look for

$$\psi\left(r,\theta,\phi\right) = R(r)Y\left(\theta,\phi\right) \tag{4.29}$$

From

$$\hat{\Delta}\psi + \frac{2m}{\hbar^2}\left[E - U(r)\right]\psi = 0 \tag{4.30}$$

$$Y\hat{\Delta}_r R - \frac{R}{r^2}\hat{l}^2 Y + (E-U)RY\frac{2m}{\hbar^2} = 0$$

Now divide both sides by RY and multiply by r^2:

$$\frac{r^2}{R}\hat{\Delta}_r R + \frac{2m(E-U)r^2}{\hbar^2} = \frac{1}{Y}\hat{l}^2 Y \tag{4.31}$$

Note that the l.h.s depends only on r while the r.h.s only on θ, ϕ. Thus, both sides should be a *const* $\equiv \lambda$. We thus achieved separation of variables using physical understanding of symmetry. The rest is math.

First consider

$$\hat{l}^2 = \lambda Y \tag{4.32}$$

now look for

$$Y\left(\theta,\phi\right) = \Phi(\phi) \times \Theta(\theta) \tag{4.33}$$

and repeat separation of variables. (*HW - do that*). Recall that key to discrete eigenvalues - BC. Periodicity in ϕ leads to

$$Y\left(\theta,\phi\right) = e^{im\phi} \times \Theta(\theta)\ , \quad m = 0, \pm 1, \pm 2, \ldots \tag{4.34}$$

(*HW - show that.*

For θ dependence harder (polynomials in $\cos\theta$, but pure math: Y_{lm} - spherical harmonics.

$$\hat{l}^2 Y_{lm} = l(l+1)Y_{lm} \tag{4.35}$$

Note no m - degeneracy of levels(!). (m - "magnetic quantum number", l - "orbital quantum number").

4.6.2 Angular momentum

$$\vec{L} = \vec{r} \times \vec{p} \to \hat{\vec{L}} = \frac{\hbar}{i} \vec{r} \times \nabla \tag{4.36}$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \hbar^2 \hat{l}^2 \tag{4.37}$$

$$\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \tag{4.38}$$

We will not need $\hat{L}_x$ and $\hat{L}_z$ - see, e.g. the Merzbacher book. Quantization:

$$L^2 = \hbar^2 l(l+1) \ , \quad l = 0, 1, ; \ldots \tag{4.39}$$

$$L_z = m\hbar \ , \quad m = 0, \pm 1, \ \ldots \ , \pm l \tag{4.40}$$

4.6.3 Rotation of molecules

Why so well separated?

$$\omega_{el} \gg \omega_{vib} \gg \omega_{rot} \tag{4.41}$$

Large parameter $\sqrt{m_e/M}$ - will explain in class.

Common to use J for l and K for m.

Here we consider heteronuclear molecules. For identical nuclei (will be discussed later) some of the energy levels are forbidden.

4.6.4 Spherical top

$$H_{rot} = \frac{L^2}{2I} \tag{4.42}$$

and the same in quantum with $L^2 \to \hat{L}^2$. Thus,

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1) \ , \quad J = 0, 1, \ldots \tag{4.43}$$

Degeneracy:

$$g_J = (2J+1)^2 \tag{4.44}$$

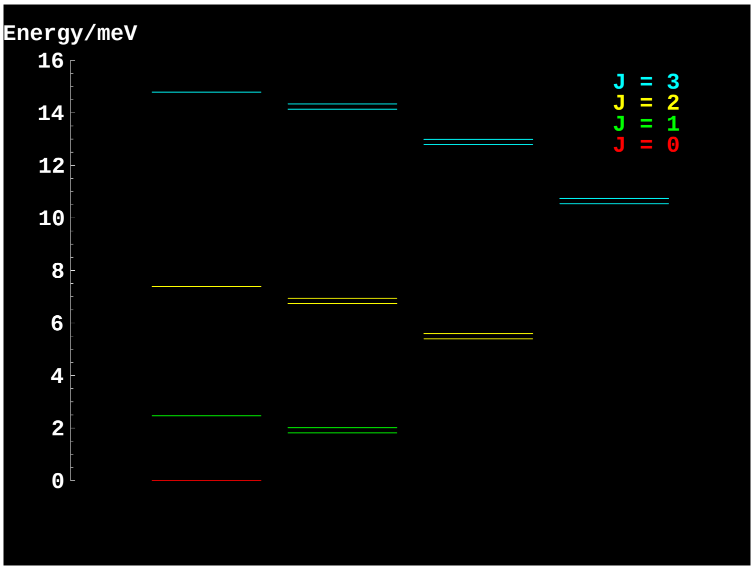

Figure 4.2: Rotational spectrum of NH_3 with $I_A = I_B = 2.816 \cdot 10^{-47} kg \cdot m^2$ and $I_C = 4.437 \cdot 10^{-47} kg \cdot m^2$ (oblate top).

4.6.5 Symmetric top

Let $I_x = I_y \equiv I$. Then,

$$H_{rot} = \frac{L_x^2}{2I} + \frac{L_y^2}{2I} + \frac{L_z^2}{2I_z} = \frac{L^2}{2I} - \frac{L_z^2}{2}\left(\frac{1}{I} - \frac{1}{I_z}\right) \tag{4.45}$$

Since eigenvalues of $\hat{L}_z^2$ are $\hbar^2 K^2$ with $K = 0, \pm 1, \ldots J^2$

$$E_{rot} = \frac{\hbar^2}{2I} J(J+1) - \frac{\hbar^2}{2}\left(\frac{1}{I} - \frac{1}{I_z}\right) K^2 \tag{4.46}$$

See Fig. 4.2 where degeneracy of levels is removed for clarity. (see *Physical Chemistry with Mathematica*, although an old version of *Mathematica* is used there)

Diatomic molecule

$$I_z \to 0$$

Thus, $K = 0$ and

$$E_{rot} = BJ(J+1)\ , \quad B = \frac{\hbar^2}{2I} \tag{4.47}$$

B-rotational quantum number.
HW - estimate B for HCl. Finish Table 3.1.

4.6.6 Asymmetric top

NOTHING!

(energy levels cannot be determined analytically)

4.7 Identical particles

Consider permutation of 2 identical particles

$$\Psi\left(x_1\ ,\ x_2\right) = e^{i\alpha}\Psi\left(x_2\ ,\ x_1\right)$$

The next permutation restores the original state:

$$e^{2i\alpha} = 1$$

Thus,

$$e^{i\alpha} = \pm 1 \tag{4.48}$$

Two possibilities depend on spin:
$s = 0, 1, \ldots$ - "+" (symmetric wave function, Bose-Einstein statistics)
$s = \frac{1}{2}\ ,\ \frac{3}{2}\ , \ldots$ - "-" (antisymmetric wave function, Fermi-Dirac statistics)

4.7.1 Implication for rotation

Consider a homonuclear diatomic molecule. Let the nuclei be Bosons (e.g. D_2). Then, for $S_N = 0$ only even J, with same degeneracies. I.e:

$$g_J = (2J+1)\ , J - \text{even} \tag{4.49}$$

$$g_J = 0\ , J - \text{odd} \tag{4.50}$$

Now let the nuclei be fermions (e.g., H_2)

$$g_J = (2J+1)\ , J - \text{odd} \tag{4.51}$$

$$g_J = 0\ , J - \text{even} \tag{4.52}$$

Formulas for $S_n \neq 0$ are more complex. We just need to know that degeneracies are different for odd and even J. The most interesting example:
Orthohydrogen: parallel nuclear spins
Parahydrogen: antiparallel nuclear spins.

4.7.2 Density of states

Will be discussed in class. Introduce

$$d\,\Gamma = d\,q_1 d\,p_1 d\,q_2 d\,p_2 \dots d\,q_{3N} d\,p_{3N} \tag{4.53}$$

which is the classical volume of phase space. If particles are different, from quasiclassical quantization the number of states is

$$\frac{d\,\Gamma}{(2\pi\hbar)^{3N}}\,, \quad \text{distinguishable particles} \tag{4.54}$$

Which is of course unrealistic for large $N \sim N_A$. If particles are identical, the number of states is much smaller

$$\frac{1}{N!}\frac{d\,\Gamma}{(2\pi\hbar)^{3N}}\,, \quad \text{identical particles} \tag{4.55}$$

4.8 The volume of phase space and the total number of states

will be done in class. Message - the number of states increases extremely rapidly with energy, and the distance between levels practically goes to zero. This will be the key to introducing statistical entropy.

4.8.1 Number of states for ideal gas

Main points: integration over $d\,q$ gives V^N. Scaling each momentum with $\sqrt{2mE}$ expresses the result through a volume of a unit n-dimensional hypersphere (with $n = 3N$ - see 641_HyperSphere.nb for detail)

$$C_n = \frac{\pi^{n/2}}{(n/2)!} \tag{4.56}$$

(I avoid using the gamma-function here not to confuse with the number of states). One has

$$\Gamma = \frac{C_{3N}}{N!}\left[\frac{V}{(2\pi\hbar)^3}\,(2mE)^{3/2}\right]^N \tag{4.57}$$

Using the Stirling approximations (leading term):

$$N! \simeq \sqrt{2\pi N}\left(\frac{N}{e}\right)^N \ , \ C_n \simeq \frac{1}{\sqrt{\pi n}}\left(\frac{2e\pi}{n}\right)^{n/2}$$

One obtains

$$\Gamma(E) = \frac{1}{\pi N\sqrt{6}}\left[\left(\frac{2\pi e^{5/2}}{3}\right) v^{2/3}\frac{2m\epsilon}{(2\pi\hbar)^2}\right]^{3N/2} \tag{4.58}$$

with

$$v = V/N \ , \ \ \epsilon = E/N$$

Or, with

$$\lambda_{dB} = 2\pi\hbar/\sqrt{2m\epsilon} \tag{4.59}$$

the de Broglie wavelength

$$\Gamma(E) = \frac{1}{\pi N\sqrt{6}}\left[\left(\frac{2\pi e^{5/3}}{3}\right)^{1/2} \frac{v^{1/3}}{\lambda_{dB}}\right]^{3N} \tag{4.60}$$

One requires

$$v^{1/3} \gtrsim 0.3\lambda_{dB}$$

to ensure the $[\ldots] > 1$ (otherwise, quantum statistics is required; strictly speaking a strong inequality, $v^{1/3} \gg \lambda_{dB}$ is needed to justify classical statistics). If, on the other hand energy is large enough (so that $v^{1/3} \gg \lambda_{dB}$) the value of $\Gamma(E)$ increases with E incredibly fast - recall that $N \sim N_A$.

4.8.2 Density of states

One has for the density of states $\Omega(E) = d\Gamma(E)/dE$

$$\Omega(E) \simeq \frac{3N}{2E}\Gamma(E) \tag{4.61}$$

Since $\Gamma(E)$ is so huge (and since ln will be of the main interest), for many applications the difference between $\Omega(E)$ and $\Gamma(E)$ can be ignored.

Part II

Foundations of statistical mechanics

Chapter 5

Distribution function

READING: **LL**, *Ch.1 (skip harder parts, such as the density matrix)*

We again consider the probability density

$$\rho(\vec{q},\ \vec{p})$$

similarly to the one we discussed in connection with the Liouville's theorem. Only now this function is static, i.e. has no explicit t-dependence [although points keep moving in the phase space!]. The best thing to imagine would be one of the lower Figs. 3.1 or 3.2, after a good mixing. We also do not keep track of normalization so far (having in mind later quantum analogies).

The average of any function $f(\vec{q},\ \vec{p})$ is given by

$$\langle f \rangle = \frac{\int f(\vec{q},\ \vec{p})\,\rho(\vec{q},\ \vec{p})\,d\vec{q}d\vec{p}}{\int \rho(\vec{q},\ \vec{p})\,d\vec{q}d\vec{p}} \tag{5.1}$$

Alternatively, one could follow a single phase point to find a time average

$$\bar{f} = \lim_{t\to\infty} \frac{1}{t}\int_0^t f\left[\vec{q}(t'),\ \vec{p}(t')\right]\,dt' \tag{5.2}$$

And they are expected to be identical

$$\langle f \rangle = \bar{f} \tag{5.3}$$

5.1 Statistically independent states

$$\rho_{12}(\vec{q}_1,\ \vec{p}_1,\ \vec{q}_2,\ \vec{p}_2) = \rho_1(\vec{q}_1,\ \vec{p}_1)\,\rho_2(\vec{q}_2,\ \vec{p}_2) \tag{5.4}$$

5.2 The role of energy

The Liouville's theorem shows that ρ is an integral of motion. Thus, one expects it to be a function of the integrals of motion. There can be many of them, but only additive can matter. Indeed, for two non-interacting parts of a body

$$\ln \rho_{12} = \ln \rho_1 + \ln \rho_2 \tag{5.5}$$

Thus, ρ can depend only on E, $\vec{\mathcal{P}}$, $\vec{L}$. In the absence of translational motion and rotation of a system ("in a box") only E remains, i.e. for a given subsystem i

$$\ln \rho_i = \alpha_i - \beta E_i \left(\vec{q}_i,\ \vec{p}_i\right) \tag{5.6}$$

The constant α_i can depend on subsystem, β is the same to ensure additivity.

Let us show that dependence of energy (Hamiltonian) indeed leads to time-independent ρ. From Liouville's theorem

$$\frac{d\,\rho}{d\,t} \equiv \frac{\partial}{\partial t}\rho + \dot{\vec{q}} \cdot \frac{\partial}{\partial \vec{q}}\rho + \dot{\vec{p}} \cdot \frac{\partial}{\partial \vec{p}}\rho = 0$$

Recall

$$\dot{\vec{q}} = \frac{\partial}{\partial \vec{p}}H\ ,\quad \dot{\vec{p}} = -\frac{\partial}{\partial \vec{q}}H$$

and for $\rho = \rho(H)$

$$\frac{\partial}{\partial \vec{q}}\rho = \frac{d\,\rho}{d\,H}\frac{\partial}{\partial \vec{q}}H\ ,\quad \frac{\partial}{\partial \vec{p}}\rho = \frac{d\,\rho}{d\,H}\frac{\partial}{\partial \vec{p}}H$$

Thus indeed

$$\frac{\partial}{\partial t}\rho = 0 \tag{5.7}$$

Chapter 6

Microcanonical ensemble

6.1 Properties of the phase volume

Having in mind the subsequent quantum discussion, introduce from the start

$$d\,\Gamma = \frac{1}{N!}\frac{d\vec{p}\,d\vec{q}}{(2\pi\hbar)^{3N}} \tag{6.1}$$

Total number of (quantum) states in the elementary phase "volume" $d\vec{p}\,d\vec{q}$ will coinside with $d\,\Gamma$.

In a finite volume

$$\Gamma(E) = \int_{H(\vec{p},\vec{q})<E} d\,\Gamma \gg 1 \tag{6.2}$$

The density of states is

$$\Omega(E) = \frac{d\,\Gamma}{d\,E} \tag{6.3}$$

Thus, for a small $\Delta \ll E$

$$\Delta\Gamma \equiv \int_{E<H(\vec{p},\vec{q})<E+\Delta} d\,\Gamma \simeq \Omega(E)\Delta \tag{6.4}$$

Due to a rapid increase of Γ with energy (recall our example with ideal gas), one has

$$\Gamma(E) \simeq \frac{\Omega(E)}{d\,\ln\Omega/d\,E} \tag{6.5}$$

Since $d\ln\Omega/d\,E$ is a "modest" function (compared to Ω), Γ and Ω are "almost the same", and so is $\Delta\Gamma$ for any reasonable Δ. This will be used below.

6.2 Equal a priori probability and Entropy

Consider an ensemble of phase points evenly distributed between E and $E+\Delta$. Again, the best thing to imagine would be one of the lower Figs. 3.1 or 3.2. Define

$$S = k_B \ln \Delta\Gamma \tag{6.6}$$

(Boltzmann). Alternatively, could use

$$S = k_B \ln \Gamma \tag{6.7}$$

or

$$S = k_B \ln \Omega \tag{6.8}$$

(although in the latter case S will slightly depend, up to an insignificant constant, on the energy units).

Additivity and equivalence will be discussed in class.

HW: *Consider one classical particle in a cubic box. Find $\Gamma(E)$ and plot $S(E)$ in all three definitions (they do not have to be too close for just one particle). Use $\Delta = 0.1E$*

6.3 Relation to "information" (non-equilibrium) entropy

Let us consider a finite phase volume $\Delta\Gamma$ and *not* assume a constant $\rho(E)$ (as in the microcanonical distribution) and define

$$\mathcal{S} = -k_B \int d\,\Gamma \rho \ln \rho \equiv -k_B \langle \ln \rho \rangle \tag{6.9}$$

A proper normalization of ρ is expected

$$\int_{\Delta\Gamma} \rho d\Gamma = 1 \tag{6.10}$$

Then, if one tries to maximize $\mathcal{S}$ with the above constrain one gets

- $\rho(E) = const = 1/\Delta\Gamma$ (microcanonical)
- $\mathcal{S} = k_B \ln \Delta\Gamma$

HW. Show this - we did a nearly identical problem in connection with information entropy and Lagrange multipliers

6.3.1 Temperature and pressure

$$\left(\frac{\partial S}{\partial E}\right)_V \equiv \frac{1}{T} \tag{6.11}$$

$$-\left(\frac{\partial E}{\partial V}\right)_S = p \tag{6.12}$$

Processes with $S = const$ are called adiabatic. They are the closest to mechanics.

Example: Ideal gas

Recall

$$\Gamma \sim v^N \epsilon^{3N/2}$$

Thus

$$s \equiv \frac{S}{N} = k_B \left(\ln v + \frac{3}{2}\ln \epsilon\right) + const \tag{6.13}$$

From definitions:

$$\frac{1}{T} = \frac{3}{2}\frac{k_B}{\epsilon}$$

or

$$\epsilon = \frac{3}{2}k_B T \tag{6.14}$$

and

$$p = \frac{2}{3}\frac{\epsilon}{v}$$

or

$$pv = k_B T \tag{6.15}$$

Dr. Vitaly A. Shneidman, Lectures on Statistical Mechanics, NJIT.

Chapter 7

Thermodynamics

Recommended reading: *Thermodynamics* by Enrico Fermi or LL, Ch.2; Ch. 1 & 2 by K. Huang are also very good.

7.1 First Law

$$dE = dR + dQ \tag{7.1}$$

$$dR = -p dV \tag{7.2}$$

R - work, Q - heat. (Joule experiment).
Note: R, Q depend on path; E -depends only on the state (thus dE is complete or "exact differential").

7.2 2d Law

$$dS \geq \frac{dQ}{T} \tag{7.3}$$

Equality is achieved for reversible processes. Then one can write

$$dE = TdS - PdV \tag{7.4}$$

Note: unlike dQ the differential of entropy dS is an exact differential.

In a general case there are irreversible processes with a ">" sign in the above. Entropy thus grows in thermally isolated systems with $dQ = 0$, reaching maximum in complete equilibrium. various formulation of the 2d law are equivalent (will be discussed in class).

7.2.1 Cycles

(see Fig. 7.1). Since the entropy (an exact differential) returns to its original value

$$\oint dS = 0$$

the 2d Law gives

$$\oint \frac{dQ}{T} < 0$$

Maximum efficiency of a heat engine

$$\eta = 1 - T_{low}/T_{high}$$

HW: *Calculate explicitly the amount of heat Q and work R for each of the 4 stages of the Carnot cycle in Fig. 7.1 (right) if the working body is ideal gas. Check explicitly the 1st Law, and the above efficiency $\eta = R/Q_{12}$. Note: in ideal gas energy remains fixed on the isothermal stage, and $s(v, \epsilon)$ depends only on volume. The numbers from the plot can be helpful (though, not required) for verification: $p_1 = v_1 = 1$, $v_2 = 2$, $v_3 = 3$, $v_4 = 3/2$, $p_2 = 1/2$, $p_4 = (2/3)^{5/3}$, $p3 = p_4/2$.*

7.2.2 Constant values of T and P in equilibrium

Will be discussed in class.

7.2.3 Absence of macroscopic motions inside a body

Consider i subsystems. Then

$$S = \sum_i S_i \left(E_i - \frac{M_i v_i^2}{2} \right)$$

with

$$\vec{\mathcal{P}} = \sum_i M_i \vec{v}_i = const$$

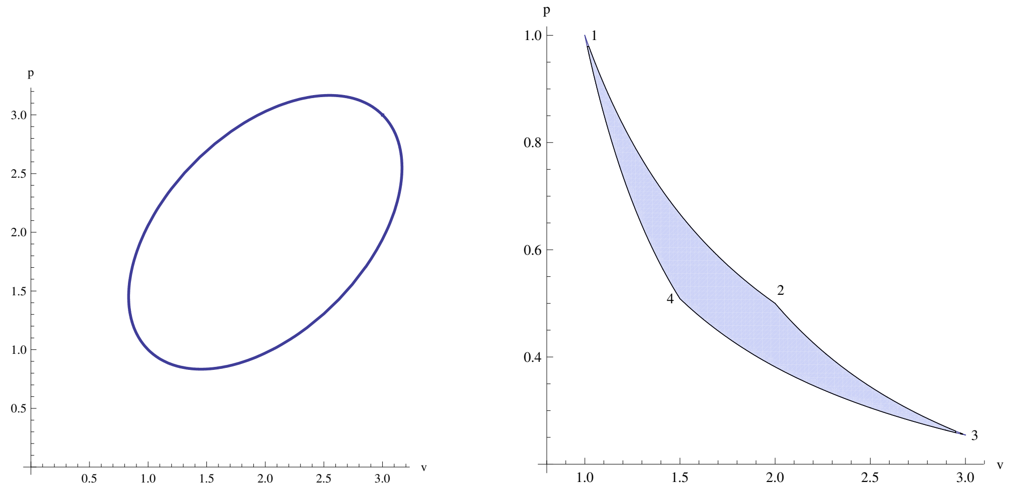

Figure 7.1: General closed cycle (left) and the Carnot cycle (right). For Carnot "12" and "34" are isotherms, and "23" and "41" are adiabats.

Then,

$$S + \vec{a} \cdot \vec{\mathcal{P}} = \max \tag{7.5}$$

From

$$\frac{\partial}{\partial \vec{v}_i} S_i = -\frac{M_i \vec{v}_i}{T}$$

get

$$v_i = const$$

(i.e. motion as a "rigid" body - Galileo).

Rotation - harder.

7.2.4 Specific heat

General definition

$$C = \frac{dQ}{dT}$$

for a given reversible process. What is constant while T is changing need to be specified. E.g.

$$C_v = T \frac{\partial S}{\partial T}\bigg|_V \tag{7.6}$$

$$C_p = T \frac{\partial S}{\partial T}\bigg|_p \tag{7.7}$$

7.3 Thermodynamic potentials (TP)

7.3.1 Energy

"Natural variables"

$$E(S, V)$$

Simple derivatives

$$T = \frac{\partial E}{\partial S}\ , \quad P = -\frac{\partial E}{\partial V} \tag{7.8}$$

(often, do not have to indicate what is constant). Also, clear physics:

$$d\,Q = d\,E\ , \quad V = const \tag{7.9}$$

$$d\,R = -d\,E\ , \quad S = const \tag{7.10}$$

Also, if there are other variables λ which can change with constrains $S = const$, $V = const$, then

$$E(S, V, \lambda) = \min$$

7.3.2 Enthalpy (heat function)

Want to go from S, V (natural variables for E) to S, P. Use Legendre transformation

$$d\,W = d\,E + d\,(PV)$$

or

$$W = E + PV \tag{7.11}$$

with

$$d\,W(S, P) = T d\,S + V d\,P \tag{7.12}$$

Now, for an isobaric process

$$d\,Q = d\,W\ , \quad P = const \tag{7.13}$$

(similar to energy for $V = const$). Similarly,

$$C_p = \left.\frac{\partial W}{\partial T}\right|_p \tag{7.14}$$

(note, need to indicate T as $const$, since T is not a "natural variable" for W.)

For thermally isolated isobaric processes, $dQ = 0$, $P = const$, one has

$$W = const$$

This is interesting, since V can change and thus work is made by the system(!)

7.3.3 Free energy (Helmholtz)

Want to use T, V as "natural variables". Again, Legendre transformation

$$dF = dE - d(TS)$$

or

$$F = E - TS \tag{7.15}$$

with

$$dF(T, V) = -SdT - PV \tag{7.16}$$

Note, work

$$dR = dF \ , \ \ T = const$$

HW: show that

$$E = -T^2 \left(\frac{\partial}{\partial T}\frac{F}{T}\right)_V \tag{7.17}$$

7.3.4 Gibbs free energy ("thermodynamic potential")

Natural variables - P, T.

$$d\Phi(P, T) = dF + d(VP) = -SdT + VdP \tag{7.18}$$

or

$$\Phi = F + PV = W - TS = E - TS + PV \tag{7.19}$$

HW: show that

$$W = -T^2 \left(\frac{\partial}{\partial T}\frac{\Phi}{T}\right)_P$$

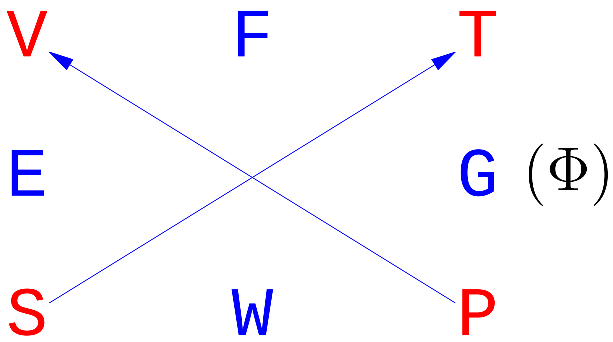

Figure 7.2: Diagram for Maxwell relations (after *K. Huang*). Each thermodynamic potential (blue) is flanked by its respective natural arguments (red). The derivative with respect to any one of the natural arguments (the other one held fixed) is determined by the corresponding arrow, with a "-" sign if moving against the arrow direction.

7.4 Maxwell relations

We thus defined four major thermodynamic potentials

$$E(S,V)\ ,\quad W(S,P)\ ,\quad F(T,V)\ ,\quad \Phi(T,P)$$

respectively energy E, enthalpy (heat function) W, (Helmholtz) free energy F, and Gibbs free energy Φ (or, G). (Note that **LL** use Φ for the Gibbs free energy; also other standard systems of notations, e.g., *K. Huang*, use U for E, H for W, A for F, and G for Φ). Connections between various derivatives are conveniently summarized by a diagram in Fig. 7.2. For example,

$$\begin{aligned} T &= \left(\frac{\partial}{\partial S}E\right)_V = \left(\frac{\partial}{\partial S}W\right)_P \\ S &= -\left(\frac{\partial}{\partial T}F\right)_V = -\left(\frac{\partial}{\partial T}\Phi\right)_P \\ P &= -\left(\frac{\partial}{\partial V}E\right)_S = -\left(\frac{\partial}{\partial V}F\right)_T \\ V &= \left(\frac{\partial}{\partial P}W\right)_S = \left(\frac{\partial}{\partial P}\Phi\right)_T \end{aligned} \tag{7.20}$$

7.4.1 Example: Ideal gas

Now with a very "minor" input from statistical mechanics, thermodynamics allows for a detailed description of a system. This path, starting from microcanonical ensemble, is not the most efficient, but instructive...

During previous class we obtained density of states of an ideal classical gas

$$\Gamma \sim \frac{1}{N}\left[v\left(\frac{m\epsilon}{\hbar^2}\right)^{3/2} \cdot const\right]^N$$

where *const* is a dimensionless number of the order of 1. Thus, entropy is given by:

$$S = Nk_B \ln\left[v\left(\frac{m\epsilon}{\hbar^2}\right)^{3/2}\right] + Nk_B \times const - \ln N - \dots \tag{7.21}$$

or per particle, $s = S/N$

$$s = k_B \ln\left[v\left(\frac{m\epsilon}{\hbar^2}\right)^{3/2}\right] + k_B \times const + O\left(\frac{\ln N}{N}\right) \tag{7.22}$$

This is all we need from Statistical Mechanics. To get a full thermodynamic description we need the equation of state, i.e. the relation between v, P and T. We do not have P and T yet, but we have connection between s, v and ϵ. Thus, if ϵ is expressed through natural variables s, v pressure and temperature can be obtained from Maxwell relations.

Inverting the expression for entropy one obtains

$$\epsilon(s, v) = \frac{\hbar_2}{m} v^{-2/3} \exp\left[\frac{2}{3}\left(s/k_B - const\right)\right] \tag{7.23}$$

Then,

$$T = \left(\frac{\partial}{\partial s}\epsilon\right)_V = \frac{2\epsilon}{3k_B} \tag{7.24}$$

Then, equation of state:

$$P = -\left(\frac{\partial}{\partial v}\epsilon\right)_s = \frac{2\epsilon}{3v} = k_B T/v \tag{7.25}$$

Similarly, free energy per particle $f \equiv F/N$

$$f = \epsilon - Ts = \frac{3}{2}k_B T - k_b T \ln\left[v\left(\frac{m \cdot (3/2)k_B T}{\hbar^2}\right)^{3/2}\right] - k_B T \cdot const \tag{7.26}$$

HW: *Construct the equation of state from f (it is easier than from ϵ since there is already no entropy)*

HW: *Construct the enthalpy and the Gibbs free energy*

7.4.2 Additional independent variables and corrections to TP

$$dE = T\,dS - P\,dV + \Lambda\,d\lambda$$

If λ is an independent variable, same corrections appear in dF, $d\Phi$ and dW. For small changes (only!)

$$(\delta E)_{S,V} = (\delta F)_{T,V} = (\delta\Phi)_{P,T} = (\delta W)_{S,P} \tag{7.27}$$

If λ is allowed to change when either T, V or T, P are *const*, then the corresponding derivatives are negative, and when equilibrium with respect to λ is reached

$$F = \min\ , \quad T, V = const \tag{7.28}$$

or

$$\Phi = \min\ , \quad T, P = const \tag{7.29}$$

7.4.3 Dependence on the number of particles

The first, and most important example of an extra independent variable is the number of particles, N. Then, all thermodynamic potentials get a correction

$$\mu\,dN$$

with μ being the "chemical potential". In addition, if s, v,... are entropy, volume, etc. per particle, we expect that

$$E = Ne(s,v)\ , \quad F = Nf(v,T)\ , \quad W = Nw(s,P)\ , \quad \Phi = N\phi(P,T)$$

Thus, immediately

$$\mu = \Phi/N \tag{7.30}$$

and

$$d\,\mu = -s\,dT + v\,dP \tag{7.31}$$

Condition of equilibrium
Consider a system of two parts with not necessarily same pressure. Then, will show

$$\mu_1 = \mu_2$$

or

$$\mu = const \tag{7.32}$$

in the body.
Equilibrium in external field Now, correction to energy is

$$\mu_0 d\,N + u\,(\vec{r})\,d\,N$$

so that $\mu = \mu_0 + u$ is the new chemical potential. Or,

$$\mu_0 + u\,(\vec{r}) = const \tag{7.33}$$

HW: *Find the elevation-dependence of pressure of an ideal gas placed in gravitational field. Hint: an explicit expression for $\mu_0(P)$ is given below.*

7.4.4 Potential Ω

One has

$$d\,F = -Sd\,T - Pd\,V + \mu d\,N$$

Now want to have μ as independent variable. Legendre transformation gives

$$d\,\Omega(T,V,\mu) = d\,F - d\,(\mu N) = -Sd\,T - Pd\,V - Nd\,\mu \tag{7.34}$$

with

$$\Omega = F - \mu N = F - \Phi = -PV \tag{7.35}$$

Looks like the simplest potential, but watch the independent variables!

7.4.5 Example: Ideal gas

Need P as a function of μ, v, T

$$\mu = f - Pv = 3/2k_BT\left\{1 - \ln\left[\left(\frac{k_BT}{P}\right)^{2/3}\frac{3k_BTm}{2\hbar^2}\right] - (2/3)\cdot const\right\}$$

Thus,

$$\omega \equiv \Omega/N = P(T,V,\mu)v = v\,(k_BT)^{5/2}\left(\frac{3m}{2\hbar^2}\right)^{3/2}\exp\left(\frac{\mu}{k_BT} - \frac{3}{2} + const\right)$$

7.5 Two non-trivial applications

7.5.1 Expansion of gas in vacuum

will be discussed in class

7.5.2 The Joule-Thompson process

will be discussed in class

7.6 Some general relations and theorems

7.6.1 Minimal values of $F(T, V, \lambda)$ and $\Phi(T, P, \lambda)$

For $T, V = const$

$$\frac{dF}{dt} = \frac{dE}{dt} - T\frac{dS}{dt} = \frac{dQ}{dt} - T\frac{dS}{dt} \leq 0 \tag{7.36}$$

For $T, P = const$

$$\frac{d\Phi}{dt} = \frac{dW}{dt} - T\frac{dS}{dt} = \frac{dQ}{dt} - T\frac{dS}{dt} \leq 0 \tag{7.37}$$

7.6.2 Connection between the change of entropy and work

Suppose we want to bring a small part of a system out of equilibrium. This will reduce the entropy and will require some work R. The work is minimum for a quasistatic process. One has

$$\Delta S = -\frac{R_{\min}}{T_0} \tag{7.38}$$

We indicate T_0, the original temperature, since it can become different in the subsystem during the process. We will not prove this relation (it is not hard, but requires some patience and time - see LL), but it will be important when describing fluctuations.

For $T = T_0 = const$ and $V = const$

$$R_{\min} = \Delta F \ , \quad T, V = const \tag{7.39}$$

or

$$R_{\min} = \Delta \Phi \ , \quad T, P = const \tag{7.40}$$

7.6.3 Thermodynamic inequalities

Follow from consideration of a small subsystem in a "thermostat" and requirement that the *total* entropy can only be reduced upon infinitesimal changes. First derivatives give $T, P > 0$. Second derivatives give - see LL

$$C_V > 0 \tag{7.41}$$

and

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \tag{7.42}$$

Metastable states: above holds, but for a *finite* deviation the total entropy is increased.

7.7 Transformation of thermodynamic variables

7.7.1 Jacobians

$$\frac{\partial(u,v)}{\partial(x,y)} \equiv \begin{vmatrix} \frac{\partial}{\partial x}u & \frac{\partial}{\partial y}u \\ \frac{\partial}{\partial x}v & \frac{\partial}{\partial y}v \end{vmatrix} \tag{7.43}$$

Properties:

$$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(s,t)} \cdot \frac{\partial(s,t)}{\partial(x,y)} \tag{7.44}$$

HW: *Demonstrate the first of the above .*
Also

$$\frac{\partial(u,y)}{\partial(x,y)} = \left(\frac{\partial}{\partial x}u\right)_y \tag{7.45}$$

HW: *Demonstrate the above*

7.7.2 C_p vs. C_v

Preliminaries:

$$\left(\frac{\partial}{\partial p}S\right)_T = -\frac{\partial}{\partial p}\left(\frac{\partial}{\partial T}\Phi\right)_p = -\left(\frac{\partial}{\partial T}V\right)_p \tag{7.46}$$

i.e., "-" the thermal expansion coefficient.

$$\begin{aligned}\frac{1}{T}C_v = \frac{\partial(S,V)}{\partial(T,V)} &= \frac{\partial(S,V)}{\partial(T,P)}\left(\frac{\partial}{\partial V}p\right)_T = \left(\frac{\partial}{\partial V}p\right)_T \begin{vmatrix} \left(\frac{\partial}{\partial T}S\right)_p & \left(\frac{\partial}{\partial p}S\right)_T \\ \left(\frac{\partial}{\partial T}V\right)_p & \left(\frac{\partial}{\partial p}V\right)_T \end{vmatrix} = \\ &= \left(\frac{\partial}{\partial V}p\right)_T \begin{vmatrix} C_p/T & -\left(\frac{\partial}{\partial T}V\right)_p \\ \left(\frac{\partial}{\partial T}V\right)_p & \left(\frac{\partial}{\partial p}V\right)_T \end{vmatrix} = C_p/T + \left(\frac{\partial}{\partial V}p\right)_T \left(\frac{\partial}{\partial T}V\right)_p^2\end{aligned} \tag{7.47}$$

Note: $C_V < C_p$ since $\left(\frac{\partial}{\partial V}p\right)_T < 0$.Also, $C_p - C_V$ is entirely determined by equation of state $p(V,T)$.
HW: *Find $C_p - C_V$ for ideal gas .*

7.8 3d Law

$$S\,(T \to 0\,,\,\ldots\; - \;\text{fixed}) \;\to\; 0 \tag{7.48}$$

From the 3d Law, the following tends to zero as $T \to 0$:

$$C_V\,,\; C_p\,,\; C_p - C_V\,,\; \frac{C_p - C_V}{C_p}\,,\; \left(\frac{\partial}{\partial T}V\right)_p$$

HW: *Prove for any two of the above; use $\frac{\partial}{\partial p}V$ finite, if you select $(C_p - C_V)/C_p$*
HW: *Show that at $T = 0$ one has $F = E$ and $\Phi = W$*

Chapter 8

Phase Transitions

READING: Ch. VIII in **LL**

8.1 Phase equilibrium

$$\mu_1(P,T) = \mu_2(P,T) \tag{8.1}$$

Solution (a one-dimensional curve):

$$P_{eq} = P(T) \tag{8.2}$$

8.1.1 Latent heat

Latent heat (per molecule):

$$q \equiv w_2 - w_1 = T\,(s_2 - s_1) \tag{8.3}$$

Positive q for transition to a high-temperature stable phase (in class).

HW. Find q/k_BT^B, the boiling temperature for steam and any other saturated vapor. Use CRC Handbook (better), or R. Reid et al. Properties of Gasses and Liquids.

8.1.2 Triple point

Consider *three* phases at equilibrium (e.g., ice, water, vapor). One has

$$\mu_1(P,T) = \mu_2(P,T) = \mu_3(P,T) \tag{8.4}$$

These are two equations with 2 unknowns, P, T. Solution - "triple point". Note: for 2 phase equilibrium everything is determined by T - 1 degree of freedom, a line in (P,T) diagram. For 3 phase equilibrium - one fixed point, zero degrees of freedom. (Alternatively, for just one phase both P and T are free to choose, i.e. two degrees of freedom). All these are examples of the Gibbs rule of phases - will discuss more with multicomponent systems:

8.1.3 Clapeyron equation

Take a derivative of eq. (8.1) for $P = P_{eq}(T)$ to get

$$\frac{d\,P_{eq}}{d\,T} = \frac{q}{T\,(v_2 - v_1)} = \frac{s_2 - s_1}{v_2 - v_1} \tag{8.5}$$

Similarly, $d\,T_{eq}/d\,P$.
HW. Use CRC Handbook for Chemistry and Physics. Find q, v_1, v_2 for ice-water. Which pressure is required for ice to melt at -20^oC?. How realistic is it for skates?

Liquid-gas transition:
Here

$$v_2 \gg v_1\ , \quad Pv_2 \simeq k_B T$$

and

$$\frac{d\,\ln P_{eq}}{d\,T} = \frac{q}{k_B T^2} \tag{8.6}$$

If $q \approx const$

$$P_{eq} \propto \exp\left(-\frac{q}{k_B T}\right) \tag{8.7}$$

HW: *Plot the main thermodynamic potentials for H_2O in a broad region of temperatures, starting from ice and ending with hot steam. Use the CRC Handbook or equivalent - do not try to be too precise, use some approximate formulas or simply points. Pay special attention to the vicinity of melting and of boiling. Which* *thermodynamic potentials are continuos and which are not? Note that many standard Tables refer to the triple point (near $0^O C$) and not to absolute zero ($0^O K$) as a reference. (Alternatively, you can plot thermodynamic potential of another material, e.g. mercury. Just cover the melting and the boiling points.)*

8.2 Critical point and corresponding states

in class + handout

8.2.1 Metastability and termination of isotherms

in class

8.2.2 The van der Waals equation

$$\left(P + \frac{a}{v^2}\right)(v - b) = k_b T \tag{8.8}$$

Here v is the volume per molecule. The isotherms are shown in Fig. 8.1.

HW: *Find the critical parameters for the van der Waals equation. Use vanderWaals.nb (and Ch.8-84 in* **LL***) if you need help.*

8.2.3 Corresponding states

in class

HW: *find the critical parameters, as well as the van der Walls parameters a and b for water. Use the CRC Handbook or equivalent.*

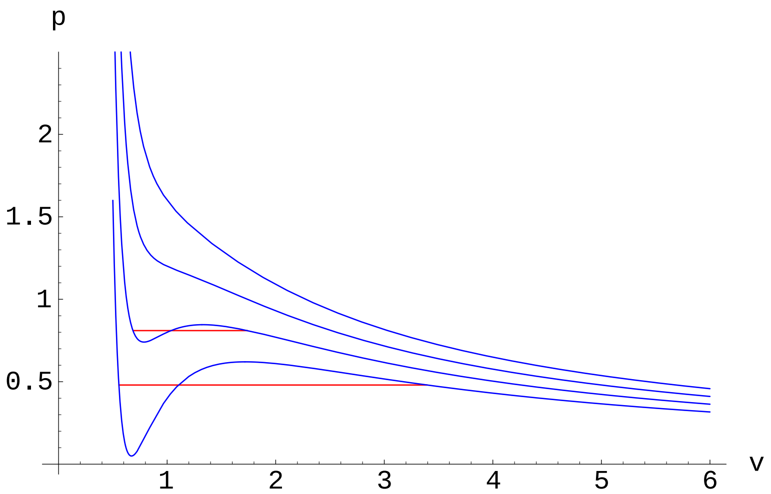

Figure 8.1: Van der Waals isotherms for reduced pressure $p = P/P_c$ and volume $v = V/V_c$. The reduced temperature $t = T/T_c$ (from top to bottom) is 1.15, 1.05, 0.95 and 0.85. Note that for $t < 1$ part of the blue isotherm is not stable and will be replaced by a horizontal red line. The latter follows from Maxwell construction with the areas below and above the line being equal.

Chapter 9

Solutions

READING: Ch. IX-85 - IX-87 [up to eq. (87-1)] in **LL**. *Skip eq. (85-4)*

9.1 Introduction

For several components

$$\mu \neq \Phi/N$$

since there are many μ's. Instead,

$$d\Phi = -SdT + VdP + \sum_i \mu_i \, dN_i \tag{9.1}$$

Thus,

$$\mu_i \left(T, P, \, , c_1 \, , c_2 \, , \ldots\right) = \left(\frac{\partial}{\partial N_i}\Phi\right)_{P,T} \tag{9.2}$$

Thus, from Euler theorem

$$\Phi = \sum_i \mu_i N_i \tag{9.3}$$

The equilibrium conditions remain the same and for *every* component the chemical potential remains constant, and if there are several phases $I, II, \ldots$

$$\mu_i^I = \mu_i^{II} = \ldots \tag{9.4}$$

for every i.

9.2 Gibbs phase rule

Consider L phases in contact and n components, with

$$\Phi^M\left(P, T, N_1^M, \ldots\ N_n^M\right)$$

being the Gibbs free energy of the M-th phase. The chemical potentials for each phase and component are

$$\mu_i^M = \frac{\partial}{\partial N_i^M}\Phi^M\ , \quad 1 \le i \le n;\ , \quad 1 \le M \le L \tag{9.5}$$

Then,

$$\mu_i^M = \mu_i^L\ , \quad \text{for any} \quad i \le n\ , \quad M \le L-1 \tag{9.6}$$

(note: i is same, phases can be different. This gives a total of

$$n \times (L-1)$$

equations for $2 + L(n-1)$ independent variables

$$P, T \text{ and } c_2^M\ ,\ \ldots c_n^M$$

in each phase, with $c_k^M \equiv N_k^M / N_1^M$ (e.g.)

One thus has the difference between the number of unknowns and the number of equations:

$$2 + L(n-1) - n\,(L-1) = 2 + n - L \tag{9.7}$$

which is the number of "degrees of freedom".

9.3 Weak solutions

Let the Gibbs potential $N\mu_0$ of pure solvent change by $\alpha(N)$ when *one* molecule of the solute is introduced. One has for n molecules

$$\Phi = N\mu_0 + n\alpha + k_bT\ln n! \tag{9.8}$$

The last term is *the only* contribution from Statistical Mechanics. It follows from $1/n!$ in statistical weight Γ, then $S = k_B \ln\Gamma$ gives a correction $-k_B \ln n!$

to entropy, and starting from energy (which does not have this term) one gets $k_BT \ln n!$ in both F and Φ.

Using Stirling approximation for large n and selecting $\alpha = k_BT\,[\psi(p,T) - lnN]$ to ensure homogenuity of Φ in n and N, one obtains

$$\Phi = N\mu_0 + nk_BT \ln \frac{n}{eN} + n\psi(P,T) \tag{9.9}$$

The function $\psi(P,T)$ has to be measured, unless the solvent is also an ideal gas.

HW: *Introducing concentration $c = n/N$ find the chemical potentials of the solvent (μ) and the solute (μ'). Hint: the answer is given below, but show the detail.*

$$\mu(P,T,c) = \mu_0(P,T) - k_BTc \tag{9.10}$$

$$\mu'(P,T,c) = k_BT \ln c + \psi(P,T) \tag{9.11}$$

9.4 Shift of the equilibrium curve

READING: Ch. IX-89 in **LL**

Apply the first of eqs. (9.11) for both phases (with different concentrations c_I and c_{II}). Chemical potentials are equal, thus the Clapeyron equation gets a correction

$$-\Delta s\, dT + \Delta v\, dP = \Delta c\, k_BT \tag{9.12}$$

(in all cases Δ is the difference between the values for the two phases, $I - II$, and $q = -T\Delta s$). E.g. for the same P

$$dT = \frac{k_bT^2\Delta c}{q} \tag{9.13}$$

For example if I is ice with $c_I \simeq 0$ and II is water,

$$dT = -\frac{k_bT^2c_{II}}{q} < 0$$

Let now $T = const$. Then,

$$dP = \frac{k_BT\Delta c}{\Delta v}$$

For an ideal gas (I) in equilibrium with liquid (II) $\Delta v \simeq v_I = k_B T/P$. Thus

$$dP = P\Delta c$$

If the solvent does not evaporate ($c_I = 0$)

$$dP/P = -c_{II} < 0$$

(*Raul's law*).

Chapter 10

The Gibbs distribution

READING: **LL**, *Ch.III: 28 - 31, 35, 36*

10.1 Microcanonical (reminder)

10.1.1 Example: Entropic elasticity

This is a simplest model of elasticity of rubber - see R. Kubo and references to texts on polymer therein. For us, the interesting part is that there is no energy in the system, but there is length-dependent degeneration of states which leads to non-zero tension. [one-dimensional analog of pressure]. The microcanonical ensemble is at its height.

The model and Γ

A chain consists of n links with length a each. Let is calculate Γ as a function of the length of the chain, $x = a\,(n_+ - n_-)$ with $n_{+,-}$ being right- and left-oriented links, respectively. The problem is identical to the one we had in one-dimensional random walk:

$$\Gamma = C_n^{n_+} \sim \frac{n^n}{n_+^{n_+} n_-^{n_-}}$$

Thus,

$$S/nk_B = \ln n - \frac{n_+}{n}\ln n_+ - \frac{n_-}{n}\ln n_- \tag{10.1}$$

Thermodynamics

$$F = 0 - TS = const + k_B T \left(n_+ \ln n_+ + n_- \ln n_- \right)$$

With

$$f = \left(-\frac{\partial}{\partial x} F \right)_T = \frac{d\, n_+}{d\, x} k_B T \ln \frac{n_+}{n_-}$$

The first term leads to Hook's law (will be completed in class).

10.1.2 Strong and weak sides of microcanonical ensemble

to be discussed in class

10.2 Entropy vs density of states

So far we considered a microcanonical distribution with a constant energy and with entropy defined as

$$S = k_B \ln \Delta\Gamma$$

Now that know more about entropy, we will mostly use the inverse of the above relation

$$\Delta\Gamma \propto \exp \frac{S}{k_b} \tag{10.2}$$

for the statistical weight.

10.2.1 Quantum

Since even in the classical approach we already count the number of states correctly (due to $(2\pi\hbar)^{3N}$ and $N!$), at this point the main modification is the discrete sum over energy levels, instead of integrals over phase space. Degeneration of levels should be accounted for. Thus,

$$\Gamma(E) = \sum_{E_i \leq E} g_i \tag{10.3}$$

The rest is the same. The Boltzmann definition of entropy, eq.(6.6) is the best, provided Δ exceeds splitting of the energy levels (and if there is no splitting Δ will not matter at all!). Note that the lowest energy level, E_0 is always non-degenerate, $g_0 = 1$. Thus $\Gamma(E_0) = 1$, with $S = 0$. This corresponds to the 3d Law.

HW: *Consider one quantum particle in a cubic box. (a) For a few lowest levels find the degeneracies g_i. (b) Calculate and plot Γ for the first few levels and entropy in two definitions (via $\Delta\Gamma = g_i$ and via Γ; (c) compare with classical; (d) for the few lowest levels remove the degeneracies by making the box slightly non-cubic, $a \times b \times c$ with, say $b = 0.95a$ and $c = 1.05a$. Examine the structure of energy levels (make a picture). (e -optional) Examine the limit of large E.*

10.2.2 Fluctuations

Probability of fluctuation

$$w' = \Gamma'/\Gamma \simeq \exp\left[(S' - S)/k_B\right] \tag{10.4}$$

Note that $S = \max$ in equilibrium so that $S' - S < 0$.

10.3 Canonical ensemble

Consider a subsystem which is part of a large system (a "thermostat"). Then the probability w_n to find this subsystem in a state with energy E_n is given by

$$w_n = \frac{1}{Q} e^{-E_n/k_B T} \ , \quad Q = \sum_n e^{-E_n/k_B T} \tag{10.5}$$

with Q known as the *partition function.* Similarly, in classical statistics (with corrected $d\,\Gamma$)

$$\rho(p,q) = \frac{1}{Q} e^{-E(p,q)/k_B T} \ , \quad Q = \int e^{-E(p,q)/k_B T} d\,\Gamma \tag{10.6}$$

or in terms of energy and density of states $d\,\Gamma/d\,E$ (for which we also used Ω in the previous lecture)

$$\rho(E) = \frac{d\,\Gamma}{d\,E}\frac{1}{Q} e^{-E/k_B T} \ , \quad Q = \int e^{-E/k_B T} \frac{d\,\Gamma}{d\,E} d\,E \tag{10.7}$$

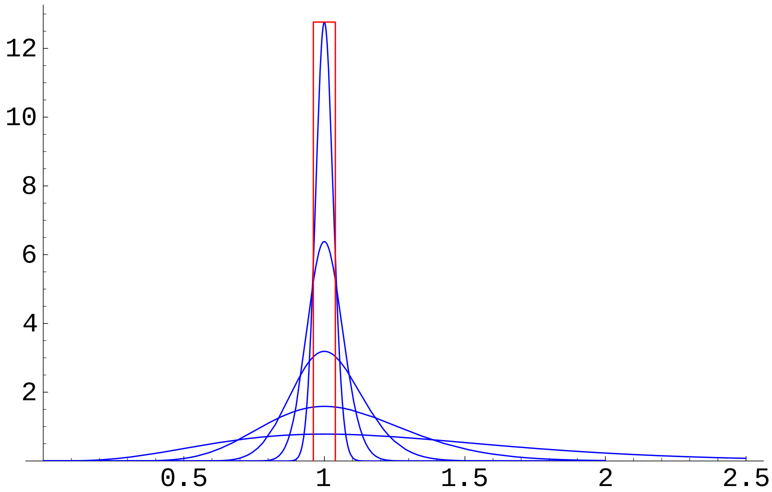

Figure 10.1: Distribution of energies, $d\,\Gamma/d\,E\,\exp\left(-E/k_BT\right)$ in the Gibbs ensemble as a function of reduced energy $E/(Nk_BT)$ for an ideal gas for different values of the number of particles, N. From down up (blue lines): $N = 4, 16, 64, 256, 1024$. A sharp maximum appears due to competition of an increasing density of energy levels and a decaying exponential. [Imagine what happens for $N \sim 10^{23}$ (!)]. The red box indicates the corresponding microcanonical distribution for the largest N.

In a sense, the last classical expression is the most instructive since it shows the presence of a rapidly growing term, $\frac{d\Gamma}{dE}$ and a rapidly decaying exponential e^{-E/k_BT}. The competition of those leads to a sharp maximum near some $\bar{E}$, which corresponds to the actual average energy of a subsystem (see below) -see Fig. 10.1.

10.4 Justification(s) of the Gibbs Distribution (GD)

10.4.1 From microcanonical

There are several ways to introduce the GD. For example, one could treat the entire large system as a microcanonical ensemble with a large energy E^0 and then consider the probability to get a certain energy $E_n \ll E^0$ in the subsystem.

Note that the subsystem is in pure state, i.e. a single energy level E_n (quantum) or a single cell in the phase space (quasiclassical). Thus, all entropy is in the remaining part of the system which has energy

$$E^0 - E_n$$

The entropy is

$$S'\left(E^0 - E_n\right) \simeq S'\left(E^0\right) - E_n \left.\frac{dS}{dE}\right|_{E=E^0} = S'\left(E^0\right) - E_n/T$$

Thus, accurate to proportionality coefficient

$$w_n \propto \exp\left(-E_n/k_B T\right)$$

The other way described below does not rely on the microcanonical distribution, but will allow to highlight once again the condition of maximum entropy.

10.4.2 From maximization of entropy

Consider

$$\left(\int -\rho \ln \rho + \alpha\rho - \beta E \rho\right) d\,\Gamma = \max \tag{10.8}$$

with α, β the Lagrange multipliers. From here

$$\rho = \frac{1}{Q} \exp\left(-\beta E\right)$$

with a constant Q given by normalization. For entropy one has

$$S = -k_B \left\langle \ln \rho \right\rangle = k_B \beta \bar{E} + k_B \ln Q \tag{10.9}$$

Compare this to

$$S = \frac{\bar{E} - F}{T}$$

Thus,

$$\beta = \frac{1}{k_B T} \tag{10.10}$$

and

$$F = -k_B T \ln Q \tag{10.11}$$

and the canonical distribution can be written as

$$w_n = \exp\left(\frac{F - E_n}{k_B T}\right) \tag{10.12}$$

The last form is the most useful in practice and is also valid for classical statistics with $w_n \to \rho(p,q)$, $E_n \to E(p,q)$.

HW: *(a) Show that*

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln Q = -T^2\frac{\partial}{\partial T}\frac{F}{T} \tag{10.13}$$

(b) Calculate Q for classical ideal gas; find $F(V,T)$, $\bar{E}(V,T)$ and the equation of state

10.5 Maxwell distribution (MD)

For classical energy

$$E = \sum_i \frac{1}{2} m v_i^2 + U(\vec{q}) \tag{10.14}$$

one has

$$\rho(\vec{p},\vec{q}) = \frac{1}{Q} e^{-U/k_B T} \prod_i e^{-p_i^2/2mk_B T} \tag{10.15}$$

Thus, can write a probability distribution for an individual momentum

$$d\,w_{\vec{p}} = a \exp\left(-\frac{p^2}{2mk_B T}\right) d\,p_x d\,p_y d\,p_z \tag{10.16}$$

with the constant a given by the normalization condition

$$\int d\,w_{\vec{p}} = 1$$

HW: *Find a; note that $p^2 = p_x^2 + p_y^2 + p_z^2$, leading to a product of three integrals*

Similarly, for the velocity distribution

$$d\,w_{\vec{v}} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) d\,v_x d\,v_y d\,v_z \tag{10.17}$$

Note: MD is applicable to very non-ideal systems (!), as long as motion is classical. In practice, MD mostly describes translational motion of molecules (since motion of atoms in a molecule, as well as rotations are often quantum).

Since the exponential depends only on v^2, convenient to re-write in spherical coordinates

$$d\,w_{\vec{v}} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) v^2 \sin\theta d\,\theta d\,\phi d\,v \tag{10.18}$$

Or, distribution in v

$$d\,w_v = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) v^2 d\,v \tag{10.19}$$

HW: *Check normalization*

HW: *(a) Plot the MD for neutrons at $300^o K$ and $3000^o K$.*
(b) write the normalized distribution in energies
(c) Find the mean energy and the mean square energy

10.6 Equipartition of energy

in class

10.7 Harmonic oscillator

in class - see Fig. 10.2.

HW: *MD (solutions). For normalization and constants - see maxwell.nb which also derives different versions of MD and averages, and has graphics.*

Distribution of energies:

$$w_E(E) = \frac{2\sqrt{E}}{\sqrt{\pi}\,(k_B T)^{3/2}} e^{-E/k_B T} \tag{10.20}$$

$$\bar{E} = \int_0^\infty E w_E(E) d\,E = \frac{3}{2} k_B T \tag{10.21}$$

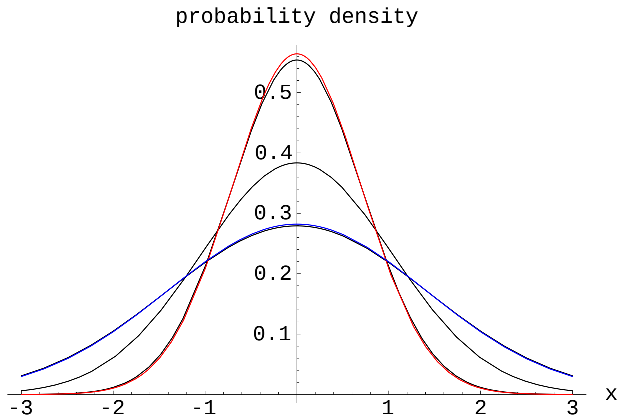

Figure 10.2: Probability density for a harmonic oscillator at various reduced temperatures $t = k_B T/\hbar\omega$ (black lines, $t = 0.25$, $t = 1$ and $t = 2$). Red line - pure quantum limit, $\psi_0^2(x)$; blue line - classical expression for $t = 2$. Note that either the quantum or the classical limits are quickly approached away from $t = 1$.

$$\langle E^2 \rangle = \int_0^\infty E^2 w_E(E) d\,E = \frac{15}{4} k_B^2 T^2 \tag{10.22}$$

$$\langle E^2 \rangle - \left(\bar{E}\right)^2 = \frac{3}{2} k_B^2 T^2$$

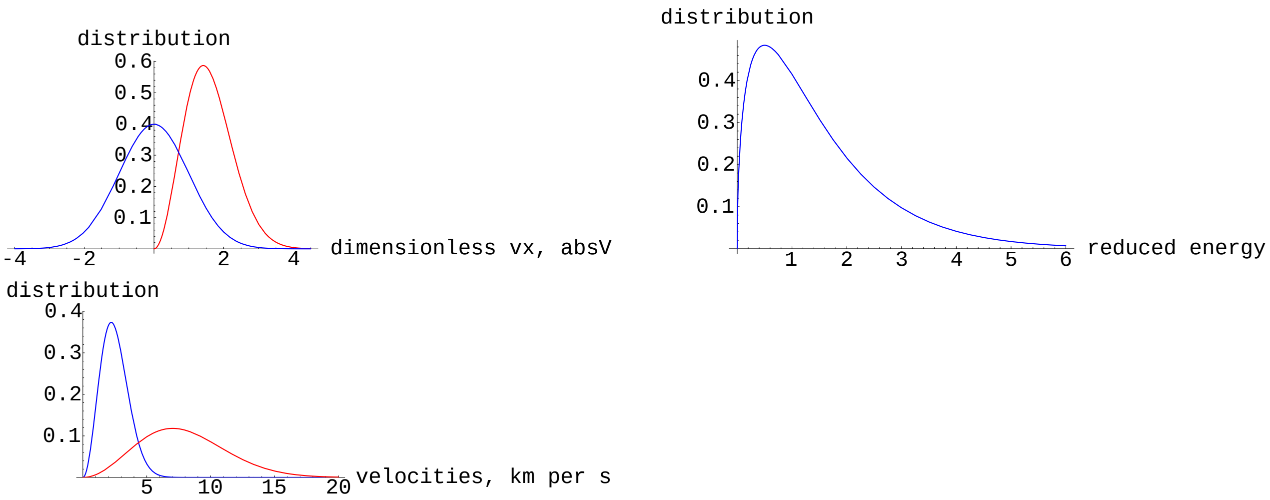

Figure 10.3: Maxwell distribution in various coordinates. Upper figure: distribution of $v_x/\sqrt{k_BT/m}$ (blue) and $v/\sqrt{k_BT/m}$ (red). Middle figure - distribution of dimensionless energies, E/k_BT. Lower figure: distribution of thermal neutrons over absolute velocities for $T = 300\ K$ (blue) and $T = 3000\ K$ (red).

Chapter 11

Grand canonical ensemble

READING: **LL**, *§35*

11.1 General

Unlike the canonical ensemble allow the number of particles N in the subsystem to fluctuate together with its energy E. Then, probability to find the subsystem with exactly N particles and in a pure state with energy E is proportional to

$$\exp\left[\frac{\mu N - E}{k_B T}\right]$$

Note that energy can depend on N. The proportionality coefficient is determined by normalization condition and its inverse is known as Ξ, the "grand canonical partition function". Connection with thermodynamics is established by

$$\Omega(T, V, \mu) = -k_B T \ln \Xi$$

Thus, with the proportionality constant the distribution function is given by

$$w_{nN} = \exp\left(\frac{\Omega + \mu N - E_{nN}}{k_B T}\right) \tag{11.1}$$

The grand canonical distribution is not postulated but derived either from microcanonical ensemble or from maximization of entropy.

11.2 From microcanonical

Let us treat the "big" system - thermostat plus our subsystem as a microcanonical ensemble with a total fixed energy E^0 and number of particles N^0. Volume of the subsystem is fixed.

If the subsystem is empty, the total entropy is given by

$$S'\left(E^0, N^0\right) \equiv S'_0$$

where prime indicates the thermostat. Now even if some particles $N \ll N^0$ and some energy $E \ll E^0$ are transferred to the subsystem, the total entropy is still the entropy of the thermostat (recall that the subsystem is in pure state, thus it has zero entropy once we fix E and N). Thus, the probability for this to occur is proportional to

$$\exp\left[S'\left(E^0 - E, N^0 - N\right)/k_B\right] \simeq \exp\left[\frac{S'_0}{k_B} - \frac{E}{k_B T} + \frac{\mu N}{k_B T}\right]$$

While the temperature and the chemical potential thus derived are the values for the thermostat, in equilibrium they are the same for the subsystem as well. The value of S'_0 does not matter since we will use the condition of normalization to find the proportionality factor. Thus, the grand canonical distribution is not affected by the specifics of the thermostat.

11.3 From maximization of entropy

Let us relax the condition $N = const$ and require only a fixed

$$\bar{N} \equiv \sum_N N \int \rho_N d\Gamma_N$$

The earlier conditions remain the same, only now summation in N is added:

$$\sum_N \int \rho_N d\Gamma_N = 1\ , \quad \sum_N \int E_N(p,q)\rho_N d\Gamma_N = \bar{E}$$

Look for (omit sub-index N in $\rho, E, d\Gamma$)

$$\sum_N \int \rho_N d\Gamma \left(-\rho \ln \rho + \alpha\rho - \beta E\rho + \gamma N\rho\right) d\Gamma = \max \tag{11.2}$$

with α, β, γ being Lagrange multipliers. Thus,

$$-\ln\rho - 1 + \alpha - \beta E + \gamma N = 0$$

or

$$\rho \propto \exp\left(-\beta E + \gamma N\right)$$

With normalization,

$$\rho_N\left(p, q\right) = \frac{1}{\Xi}\exp\left(-\beta E + \gamma N\right) \tag{11.3}$$

$$\Xi = \sum_N e^{\gamma N}\int e^{-\beta E} d\,\Gamma_N \tag{11.4}$$

Consider the entropy

$$S = -k_B\left\langle \ln\rho\right\rangle = k_B\beta\bar{E} - k_B\gamma\bar{N} + k_B\ln\Xi$$

and compare this with

$$\Omega = \bar{E} - TS - \mu\bar{N}$$

Thus, the same $\beta = 1/k_BT$ and

$$\gamma = \frac{\mu}{k_BT} \tag{11.5}$$

with

$$-\Omega = k_BT\ln\Xi = k_BT\ln\left(\sum_N e^{\mu N/k_BT}\sum_n e^{-E_{nN}/k_BT}\right) \tag{11.6}$$

for quantum (and sum over n replaced by integral over $d\,\Gamma$ for classical).

HW: *Calculate Ξ for a classical gas*

With

$$z = e^{\mu/k_BT} \tag{11.7}$$

one has

$$\Xi = \sum_N z^N Q_N(V, T) \tag{11.8}$$

Next,

$$\bar{N} = \frac{\partial}{\partial\ln z}\ln\Xi \equiv k_BT\frac{\partial}{\partial\mu}\ln\Xi \tag{11.9}$$

11.4 Absence of a phase transition for a finite V

in class

Part III

Ideal systems

Chapter 12

Introduction: the simplest classical gas.

12.1 Canonical

Since

$$E = \sum_i E_i$$

$$Q_N = \frac{1}{N!} \prod_i \int d\Gamma_i e^{-E_i/k_B T} = \frac{1}{N!} q^N \ , \quad q \equiv \int d\Gamma_i e^{-E_i/k_B T}$$

For

$$E_i = p_i^2/2m \ , \quad d\Gamma = \frac{dp_x\, dx\, dp_y\, dy\, dp_z\, dz}{(2\pi\hbar)^3}$$

one obtains

$$q = \frac{V}{(2\pi\hbar)^3} \left[\int_{-\infty}^{\infty} dp_x \, \exp\left(-\frac{p_x^2}{2mk_B T} \right) \right]^3 = \ldots$$

12.2 Grand canonical

$$\Xi = \sum_N Q_N e^{\mu N/k_B T} = \sum_N \frac{1}{N!} q^N e^{\mu N/k_B T} = \exp\left(q \, e^{\mu/k_B T} \right)$$

Chapter 13

Classical gas (with quantum molecules)

13.1 General and Boltzmann distribution

READING: **LL**, *§37*

For non-classical

$$E = \sum_i n_k \epsilon_k \ , \quad N = \sum_k n_k \tag{13.1}$$

Note: summation is now over energy levels (not over particles!).

Now,

$$\Xi = \prod_k \Xi_k \ , \quad \Omega = \sum_k \Omega_k$$

and

$$w_{n_k} = \exp\left[\frac{\Omega_k + (\mu - \epsilon_k)\, n_k}{k_B T}\right] \tag{13.2}$$

Note:

$$w_0 = e^{\Omega_k / k_B T}$$

is the probability *not* to have any particles in a given state. Classical (Boltzmann)

$$w_0 \simeq 1 \ , \quad w_1 \simeq \exp\frac{\mu - \epsilon_k}{k_B T} \ll 1 \ , \quad w_n \simeq 0, n \geq 2$$

The average number of particles

$$\langle n_k \rangle = \sum_{n_k} n_k w_{n_k} \simeq w_1$$

or

$$\langle n_k \rangle \equiv \bar{n}_k = \exp \frac{\mu - \epsilon_k}{k_B T} \tag{13.3}$$

The above is the Boltzmann distribution, often used just as

$$\bar{n}_k = a e^{-\epsilon_k / k_B T}\ , \quad N = \sum n_k \tag{13.4}$$

(the second equation gives a).

Note: so far we do not specify the nature of states ϵ_k, quantum or classical. Boltzmann statistics requires only $\bar{n}_k \ll 1$ which is equivalent to $\epsilon_k - \mu \gg k_B T$. (Once we get an explicit $\mu(N)$ we will see that small N/V give a negative μ, ensuring the Boltzmann statistics).

Note: Boltzmann distribution follows directly from the canonical (Gibbs) distribution since for a classical gas each molecule can be treated as an independent "subsystem" (i.e. energy of particles can be just added). However, in quantum case molecules are not independent any more and it becomes hard to use Gibbs distribution directly. Nevertheless, different quantum states (which we labeled by k) remain independent, which allows an easy use of the grand canonical distribution.

13.2 Barometric formula

READING: §38 in **LL**

$$n(z) = n_0 \exp\left[-\frac{u(z) - u(0)}{k_B T} \right] \tag{13.5}$$

For a moderate hight z, $u(z) - u(0) \simeq mgz$. For large z one has $u(z) \sim -1/z^2$ and density does not vanish for $z \to \infty$ [equilibrium is impossible!]

HW: *Problem 1 for §38; use "centrifugal energy"* $(1/2)m\omega^2 r^2$

HW: *Problem 2 for §38, but use only ultra relativistic limit with* $\epsilon = cp$.

13.2.1 Brownian motion

Consider now a suspension of tiny particles with concentration $c(\vec{r})$. Every particle can be treated as a subsystem (independent from each other but not from the carrier gas/liquid molecules). Thus, Gibbs distribution applies, and if the system is placed in external field with each particle having energy $u(\vec{r})$, the equilibrium concentration is given by the analog of barometric formula

$$c_{eq} \propto \exp\left[-u(\vec{r})/k_B T\right] \tag{13.6}$$

For a general non-equilibrium distribution there will be a flux of particles

$$\vec{j} = -D\hat{\nabla}c + \vec{v}c \tag{13.7}$$

with D being the (yet unknown) diffusion coefficient and $\vec{v}$ the "drift" velocity - in fact the average speed with which a single particle sinks. The latter can be calculated from standard hydrodynamics; if a force $\vec{F} = -\hat{\nabla}u$ acts on a particle, it will get a velocity

$$\vec{v} = \text{mobility} \cdot \vec{F}$$

In equilibrium $\vec{j} = 0$, thus

$$D = \text{mobility} k_B T \tag{13.8}$$

Einstein, 1905. Example: spherical particles

$$F = 6\pi r\eta v$$

(η - viscosity) (*Stokes*). Thus,

$$D = \frac{k_B T}{6\pi r\eta}$$

13.3 Monatomic gas: summary of examples and thermodynamics

Notations: $k_B \to k$ and often $\beta = 1/kT$ will be used. No bar is used over E or N - their thermodynamic values are always implied.

We considered before almost all relation as examples. Here is a summary, see also §45 and §42 in **LL**.

13.3.1 Canonical

For Boltzmann statistics:

$$Q_N(V,T) = \frac{1}{N!} q^N \simeq \left(\frac{eq}{N}\right)^N$$

$$q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \tag{13.9}$$

Free energy:

$$F = -kT \ln Q = -NkT \ln \frac{qe}{N} = -NkT \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{Ve}{N}\right] \tag{13.10}$$

$$P = -\frac{\partial F}{\partial V} = NkT/V$$

(equation of state)

$$E = -\frac{\partial}{\partial \beta} \ln Q = \frac{3}{2} NkT \tag{13.11}$$

Entropy:

$$S = (E - F)/T = \dots$$

Specific heat:

$$c_v = \frac{3}{2} k_B \ , \quad c_p = c_v + k_B = \frac{5}{2} k_B \tag{13.12}$$

HW: *make sure you can reproduce all the above relations in detail*

Some standard notations:

$$\zeta = \frac{3}{2} k_B \ln \frac{2\pi m}{h^2} \tag{13.13}$$

"chemical constant". Then,

$$F = -NkT \ln \frac{eV}{N} - Nc_v T \ln(kT) - N\zeta T$$

and

$$S(V,T) = kN \ln \frac{eV}{N} + Nc_v \ln(kT) + (\zeta + c_v) N \tag{13.14}$$

Such relations are of more general validity if ζ and c_v are different from those for monatomic gas. Energy is given by

$$E = Nc_v T \tag{13.15}$$

13.3.2 Grand canonical

This is an overkill for ideal classical gas since everything can be obtained from a canonical distribution. Nevertheless

$$\Xi(V,T,\mu) = \sum_N Q_N e^{\beta\mu N} = e^{qz} \ , \quad z \equiv e^{\mu\beta} \tag{13.16}$$

$$N = \frac{\partial}{\partial \ln z} \ln \Xi = qz \tag{13.17}$$

Thus,

$$\mu = kT \ln \frac{N}{q} = kT \ln \left[\frac{P}{(kT)^{5/2}} \left(\frac{2\pi\hbar^2}{m} \right)^{3/2} \right] = kT \ln \left[\frac{N}{V} \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} \right] \tag{13.18}$$

(of course, could get as $\frac{\partial}{\partial N} F$ - **HW**: *show that*).

HW: *derive q, c_v and ζ for a two-dimensional gas, with N particles over an area σ*

13.4 General: corrections for atomic/molecular energy levels

READING: **LL**, *§§41, 42*

Will use index "0" for monatomic gas. One has

$$\epsilon_k = \frac{p^2}{2m} + \epsilon'_k$$

Then

$$q = q_0 q' \ , \quad q' = \sum_k e^{-\epsilon'_k / k_B T}$$

Note:

$$q' = q'(T) \ \text{ only!}$$

Thus,

$$F = F_0 - N k_B T \ln q'(T) \tag{13.19}$$

Pressure:

$$P = -\frac{\partial}{\partial V} F = P_0 = N k_B T/V$$

Energy:

$$E = E_0(T) + \delta E'(T)$$

still depends only on temperature (not on volume!).

HW: *Consider a model gas with equal distance between energy levels $\epsilon_k = k \cdot \epsilon_0$. Find q' (Boltzmann).*

13.4.1 Electronic partition function

$$\hat{H} = \frac{p_n^2}{2m} + \hat{H}_{el}$$

$$q = q_{trans} q_{el} \ , \quad q_{el} = \sum_i g_i e^{-\beta \epsilon_i} \tag{13.20}$$

with g_i being the degeneration.

Meaning - only a few lowest levels - otherwise ionization(!).

One has (with subindex "0" corresponding to above translational part):

$$F = F_0 - NkT \ln q_{el} \tag{13.21}$$

$$E = E_0 + (N/q_{el}) \left[g_1 (\epsilon - \epsilon_0) e^{-\beta(\epsilon - \epsilon_0)} + \ldots \right] \tag{13.22}$$

HW: *derive this*

$$P = NkT/V$$

(same, since q_{el} does not depend on V)

$$\mu = \mu_0 - kT \ln q_{el} \tag{13.23}$$

$$S = S_0 - \ldots \tag{13.24}$$

HW: *Calculate corrections to E/N, F/N, S/N, μ for hydrogen atoms at $T = 1000^o K$. (use only one lower level). (optional) plot those as a function of T*

13.5 Diatomic gas

We will still use E_0, F_0, etc. for the translational part (same formulas with $m \to M$).

$$\hat{H} = \frac{p_{CM}^2}{2M} + \hat{H}_{int} \tag{13.25}$$

where $M = m_1 + m_2$ is the mass of molecule. Thus,

$$q = q_{trans} q_{int} \tag{13.26}$$

Next,

$$\hat{H}_{int} \simeq \hat{H}_{el} + \hat{H}_{rot} + \hat{H}_{vib} \tag{13.27}$$

and

$$q_{int} = q_{el} q_{vib} q_{rot} \tag{13.28}$$

Ignore the electronic excitations for simple molecules - they are of the order of $eV \gg kT_{room}$, so that higher levels are not excited.

Thus,

$$E \simeq E_0 + E_{vib} + E_{rot} \tag{13.29}$$

and similarly for F, etc.

13.5.1 Vibrational partition function

Classical:

$$\omega = \sqrt{k'/m'} \tag{13.30}$$

with k' being the force constant and

$$m' = m_1 m_2 / (m_1 + m_2) \tag{13.31}$$

the reduced mass.

Then,

$$q_{vib,clas} = kT/\hbar\omega \tag{13.32}$$

HW: *show this*

Thus,

$$E_{vib,clas} = NkT$$

("equipartition theorem") and

$$F_{vib,clas} = NkT \ln\left(\hbar\omega/kT\right)$$

HW: *show this*

Quantum

$$\epsilon_n - \epsilon_0 = n\hbar\omega \ , \quad \epsilon_0 = \hbar\omega/2 \tag{13.33}$$

Thus,

$$q_{vib} = \frac{1}{1 - e^{-\Theta_{vib}/T}} \tag{13.34}$$

with

$$\Theta_{vib} = \frac{\hbar\omega}{k} \ , \quad [\Theta_{vib}] =^o K \tag{13.35}$$

HW: *Fill out a Table for Θ_{vib} for several main molecules*

Then,

$$F_{vib} = NkT \ln\left(1 - e^{-\Theta_{vib}/T}\right) \tag{13.36}$$

$$E_{vib} = Nk\Theta_{vib}/\left(e^{\Theta_{vib}/T} - 1\right) \tag{13.37}$$

and

$$C_{vib} = Nk\left(\Theta_{vib}/T\right)^2 \frac{e^{\Theta_{vib}/T}}{\left(e^{\Theta_{vib}/T} - 1\right)^2} \tag{13.38}$$

HW: *Check the above 2 relations* **HW**: *Explore the classical limit for $T \gg \Theta_{vib}$; there will be a constant difference with the strictly classical expression since we calculate the energy from ϵ_0 in the quantum case.*

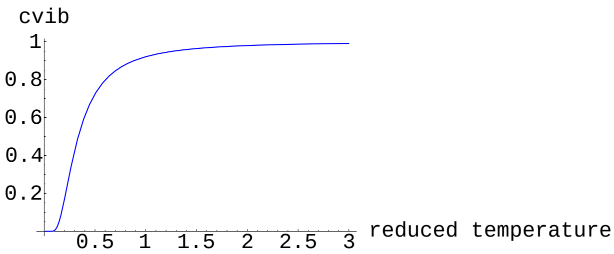

Figure 13.1: Vibrational contribution to specific heat, C_{vib}/Nk as a function of T/Θ_{vib}

13.5.2 Rotational partition function (different nuclei)

Classical:

$$\epsilon_r = \frac{(p_\theta)^2}{2I} + \frac{(p_\phi)^2}{2I\sin^2\theta}$$

$$q_{r,clas} = \frac{1}{(2\pi\hbar)^2}\int\int \exp\left\{-\beta\epsilon_r\left(p_\theta, p_\phi, \theta\right)\right\} d\,p_\theta d\,p_\phi d\,\theta d\,\phi = \frac{T}{\Theta_r} \tag{13.39}$$

with

$$\Theta_r \equiv \frac{\hbar^2}{2Ik} \tag{13.40}$$

HW: *Show this*

HW: *Fill out a Table for Θ_r for several main molecules*

The rest is the same as for vibrations, with $\Theta_{vib} \to \Theta_r$; in particular the equipartition theorem holds, and

$$C_{r,clas} = Nk \tag{13.41}$$

Quantum:

$$\epsilon_{r,J} = k\Theta_r J(J+1)\ , \quad J = 0, 1, \ldots \tag{13.42}$$

Notations:

$$z_r = e^{-\Theta_r/T} \tag{13.43}$$

Then,

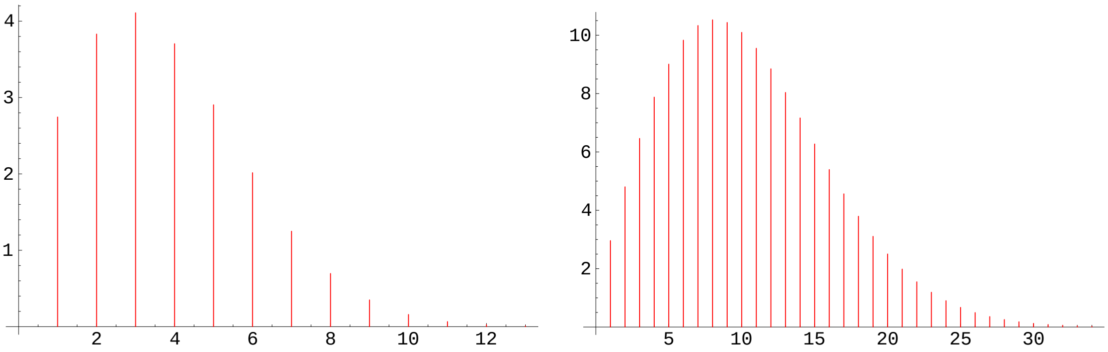

Figure 13.2: Relative populations of rotational levels at lower (left) and higher (right) temperatures [in both cases, however, temperature is noticeably larger than Θ_r - otherwise only a handful of levels would be visible] . On the x-axes is the number J.

$$q_r(z) = \sum_{J=0}^{\infty}(2J+1)z^{J(J+1)} \tag{13.44}$$

Limits:
$T \to 0$, $z \to 0$ (much faster !).

$$q_r = 1 + 3z^2 + 5z^6 + \dots \tag{13.45}$$

$T \to \infty$, $z \to 1$, series almost diverges. $\sum_J \to \int dJ$. Goes to classical limit.

HW: *Check this. Hint: replace summation by integration.*

13.5.3 Rotational specific heat

Generally, needs to be considered numerically (see the Mathematica notebook *vibrot.nb* for details). The major contribution to the sum for $q_r(z)$ (see also Fig. 13.2) comes from

$$J_{\max} \simeq \frac{1}{\sqrt{-2\ln z}} - 1/2 = \left(\frac{T}{2\Theta_r}\right)^{1/2} - 1/2$$

The number of contribution terms around $J_{\max}$ is also of the order of $J_{\max}$ [this can be found from the second derivative, or from the integral representation which is just an exponential of $-J(J+1)\Theta_r/T$]. About $5J_{\max}$ will be sufficient for an accurate q_r with an error of about 1%.

To get the specific heat we need a symbolic derivative. Note that:

$$\frac{\partial}{\partial\beta} = -k\Theta_r z\frac{\partial}{\partial z}\ , \quad \frac{\partial}{\partial T} = \frac{\Theta_r}{T^2}z\frac{\partial}{\partial z}$$

(which is useful when calculating the energy and the specific heat, respectively). When taking a second derivative of q_r, a typical term is

$$J^2(1+J)^2(1+2J)z^{J(J+1)}$$

which has a slightly larger maximum at

$$J_{c,\max} \approx \left(\frac{3T}{2\Theta}\right)^{1/2}$$

If the numerical goal is to reproduce Fig. 3 in LL (with $T \lesssim 1.5\Theta_r$), then $J_{c,\max}$ is not large, and taking 15 terms will be more then enough. The expected error, of the order of the first neglected term at the highest T, is virtually zero (about 10^{-60}); on the other hand, the 15-term approximation will become inapplicable for $T \gtrsim (2/3)\Theta_r \times (15)^2 \sim 150\Theta_r$.

The specific heat is shown by a blue line in Fig. 13.3. To get the asymptotes (red lines) we do the following. At high T the Euler-MacLaurin formula is used which approximates the infinite sum by an integral, and provides further corrections. One has:

$$q_r \simeq \frac{T}{\Theta_r} + \frac{1}{3} + \frac{\Theta_r}{T} + \dots\ , \quad T \gg \Theta_r$$

The first term is classical; two extra terms are needed for the second derivative in C_r. Thus, we get for energy:

$$E = Nk\left(T - \Theta_r/3 - \frac{\Theta_r^2}{45T} + \dots\right) \tag{13.46}$$

and

$$C_r = Nk\left(1 + \frac{\Theta_r^2}{45T^2} + \dots\right)\ , \quad T \gg \Theta_r \tag{13.47}$$

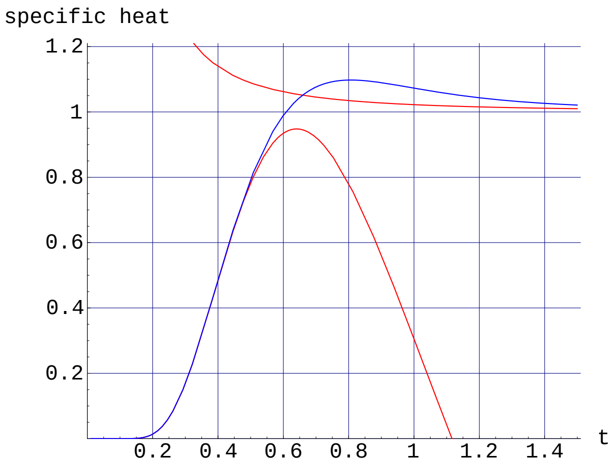

Figure 13.3: Reduced rotational specific heat C_r/Nk as a function of reduced temperature $t = T/\Theta_r$ (blue line). Red lines are the low- and the high-temperature asymptotes, eqs. (13.48) and (13.47), respectively.

This indicates an overshoot over the classical value, but otherwise is not an accurate approximation, as seen from Fig. 13.3.

For $T \ll \Theta_r$ we use eq.(13.45). Then,

$$E = 6Nk\Theta_r e^{-2\Theta_r/T}\left(1 - 3e^{-2\Theta_r/T}\right)$$

and

$$C_r = 12Nk\left(\frac{\Theta_r}{T}\right)^2 e^{-2\Theta_r/T}\left(1 - 6e^{-2\Theta_r/T}\right) \ , \quad T \ll \Theta_r \tag{13.48}$$

When applicable, this approximation is very accurate - see Fig. 13.3.

13.6 Thermodynamic consequences

work-through: §42,43 and problems (!)

Reminder:

$$Q = \frac{1}{N!}q^N \ , \ q = q_{trans}(V,T)q_{int}(T) \ , \quad q_{trans} = V\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}$$

$$q_{int} = \sum e^{-\beta\epsilon'} \simeq q_{el}q_{rot}q_{vib}$$

Thus,

$$F(V,T,N) = -kT\ln Q \simeq -kTN\ln\frac{eq}{N} = -NkT\ln\frac{eV}{N} + Nf(T) \tag{13.49}$$

with

$$f(T) = -kT\ln q_{int} \tag{13.50}$$

which can be complicated. Thus, dependences on V, P remain similar to monatomic gas, but T-dependence is sensitive to inner motions/structure of molecules.

Entropy:

$$S = kN\ln\frac{eV}{N} - Nf'(T) \tag{13.51}$$

Energy:

$$E = N\left[f(T) - Tf'(T)\right] \tag{13.52}$$

Enthalpy:

$$W = N\left[f(T) - Tf'(T) + kT\right] \tag{13.53}$$

and

$$C_p - C_v = NkT \tag{13.54}$$

HW: *Derive the above 4 equations*

13.6.1 Gas with constant specific heat

T far away from Θ_r , Θ_{vib} , etc.:

$$E = Nc_vT + N\epsilon_0\,,\ W = Nc_pT + N\epsilon_0 \tag{13.55}$$

Let us find $f(T)$:

$$C_v \equiv Nc_v = dE/dT = -NTf''(T)$$

$$f(T) = -c_vT\ln T - \zeta T + \epsilon_0 \tag{13.56}$$

with ζ - some *const*. Thus,

$$F = -Nk_BT\ln\frac{eV}{N} - Nc_vT\ln T - NT\zeta + N\epsilon_0 \tag{13.57}$$

$$S = -\frac{\partial}{\partial T}F = Nk_B\ln\frac{eV}{N} + Nc_v\ln T + N(\zeta + c_v) \tag{13.58}$$

Can use $PV = Nk_BT$ to replace V or T by P, e.g.

$$S = Nk_B\ln V + Nc_v\ln PV + N\cdot const \tag{13.59}$$

or with $c_p = c_v + k_B$

$$S = N\left(\ln V^{c_p} + \ln P^{c_v} + const\right)$$

For $S = const$ (adiabatic):

$$PV^\gamma = const\ ,\quad \gamma = c_p/c_v \tag{13.60}$$

HW: *Describe problem 1 to §43. How the result is modified if gasses are distinct from each other?*

Chapter 14

Fermi-Dirac (FD) and Bose-Einstein (BE) statistics

14.1 Introduction: the simplest example

in class

14.2 Grand canonical partition function

in class

14.2.1 Occupation numbers

$$E = \sum_k \epsilon_k n_k \ , \quad N = \sum_k n_k \tag{14.1}$$

$$Q_N = \sum_{\{n_k\}}{}' \prod_k \left(e^{-\beta\epsilon_k}\right)^{n_k}$$

(where prime means that the sum is restricted by $\sum n_k = N$).

FD:

$$n_k = 0, 1 \tag{14.2}$$

BE:

$$n_k = 0, 1, 2, \ldots \tag{14.3}$$

Actual evaluation of Q_N for finite N is very hard.

14.2.2 Evaluation of Ξ

READING: **LL**, *§§53, 54, although they do not use Ξ but go directly to $\Omega = -kT\ln\Xi$.*

$$\Xi = \sum_N e^{\beta\mu N} Q_N = \sum_N \sum_{\{n_k\}}{}' \prod_k \left(e^{\beta\mu} e^{-\beta\epsilon_k}\right)^{n_k} \tag{14.4}$$

0r,

$$\Xi = \prod_k \left\{ \sum_{n_k=0}^{n_k^{\max}} \left(e^{\beta(\mu-\epsilon_k)}\right)^{n_k} \right\} \tag{14.5}$$

With the FD and BE restrictions on $n_K^{\max}$ one has, respectively

$$\sum_{n_k=0}^{n_k^{\max}} \left(e^{\beta(\mu-\epsilon_k)}\right)^{n_k} = \left(1 \pm e^{\beta(\mu-\epsilon_k)}\right)^{\pm 1}$$

Thus, with upper sign for FD and lower for BE

$$\Xi \equiv \prod_k \Xi_k = \prod_k \left(1 \pm e^{\beta(\mu-\epsilon_k)}\right)^{\pm 1} \tag{14.6}$$

Note: despite formal similarities, in FD we have a sum, while in BE an infinite series. Thus, $\mu_{BE} < 0$ (otherwise the series diverges), while there are no restrictions on the sign of μ_{FD} .

14.2.3 Average occupation numbers

$$\bar{n}_k = k_B T \left(\frac{\partial}{\partial\mu} \ln \Xi_k\right)_{V,T} = \frac{1}{e^{\beta(\epsilon_k-\mu)} \pm 1} \tag{14.7}$$

Then,

$$N = \sum_k \bar{n}_k \tag{14.8}$$

$$E = \sum_k \bar{n}_k \epsilon_k \tag{14.9}$$

$$\Omega = \sum_k \Omega_k \ , \ \ \Omega_k = -k_B T \ln \Xi_k = \mp k_B T \ln\left(1 \pm e^{\beta(\mu - \epsilon_k)}\right) \tag{14.10}$$

(and $pV = -\Omega$).

Boltzmann limit: for $\epsilon_k - \mu \gg kT$

$$\bar{n}_k = e^{\beta(\mu-\epsilon_k)} \ll 1$$

14.3 Non-equilibrium quantum gas

Reading: class notes or LL, Ch.IV-§55.

Fermi: for each level j with degeneracy G_j there are

$$\Delta\Gamma_j = C_{G_j}^{N_j}$$

ways to distribute N_j particles.

Using the Stirling formula for large G_j, n_j one obtains for the entropy

$$S = k \sum_j \ln \Delta\Gamma_j \simeq k \sum_j \left\{G_j \ln G_j - N_j \ln N_j - (G_j - N_j) \ln (G_j - N_j)\right\}$$

HW: *check this*

With

$$\bar{n}_j \equiv N_j / G_j \leq 1 \ \ (\text{forFermi})$$

one has

$$S = -k \sum_j G_j \left\{\bar{n}_j \ln \bar{n}_j + (1 - \bar{n}_j) \ln (1 - \bar{n}_j)\right\} \tag{14.11}$$

Using method Lagrange multipliers, find maximum of S with constrains

$$\sum_j G_j \bar{n}_j = N \ , \ \ \sum_j \epsilon_j G_j \bar{n}_j = E$$

this gives

$$\bar{n}_j = 1/\left(e^{\alpha + \beta\epsilon_j} + 1\right)$$

HW: *show that*

For Bose

$$\Delta\Gamma_j = C_{G_j + N_j - 1}^{N_j}$$

(check with the elementary example above). The rest is similar, giving

$$S = -k \sum_j G_j \left\{ \bar{n}_j \ln \bar{n}_j - (1 + \bar{n}_j) \ln (1 + \bar{n}_j) \right\} \tag{14.12}$$

HW: *show this*

Maximization with the same constrains gives

$$\bar{n}_j = 1/\left(e^{\alpha + \beta \epsilon_j} - 1\right)$$

HW: *show that*

14.4 Role of spin and density of levels

14.4.1 Standard case: 3D and $\epsilon = p^2/2m$

$$d\Gamma = g dV \frac{dp_x dp_y dp_z}{h^3} \;\rightarrow\; gV 4\pi p^2\, dp/h^3 \tag{14.13}$$

with

$$g = 2s + 1 \tag{14.14}$$

s-spin. Note this result depends *only* on 3-dimensional space, but not on the statistics (BE or FD) or the dispersion law $\epsilon = \epsilon(p)$ (non-relativistic or relativistic).

$$dN\left(\vec{p}\right) = \bar{n}\left(\epsilon(p)\right) d\Gamma$$

$$dN_p = \frac{4\pi g V p^2 dp}{h^3} \bar{n}(\epsilon) \tag{14.15}$$

Note: $p^2 = 2m\epsilon$, thus

$$p^2\, dp = \sqrt{2} m^{3/2} \sqrt{\epsilon}\, d\epsilon$$

One has

$$dN_\epsilon = \frac{dN_p}{d\epsilon} d\epsilon = gV \frac{m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \sqrt{\epsilon} d\epsilon \bar{n}(\epsilon) \equiv VR \frac{\sqrt{\epsilon} d\epsilon}{e^{\beta(\epsilon - \mu)} \pm 1} \tag{14.16}$$

with

$$R \equiv g \frac{m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \tag{14.17}$$

HW: *Show that this tends to Maxwell distribution in the classical limit. Hint: consider large negative μ and use the classical expression for $\mu = \mu_{Bol}$ - see below.*

14.4.2 Other dimensions d and other dispersion relation

Note: $n(\epsilon)$ will be the same(!). The only changes will be: $d\Gamma(p) \propto L^d p^{d-1}\, dp/\hbar^d$ will change with dimension (not sensitive to dispersion or statistics) while a different $\epsilon(p)$ will modify $dp/d\epsilon$ encountered when making a transition from N_p to N_ϵ.

Examples:

$2D$: V is now the area

$$d\Gamma \;\to\; gV2\pi p\, dp/h^2 \tag{14.18}$$

HW: *Write explicitly N_ϵ for a 2D gas*

Ultra-relativistic dispersion: $\epsilon = cp$:

$$p^2\, dp = \frac{1}{c^3}\epsilon^2\, d\epsilon$$

HW: *Write explicitly N_ϵ for a 3D ultra-relativistic gas - will need this later*

14.4.3 Mathematical intermission - polylogarithm

LL do not use this function explicitly, but all their integrals are expressed through it. It thus allows to represent (and plot) the results in a compact unified way for both BE and FD cases.

Definition

$$Li_s(z) \equiv \sum_{k=1}^{\infty} \frac{z^k}{k^s} = \frac{1}{(s-1)!}\int_0^\infty \frac{x^{s-1}\, dx}{\frac{1}{z}e^x - 1} \tag{14.19}$$

The integral relation is useful for general expressions and the extreme quantum limits; the series is convenient for understanding the Boltzmann limit and corrections. s does not have to be integer, but I do not want to use Gamma-function (since Γ is reserved for statistical weight); we will need $s = 3/2\,, 5/2\,, 1/2$ and 2.

A useful identity is

$$\frac{d}{dz}Li_s(z) = \frac{1}{z}Li_{s-1}(z) \tag{14.20}$$

HW: *prove the above using alternatively the series or the integral representations*

At $z = 1$ one has

$$Li_s(1) = \sum_{k=1}^{\infty} \frac{1}{k^s} \equiv \zeta(s) \tag{14.21}$$

which is the Riemann zeta-function.

14.5 Evaluation of chemical potential

Return to standard $3D$ case. The total number of particles is

$$\frac{N}{V} = \frac{gm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^{\infty} \frac{\sqrt{\epsilon}d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1} \tag{14.22}$$

This is an implicit equation for the chemical potential as a function of density.
With

$$z = \mp e^{\beta\mu} \tag{14.23}$$

and $x = \beta\epsilon$ one can write

$$\frac{N}{V} = \mp \frac{g(mkT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^{\infty} \frac{\sqrt{x}dx}{\frac{1}{z}e^x - 1} \tag{14.24}$$

The integral can be expressed through a special function, Polylogarithm
:

$$\nu(z) \equiv \left| \int_0^{\infty} \frac{\sqrt{x}dx}{\frac{1}{z}e^x - 1} \right| = \left| \frac{\sqrt{\pi}}{2} \mathrm{Li}_{3/2}(z) \right| \tag{14.25}$$

(see http://mathworld.wolfram.com/Polylogarithm.html or the function "PolyLog[n, z]" in *Mathematica*).

The equation for the chemical potential can be written as

$$\frac{N}{V} = \mp \frac{g(mkT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \frac{\sqrt{\pi}}{2} \mathrm{Li}_{3/2}(z) \equiv R\,(kT)^{3/2}\,\nu(z) \tag{14.26}$$

and is shown in Fig. 14.1. Results of the actual (numerical) solution of this equation using *Mathematica* are shown in Fig. 14.2.

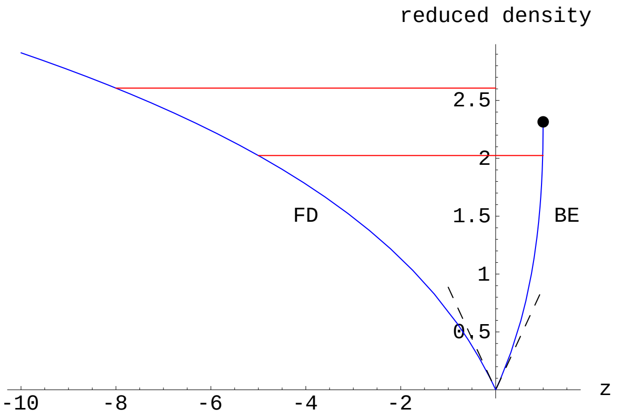

Figure 14.1: Reduced density $\nu(z)$ (see caption to next figure) as a function of $z = \mp e^{\beta\mu}$, as follows from eq. (14.26). Negative z correspond to Fermi-Dirac (FD) and positive z to Bose-Einstein (BE) statistics, respectively. For a given density (horizontal red line) interchapter with the curve determines the value of z and thus the chemical potential. Note that the BE curve stops at $z = 1$ at the value of 2.31516, and for higher density there are no solutions for the BE statistics (upper red line). This corresponds to the Bose-Einstein condensation. Dashed line -$|z|\sqrt{\pi}/2$, the Boltzmann limit.

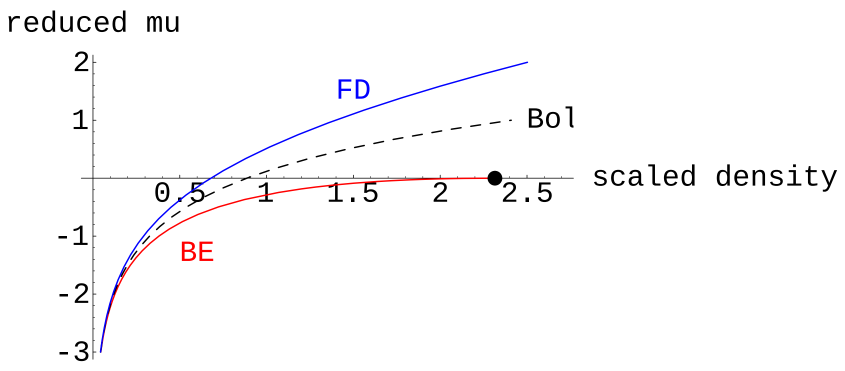

Figure 14.2: Reduced chemical potential μ/kT as a function of the scaled density $(N/V)\cdot\left\{\sqrt{2}\pi^2\hbar^3/\left[g(mkT)^{3/2}\right]\right\}$ (which is of the order of $(N/V)\cdot\Lambda^3/g$ with the thermal deBroglie wavelength Λ and $g = 2s + 1$ the degeneration associated with the spin s). In the BE case the chemical potential is strictly zero if density exceeds the critical value. The dashed line corresponds to Boltzmann statistics and coincides with both quantum statistics for large negative μ; extension of the Boltzmann curve into the region of large positive μ is formal since any real particles will act as quantum here.

14.6 Energy

$$E = RV\int_0^\infty \frac{\epsilon^{3/2}d\epsilon}{e^{\beta(\epsilon-\mu)}\pm 1} = RV\,(kT)^{5/2}\,\nu_\epsilon(z) \tag{14.27}$$

with

$$\nu_\epsilon(z) \equiv \left|\int_0^\infty \frac{dx\,x^{3/2}}{\frac{1}{z}e^x - 1}\right| = \left|\frac{3}{4}\sqrt{\pi}\mathrm{Li}_{5/2}(z)\right| \tag{14.28}$$

HW: *check this - Mathematica can be helpful*

14.7 Equation of state

$$\Omega \equiv -PV = \mp kTRV\int_0^\infty \sqrt{\epsilon}d\epsilon\ln\left(1\pm e^{\beta(\mu-\epsilon)}\right) \tag{14.29}$$

Integrating by parts, get

$$PV = \frac{2}{3}E \tag{14.30}$$

HW: *show that*

This is just like classical(!).

Correction to classical ideal gas equation

$$PV/NkT = 2\nu_\epsilon(z)/3\nu(z) \tag{14.31}$$

Expand for small z

$$PV/NkT \approx 1 - \frac{z}{4\sqrt{2}} \tag{14.32}$$

HW: *check this - Mathematica can be useful*

For the first quantum correction the Boltzmann approximation can be sufficient when evaluating z.

$$\mu_{Bol}(P,T) = kT \ln \left[\frac{P}{g(kT)^{5/2}} \left(\frac{2\pi\hbar^2}{m} \right)^{3/2} \right] = kT \ln \left[\frac{N}{gV} \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} \right] \tag{14.33}$$

With

$$z \approx z_{Bol} = \mp e^{\mu_{Bol}/kT} \tag{14.34}$$

one has

$$\frac{PV}{NkT} = 1 \pm \frac{\pi^{3/2}}{2g} \frac{N\hbar^3}{V(mkT)^{3/2}} + \ldots \tag{14.35}$$

Note that pressure is increased for Fermi and reduced for Bose. Also, correction is of the order $N\Lambda^3/Vg$, and should be small.

14.8 Ultra-relativistic gas

READING: **LL**, *§61, although they consider specifically electrons, which correspond to $g = 2$ and "+" sign in equations below. The Bose case - "$-$" sign with $g = 2$- will be useful for black-body radiation.*

The average occupation numbers for a given energy level $\bar{n}(\epsilon)$, as in eq.(14.7), remain unchanged. The quantum analog of the Maxwell distribution in momentum space, eq.(14.15) also is the same. [recall that deBroglie wave h/p which is used to count states is also valid in the relativistic case (!)]. The difference comes when one considers energy

$$\epsilon = cp$$

(instead of $p^2/2m$). This gives

$$dN_\epsilon = \frac{4\pi g}{(ch)^3} V \epsilon^2 d\epsilon \bar{n}(\epsilon) \tag{14.36}$$

The total energy

$$E = \int \epsilon dN_\epsilon = \frac{4\pi g}{(ch)^3} V \int_0^\infty \epsilon^3 d\epsilon \bar{n}(\epsilon) \tag{14.37}$$

Similarly, for Ω one has

$$\Omega = \mp \frac{gV}{2\pi^2 (\hbar c)^3} \int_0^\infty \epsilon^2 d\epsilon \ln\left(1 \pm e^{\beta(\mu-\epsilon)}\right) = -\frac{1}{3} E \tag{14.38}$$

Thus,

$$P = \frac{1}{3} \frac{E}{V} \tag{14.39}$$

14.9 More on polylogarithm

As we have seen, with $z = \mp \exp(\beta\mu)$ one needs an absolute value of a typical integral

$$\int_0^\infty \frac{\epsilon^n \, d\epsilon}{e^{\beta\epsilon}/z - 1} = (kT)^{n+1} n! \, \mathrm{Li}_{n+1}(z)$$

The index n depends on the quantity of interest (density/energy), and on the dimension and the dispersion law - see Fig. 14.3 for typical values in 3D.

Limis:

- $z \to 0$ (i.e. $\mu \to -\infty$, Boltzmann with first quantum correction). From series

$$\mathrm{Li}_s(z) \sim z + z^2/2^s \tag{14.40}$$

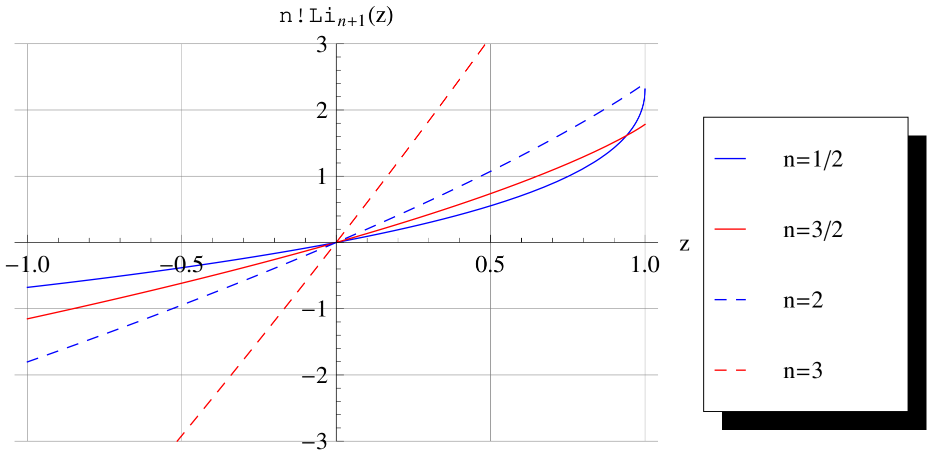

Figure 14.3: Typical values of the integrals for the dimensionless densities (blue) and energies (red). Solid lines - classical dispersion law $\epsilon \propto p^2$, dashed - ultrarelativistic $\epsilon \propto p$. Positive z correspond to Bose-Einstein case (with $z = 1$ being the condensation point), and $z < 0$ is the Fermi-Dirac case, when absolute value of the integral should be taken.

- $z \to -\infty$ (i.e. $T \to 0$, $\mu > 0$ - degenerate Fermi). Note the cut-off of the integral in the definition of Li_s for $x \sim \ln |z|$. Thus

$$\mathrm{Li}_s(z) \sim \frac{1}{s!} (\ln |z|)^s \tag{14.41}$$

- $z \to 1^-$ (i.e. $\mu \to 0^-$, Bose-Einstein condensation). For $z > 1$ divergence follows either from series definition of $\mathrm{Li}_s(z)$ or from the integral. For $z = 1$ convergence for $s > 1$ (from integral).

Chapter 15

Bose-Einstein condensation

What happens if eq.(14.26) has no solutions, as in the right part of Fig. 14.1? In other words,

$$\frac{N}{V}\frac{1}{R}(kT)^{-3/2} = \nu(1) = \frac{\sqrt{\pi}}{2}\zeta(3/2) \approx 2.31516 \tag{15.1}$$

determines the highest density (or the lowest temperature) when the solution is still possible.

[Again, $\zeta(x)$ is the Riemann zeta-function, which appears as the limit of PolyLogarithm as $z \to 1$:

$$\zeta(s) = \mathrm{Li}_s(1) = \sum_{i=1}^{\infty} \frac{1}{i^s}\ , \quad s > 1$$

(see any good math reference, e.g. Abramowitz and Stegun or *mathworld*)].

Since all math was done correctly, the only way one could stray was in replacing the sum over discrete energy levels by an integral. Care should be taken since the average occupation number, $\bar{n}_\epsilon$ tends to infinity (!) for $\epsilon \to 0$ and $\mu \to 0$. Indeed, the lowest level can hold a *finite* number of particles in order to ensure that eq.(15.1) (with N reduced by this number) has a solution.

[*Note: it is possible to isolate the contribution of the lowest level explicitly, obtaining a correction proportional to* $1/V$ *- see, e.g., Huang. Then all dependences are smooth across the transition. However, in the limit* $V \to \infty$*, which is of the main interest, one anyway gets cusped curves, and we shall consider this limit from the start*].

If the inverse density $v = V/N$ (volume per particle) is fixed, then

$$kT_c = \left(\frac{2}{\sqrt{\pi}Rv\zeta(3/2)}\right)^{2/3} \simeq \frac{0.5714}{(Rv)^{2/3}} \tag{15.2}$$

HW: *Check the dimension*
HW: *Estimate T_c for liquid He - use any Tables to find N/V for $T = 4K$, and assume that this density is not changing with T*

15.1 Properties of the condensed phase

15.1.1 Number of particles

Note the energy distribution at $\epsilon > 0$ is still correct at $T < T_c$. Thus,

$$N_{\epsilon>0} = RV(mkT)^{3/2}\nu(1) = N\left(\frac{T}{T_c}\right)^{3/2}\ ,\ \ T \le T_c \tag{15.3}$$

The "missing" particles are in the ground state

$$N_0 = N - N_{\epsilon>0} = N\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right] \tag{15.4}$$

see Fig. 15.1. Remarkably, the ground state which can bearly hold two electrons, can hold an Avogadro number of bosons!

15.1.2 Energy

$$\begin{aligned} E = RV(kT)^{5/2}\nu_\epsilon(1) = kTN_{\epsilon>0}\frac{\nu_\epsilon(1)}{\nu(1)} \\ \simeq 0.77kTN\left(\frac{T}{T_C}\right)^{3/2} = 0.128\frac{gm^{3/2}}{\hbar^3}(kT)^{5/2}V \end{aligned} \tag{15.5}$$

HW: *check the numbers*

Note: energy depends only on T, V, but not N - "extra" particles go to the ground state and do not contribute.

HW: *show that for $\mu = 0$ one has $F = \Omega = -2E/3$*

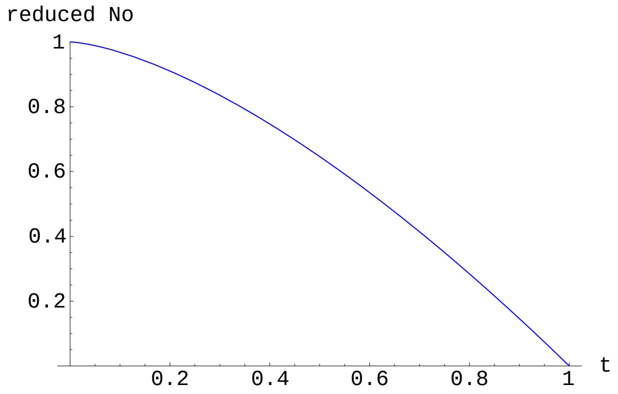

Figure 15.1: Reduced number of particles in the ground state N_0/N as a function of reduced temperature $t = T/T_c \leq 1$. For higher temperature this number is strictly zero (in the limit of infinite volume).

15.1.3 Specific heat, $T < T_c$

$$C_v = \left(\frac{\partial}{\partial T} E\right)_{V=const} = \frac{5E}{2T} \sim T^{3/2} \ , \quad T \leq T_c \tag{15.6}$$

15.1.4 Pressure

$$P = -\left(\frac{\partial}{\partial V} \Omega\right)_{T,\mu=const} = \frac{2}{3}\frac{E}{V} = \frac{2}{3} 0.128 \frac{g m^{3/2}}{\hbar^3} (kT)^{5/2} \tag{15.7}$$

Note: no dependence on volume! - horizontal isotherms, similar to two-phase mixture.

15.2 Specific heat at all T

Assuming $N, V = const$ (not to write partial derivatives)

$$C_V = \frac{dE}{dT} = RV \frac{d}{dT} (kT)^{5/2} \nu_\epsilon[z(T)] \tag{15.8}$$

or

$$C_v = \frac{3kRV\sqrt{\pi}(kT)^{3/2}}{8z}\left[5\mathrm{Li}_{5/2}(z) z + 2T \mathrm{Li}_{3/2}(z) \frac{dz}{dT}\right]$$

In order to eliminate dz/dT we differentiate the equation for the (constant) density $n \equiv N/V$

$$0 = dn = d\left(R(kT)^{3/2}\nu[z(T)]\right)$$

this gives:

$$\frac{dz}{dT} = -\frac{3z}{2T}\frac{\mathrm{Li}_{3/2}(z)}{\mathrm{Li}_{1/2}(z)} \tag{15.9}$$

Note that $\mathrm{Li}_{1/2}(z)$ diverges for $z \to 1$.

Thus,

$$C_v = \frac{3kRV\sqrt{\pi}(kT)^{3/2}}{8}\left[5\mathrm{Li}_{5/2}(z) - 3\frac{\mathrm{Li}^2_{3/2}(z)}{\mathrm{Li}_{1/2}(z)}\right] \tag{15.10}$$

Or, if we divide by the Nk

$$\frac{C_v}{Nk} = \frac{15}{4}\frac{\mathrm{Li}_{5/2}(z)}{\mathrm{Li}_{3/2}(z)} - \frac{9}{4}\frac{\mathrm{Li}_{3/2}(z)}{\mathrm{Li}_{1/2}(z)} \tag{15.11}$$

This is shown in Fig. 15.2 together with the sub-T_c part. Note that C_v is continuous at the transition, although there is a cusp. At high T it approaches the classical limit of $(3/2)Nk$. An alternative way get this formula, more straightforward in *Mathematica*-assisted derivations -see bec1.nb, is to use z as an independent variable with

$$k\,T(z) = [Rv\nu(z)]^{-2/3} \tag{15.12}$$

and

$$C_v = \frac{dE/dz}{dT/dz} \tag{15.13}$$

Note: both McQuarrie and Huang have eq.(15.11) for C_v/Nk. **LL** *do not give it, but they derive analytically the change in slope near T_c. Below we will do it with Mathematica - see bec1.nb.*

Again, we use parametric representation

$$\frac{dc_v}{dT} = \frac{dc_v/dz}{dT/dz}$$

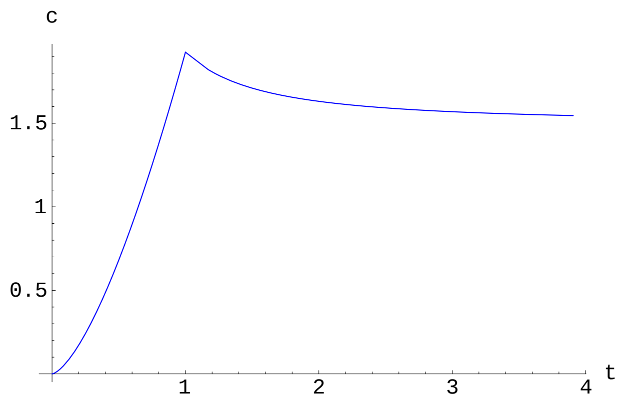

Figure 15.2: Reduced specific heat $c = C_v/(kN)$ as a function of reduced temperature $t = T/T_c$. For $t \to 0$ it is a power law: $c \sim t^{3/2}$.

This leads to a cumbersome expression, but we need only the limit $z \to 1$ - see bec1.nb. One obtains

$$\left.\frac{dc_v/dz}{dT/dz}\right|_{z=1} = 9\frac{-3 * \zeta[3/2]^3 + 10\pi\zeta[5/2])}{16\pi T_c\zeta[3/2]} \simeq -0.7772/T_c \tag{15.14}$$

Below T_c slope is positive and is given by

$$\frac{3}{2}c_v\,(T_c) = (45 * \zeta[5/2])/(8 * v * \zeta[3/2]) \simeq 2.8885/v$$

Thus, for the difference in slopes one gets $(N, V = const)$:

$$\Delta c_v = -3.66577/T_c \tag{15.15}$$

15.2.1 Pressure at all T and isotherms in parametric representation

One has

$$P = \frac{2}{3}R(kT)^{5/2}\nu_\epsilon(z) \tag{15.16}$$

Similarly,

$$V = \frac{N}{R(kT)^{3/2}\nu(z)} \tag{15.17}$$

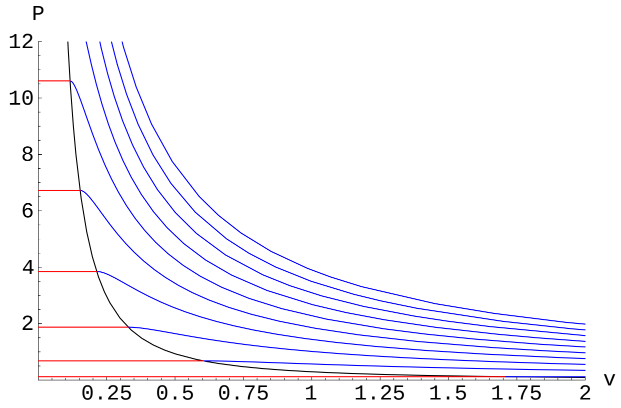

Figure 15.3: Isotherms of ideal Bose-gas in terms of reduced pressure $p \propto P$ as a function of reduced volume $v \propto V/N$. The isotherms correspond to increasing values of T (with equal increments - see *pbec.nb* for detail). At large v one has the classical ideal gas law $pv = const$. Transition between the "gas phase" (blue) and the "mixed phase" (red) is indicated by the black line with $p \propto v^{-5/3}$ (see text).

R is a constant - see eq. (14.17).

In principle, one needs to eliminate $z = z(V,T)$ (N-fixed) from the second equation, and thus obtain the equation of state $P = P(V,T)$. Technically, however, this is hard, and it is much better to treat z as a parameter which determines both P and V. The resulting curves are shown in Fig. 15.3, with z ranging from 0 to 1 (with small z corresponding to large volume and with $z = 1$ corresponding to the onset of condensation). To obtain the condensation curve we need to get rid of T. Thus

$$P_c^3 V_c^5 = N^5 R^{-2} \left(\frac{2}{3}\nu_\epsilon(1)\right)^3 \nu(1)^{-5} = const \tag{15.18}$$

which is the black curve in the figure.

15.3 Experimental

Remarkably, could observe BEC in dilute vapors - see

http://jilawww.colorado.edu/www/press/images.html for the image, or M.H. Anderson et al., Science, **269**, 198 (1995) for the description.

They used ^{87}Rb at a density $\sim 3 \cdot 10^{12} cm^{-3}$. Which spin to use is an issue, but let us use $s = 0$.

HW: *Estimate T_c. Note: should be VERY small*

Note: the actual experiment was performed in a trap, which somewhat changes the conditions of condensation - see www.physics.cornell.edu/sethna/StatMech/ for additional discussion and references

Chapter 16

Blackbody radiation

16.1 Planck distribution

One has

- ultra-relativistic gas with $g = 2$ (the latter is a subtle issue, photon has 2 states, not 3 as would a particle with spin $s = 1$, will discuss in class)
- "particles" are not conserved, thus $\mu = 0$
- energy is $\hbar\omega$

The rest is straightforward.

$$\bar{n} = \frac{1}{e^{\hbar\omega/kT} - 1} \tag{16.1}$$

is the Plank's formula.

Next

$$dN_\omega = \hbar^3 dN_\epsilon = \frac{V}{\pi^2 c^3} \frac{\omega^2 d\omega}{e^{\hbar\omega/kT} - 1} \tag{16.2}$$

(note that $\hbar$ enters only in $\bar{n}$, but not in the density of states. Indeed, the latter can be (and was) derived classically at first.

HW: *Calculate the number of photons, $\int dN_\omega$*

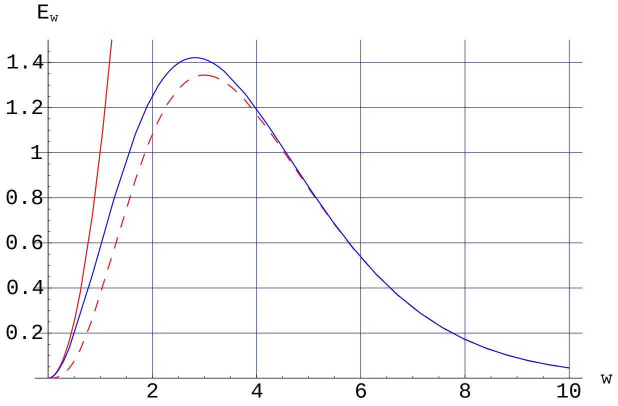

Figure 16.1: The function $E_w = w^3/\left(e^w - 1\right)$ (blue line) which determines the energy density in the Plank's formula, with $w = \hbar\omega/kT$. Maximum of the blue curve is at $\hbar\omega = 2.822\,kT$, which determines how the dominant color of radiation changes with temperature (the "displacement law"). The solid red line is the Rayleigh-Jeans approximation, and the dashed red line (much better) is the Wien's law.

Density of energy (Plank):

$$dE_\omega = \hbar\omega dN_\omega = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3 d\omega}{e^{\hbar\omega/kT} - 1} \tag{16.3}$$

This is shown in Fig. 16.1 together with the small- and large-frequency asymptotes:

$$dE_\omega \approx \frac{VkT}{\pi^2 c^3}\omega^2 d\omega\ , \quad \hbar\omega \ll kT$$

(Rayleigh-Jeans, without the restriction - they did not know $\hbar$)

and

$$dE_\omega \approx \frac{V\hbar}{\pi^2 c^3}\omega^3 d\omega e^{-\hbar\omega/kT}\ , \quad \hbar\omega \gg kT$$

(Wien, also without the restriction)

HW: *find* dE_λ *with* $\lambda = 2\pi c/\omega$; *find* $\lambda_{\max}$

16.2 Total energy and specific heat

The total energy is given by

$$E = \int dE_\omega = \frac{V(kT)^4}{\pi^2(c\hbar)^3}\int_0^\infty \frac{w^3dw}{e^w - 1} \tag{16.4}$$

The integral is $\pi^4/15$.
HW: *Check this from a handbook or software. Also, calculate the integral approximately, "by hand". Hint: see Fig. 16.1.*

Thus,

$$E = 4\frac{\sigma V}{c}T^4 \tag{16.5}$$

with

$$\sigma = \frac{\pi^2 k^4}{60\hbar^3 c^2} \tag{16.6}$$

known as the Stefan-Boltzmann constant. **HW**: *Calculate it, with units* .

$$C_v = \left(\frac{\partial}{\partial T}E\right)_V = 16\frac{\sigma V}{c}T^3 \tag{16.7}$$

16.3 Radiation pressure

As for any relativistic gas, $\Omega = -E/3$. Thus,

$$P = \frac{E}{3V} \tag{16.8}$$

16.4 Einstein's coefficients

Consider a 2-level system with $E_j > E_i$. Let
B_{ij} - probability of absorption
A_{ji} probability of spontaneous emission.

Supposedely, if $\rho(\nu)$ is the density of photons with $h\nu = E_j - E_i$, and n_i, n_j are populations of the levels (i.e., numbers of atoms in each state), the rate of absorption is

$$B_{ij}n_i\rho(\nu) - A_{ji}n_j\ , \quad \text{WRONG!}$$

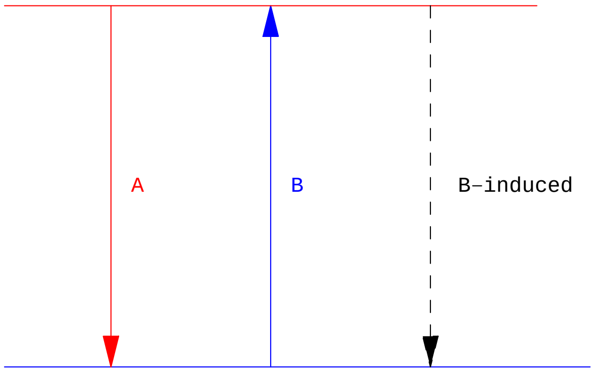

Figure 16.2:

Why?
Consider equilibrium

$$n_j^{eq}/n_i^{eq} = \exp\left\{-\frac{E_j - E_i}{k_B T}\right\}$$

(the Boltzmann distribution), then

$$\rho^{eq}(\nu) = (A_{ji}/B_{ij}) \exp\left\{-\frac{E_j - E_i}{k_B T}\right\} \quad , \quad \text{WRONG!!!}$$

must be Planck distribution. Thus, need induced transitions $B_{ji}\rho(\nu)$ ("stimulated"). Then, rate of absorption is

$$B_{ij} n_i \rho(\nu) - B_{ji} n_j \rho(\nu) - A_{ji} n_j$$

Now with $h\nu = E_j - E_i$

$$\rho^{eq}(\nu) = \frac{A_{ji}}{B_{ij} e^{h\nu/k_B T} - B_{ji}}$$

compare this with Planck

$$\rho(\nu)^{eq} = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1}$$

Thus:

$$B_{ij} = B_{ji}$$

(to ensure symmetry for very strong fields) and

$$B_{ij} = A_{ij} \left(\frac{c^3}{8\pi h \nu^3} \right)$$

Part IV

Specific heat of solids

Chapter 17

Phonons

17.1 Linear monoatomic chain

Let κ be the spring constant; u_l - displacement from equilibrium. Force

$$F_l = \kappa (u_{l+1} - u_l) - \kappa (u_l - u_{l-1})$$

or

$$m\ddot{u}_l = \kappa (u_{l+1} + u_{l-1} - 2u_l)$$

Acoustic wave:

$$a \cdot l \to x \ , \quad (\ldots) \to a^2 \frac{\partial^2 u}{\partial x^2}$$

with $m/a = \rho$, linear density, and $a\kappa = G$

$$\rho \frac{\partial^2 u}{\partial t^2} = G \frac{\partial^2 u}{\partial x^2}$$

or

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2}$$

with the "speed of sound"

$$v^2 = G/\rho = a^2 \kappa / m$$

Any $u(x - vt)$ - solution. E.g., $\exp \{i (\omega t - kx)\}$ with any $\omega, \ k$ with $\omega = kv$.

Return to discreet:
look for

$$u_l \propto \exp\left\{i\left(\omega t - kx\right)\right\} \ , \ \ x = la$$

Then,

$$-m\omega^2 = \kappa\left[e^{ika} + e^{-ika} - 2\right] = \kappa\left[e^{ika/2} - e^{-ika/2}\right]^2$$

Or,

$$\omega(k) = \sqrt{\frac{4\kappa}{m}}\left|\sin\left(\frac{ka}{2}\right)\right| \tag{17.1}$$

For $k \to 0$, $\omega \approx kv$.

$$-\frac{\pi}{a} < k < \frac{\pi}{a}$$

Brillouin zone. See Fig. 17.1 (and file phonons.nb).

Debye frequency:

$$\omega_{\max} \sim \frac{v}{a} \sim 10^{13} \ - \ 10^{14} \ Hz$$

(infrared)

17.2 1D- diatomic; optical branches

Consider the same force as above, but alternating masses m at even and M at odd positions, respectively ("red" and "blue"). Even l:

$$m\ddot{u}_l = \kappa\left(u_{l+1} + u_{l-1} - 2u_l\right)$$

Odd l:

$$M\ddot{u}_l = \kappa\left(u_{l+1} + u_{l-1} - 2u_l\right)$$

Look for a solution

$$u_{red}(l,t) = A\exp\left(ik2l - i\omega t\right) \ , \ \ u_{blue}(l,t) = B\exp\left(ik(2l+1) - i\omega t\right)$$

which should be plugged in into the dynamic equation. This gives

$$\begin{aligned} -Am\omega^2 &= \kappa\left[Be^{ika} + Be^{-ika} - 2A\right] \\ -BM\omega^2 &= \kappa\left[Ae^{ika} + Ae^{-ika} - 2B\right] \end{aligned} \tag{17.2}$$

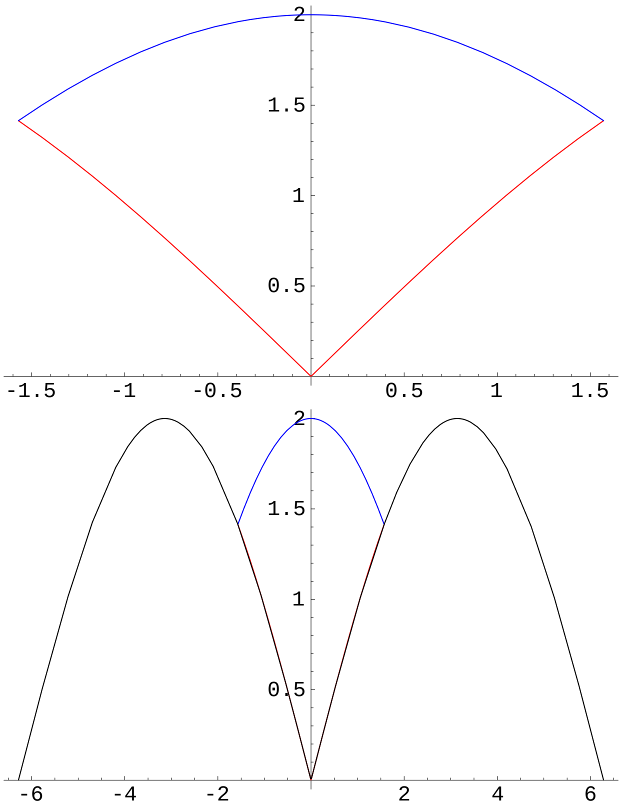

Figure 17.1:

From the condition of non-zero A, B (non-trivial solutions), find $\omega(k)$ with *two* branches. For detail, see file phonons.nb.

HW: *Restore the math, and get the two branches explicitly* .

If $m = M$ the situation is physically identical to the monatomic chain (it is just labeling of k which is different) - see Fig. 17.1. For $m \neq M$ there will be a gap in spectrum, as in Fig. 17.2 with $M = 2m$.

17.3 3D - monoatomic

Three acoustic branches - 1 longitudinal and 2 transverse.

Often hard to calculate, but can measure. E.g., neutron scattering: Consider a neutron with momentum $\hbar\vec{k}$ which is scattered to momentum $\hbar\vec{k}'$,

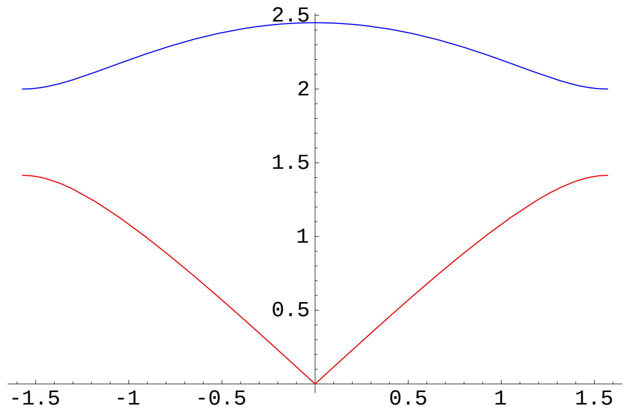

Figure 17.2:

emmiting a phonon with wave vector $\vec{K}$. Then,

$$\frac{\hbar^2 k^2}{2m_n} = \frac{\hbar^2 k'^{\,2}}{2m_n} + \hbar\omega\left(\vec{K}\right)$$

and

$$\vec{k} = \vec{k}' + \vec{K}$$

Experimentally, $\vec{k}$ and $\vec{k}'$ can be accurately measured, giving $\omega\left(\vec{K}\right)$.

Chapter 18

Contribution to specific heat

18.0.1 General density of states g_ω

Contribution of a single oscillator follows from eq. (13.38). One has

$$c_{vib}(\omega, T) = k_B (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega} - 1\right)^2}, \quad \beta \equiv \frac{1}{k_B T} \tag{18.1}$$

Now suppose the density of oscillators is given by g_ω with the total number

$$\int g_\omega d\,\omega = 3N \tag{18.2}$$

N being the number of atoms in a solid (of course, we neglect 6 compared to $3N_A$ otherwise, e.g. for a big molecule, it would be $3N - 6$).

The total contribution to specific heat is then given by

$$C_V(T) = \int c_{vib} g_\omega d\,\omega \tag{18.3}$$

If $\omega\left(\vec{K}\right)$ is known for all branches, g_ω can be determined, but need experiment. Simple approximations:

18.0.2 One-dimensional crystal

In a general case g_ω has to be measured (or assumed). It can be obtained however, if we know the dispersion relation. Let us write the previos result for a 1-dimensional monatomic chain as

$$\omega(k) = \omega_0 |\sin(ka/2)| \tag{18.4}$$

One has for a crystal with length L

$$g_k\, dk = L dk/2\pi = L \frac{dk}{d\omega} \frac{1}{2\pi}\, d\omega \equiv g_\omega\, d\omega \tag{18.5}$$

or

$$g_\omega = L \frac{dk}{d\omega} \frac{1}{2\pi} \tag{18.6}$$

Evaluating the derivative explicitly one gets

$$g_\omega \sim \frac{1}{\sqrt{\omega_0^2 - \omega^2}} \tag{18.7}$$

Note a singularity for $\omega \to \omega_0$ (*van Hove*).

18.1 Einstein model

$$g_\omega = 3N\delta\,(\omega - \omega_E) \tag{18.8}$$

and

$$C_V(T) = 3Nk_B\,(\beta\hbar\omega_E)^2\, \frac{e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E} - 1)^2} \tag{18.9}$$

The scaled picture is the same as in Fig. 13.1.

18.2 Debye model (DM)

In the DM the density of states is not assumed, but the dispersion law is taken in the long-wave length limit

$$\omega \simeq vk \tag{18.10}$$

After that, g_ω is calculated, and it is has to be truncated at some $\omega = \omega_D$ to comply with eq. (18.2).

Let us do that. Note that $g_{\vec{k}}$ is simple. One state is

$$\frac{d\,\vec{r}d\,\vec{p}}{(2\pi\hbar)^3}$$

Using $d\,\vec{p} = \hbar d\,\vec{k}$ and integrating with respect to $d\,\vec{r}$ to get volume V, one has

$$g_{\vec{k}}d\,\vec{k} = V\frac{d\,\vec{k}}{(2\pi)^3} \;\rightarrow\; V\frac{4\pi k^2 d\,k}{(2\pi)^3} = g_k d\,k \tag{18.11}$$

where we switched to spherical coordinates in k. Now with the dispersion law, eq. (18.10)

$$g_\omega d\,\omega = V\frac{\omega^2 d\,\omega}{v^3 2\pi^2}$$

and this should be multiplied by 3 to account for 3 polarizations of the phonon. More precisely, if we take into consideration different speeds of transverse ("t") and longitudinal ("l") waves, we can introduce an "average" v_0 from

$$\frac{3}{v_0^3} = \frac{2}{v_t^3} + \frac{1}{v_l^3} \tag{18.12}$$

Then,

$$g_\omega d\,\omega = 3V\frac{\omega^2 d\,\omega}{v_0^3 2\pi^2}\;, \quad \omega < \omega_D \tag{18.13}$$

and

$$g_\omega = 0;\,, \quad \omega > \omega_D$$

The value of ω_D follows from eq.(18.2), giving

$$\omega_D = v_0\left(\frac{3N}{V}2\pi^2\right)^{1/3}\;, \quad \Theta_D = \hbar\omega_D/k_B \tag{18.14}$$

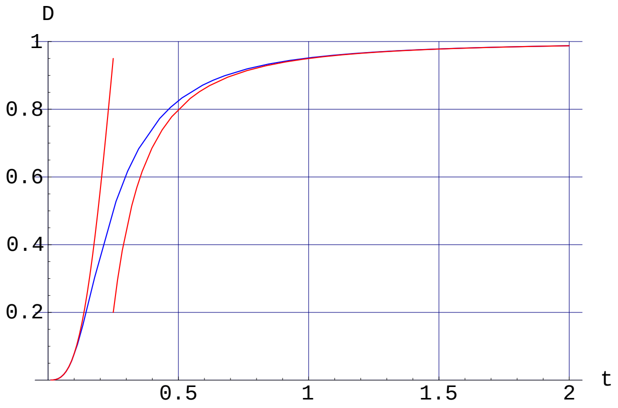

Figure 18.1: The Debye curve $D(t)$ (blue), which determines reduced specific heat $C_V/3Nk_B$ as a function of reduced temperature $t = T/\Theta_D$. Red lines indicates the low-temperature asymptote ($\sim T^3$) and the high-temperature asymptote (Dulong-Petit law $C_V = 3Nk_B$, with the first correction), respectively.

with Θ_D known as the "Debye temperature". [Note: there is no $\hbar$ in ω_D - counting of states could have been done classically(!)]. With $\omega_D \sim 10^{13} - 10^{14}\ s^{-1}$ one has

$$\Theta_D \sim 10^2 \ - \ 10^3\ {}^oK$$

Thus, with a substitution $x = \beta\hbar\omega$ one has

$$C_V = 9Nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x d\,x}{(e^x-1)^2} \equiv 3ND\left(\frac{T}{\Theta_D}\right) \tag{18.15}$$

where $D(T)$ is defined as

$$D(t) = 3t^3 \int_0^{1/t} \frac{x^4 e^x d\,x}{(e^x-1)^2} \tag{18.16}$$

The curve $D(t)$ is shown in Fig. 18.1, together with its asymptotes discused below. Note that $D(t)$ can be expressed as a combination of several elementary functions and three polylogarithms; this can be useful for plotting and for *Mathematica*-assisted evaluation of derivatives - see debye.nb.

18.2.1 Limit $T \to 0$ and connection to black-body radiation.

The upper limit of the integral tends to ∞. The value of the integral is $4\pi^4/15$ (**HW**: *Check this, or calculate the integral approximately*)

Thus,

$$C_V \simeq \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D} \right)^3 \tag{18.17}$$

HW: *show that this is N-independent, i.e. specific heat depends only on the volume of the crystal but not on the number of atoms, similar to black-body radiation.*
HW: *show that this is consistent with black-body radiation with $c \to v_0$ and $\times 3/2$ (recall that photons have only 2 polarizations)*

Note: unlike the Debye interpolation, the above expression is exact for $T \to 0$ for the phonon contribution.

Corrections to the T^3 law are discussed in *debye.nb*

18.2.2 $T \gg \Theta_D$

In the high-T limit one can linearise the denominator in the integral representation of $D(t)$, obtaining the classical Dulong-Petit law.

$$C_V \simeq 3 N k_B \tag{18.18}$$

Corrections are discussed in *debye.nb*. The leading correction is $-\left(\Theta_D/T\right)^2/20$ and is very small already at $T = 2\Theta_D$ - see Fig. 18.1.

Again note that in reality the Dulong-Petit law is more reliable than the Debye interpolation model since the former *does not* assume any specific g_ω but only that the total number of modes is $3N$.

18.2.3 Experimental

Fig. 18.2 shows data for silver superimposed on the Debye curve.

How to find Θ_D ? - fit to data at small T - see Fig. 18.3.

HW: *Plot data for C_V/T as a function of T^2 at small T; fit to a straight line. Data for C_V can be obtained from debye.nb.*

the rest will be discussed in class

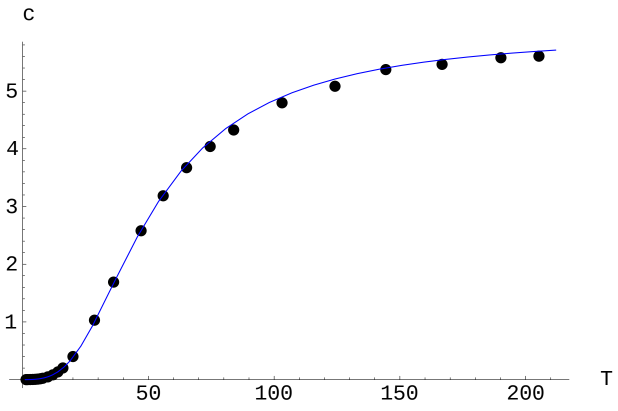

Figure 18.2: Data for Ag (points) superimposed on the Debye curve with $\Theta_D \sim 212\,^oK$

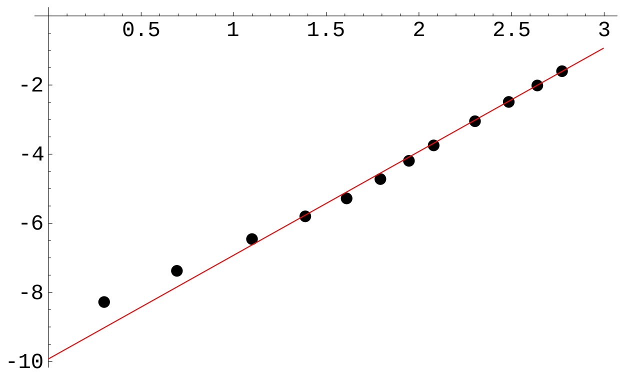

Figure 18.3: The $\ln - \ln$ plot of low-temperature data for reduced specific heat in silver (points) against the T^3 law (red line). This allows one to obtain Θ_D. Deviation at very small T is due to electronic contribution, which is linear in T. [Often, rather than using the $\ln - \ln$ plot, data for C_V/T are fitted to $a + bT^2$, giving simultaneous information about the electron (a) and phonon contributions (b), respectively.

Part V

Strongly degenerate electron gas

Notations: only electrons will be discussed in this chapter, so m will the mass of one. Subscript "F" always refers to "Fermi". The main function $f(\epsilon)$, the Fermi distribution. In addition, I will use the Fermi energy ϵ_F which is standard for physics books, and which will be taken as equivalent to μ_0. When describing the Fermi surface at $T = 0$ (and only there) I will also use notations which are standard in solid-state literature: a_0 - Bohrs radius and r_s - the "ionic radius".

Chapter 19

Fermi energy, $T = 0$

19.0.4 Formal introduction

Start with eq.(14.24) specified for fermions with $g = 2$:

$$\frac{N}{V} = R\int_0^\infty \frac{\sqrt{\epsilon}d\epsilon}{e^{\beta(\epsilon-\mu)}+1}\ ,\ R \equiv \frac{2m^{3/2}}{\sqrt{2}\pi^2\hbar^3} \tag{19.1}$$

we need the limit $\beta \to \infty$. To get the leading asymptote we introduce a cut-off at $\epsilon \sim \mu$. Then,

$$\frac{N}{V} \simeq \mu_0^{3/2}\frac{2}{3}R\ ,\ \ \epsilon_F \equiv \mu_0 = \frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{2/3} \tag{19.2}$$

The value of μ at $T = 0$, which is the Fermi energy - we will re-derive it below in more conventional units. Evaluation of further corrections (i.e., $T \neq 0$) is a challenging task and will be discussed separately (basically, the function $1/\left(e^{\beta(\epsilon-\mu)}+1\right) \simeq \theta(\mu-\epsilon)$ for large β; we will integrate by parts to get a near-delta-function).

HW: *Repeat the zero-T calculations for energy; use the integral representation, not polylogarithm.*

19.0.5 Volume of Fermi-sphere

The simplest way to count states is in the $\vec{k}$-space (no $\hbar$). I.e. instead of

$$\Delta p_x \cdot L_x = 2\pi\hbar\ ,\ \ldots$$

one has

$$\Delta k_x \cdot L_x = 2\pi \ , \ \ldots$$

The number of particles is twice the number of states inside the sphere:

$$N = 2 \cdot \frac{4}{3}\pi K_F^3 \frac{1}{\Delta k_x \cdot \Delta k_y \cdot \Delta k_z} = V\frac{K_F^3}{3\pi^2}$$

Or,

$$\frac{N}{V} = \frac{K_F^3}{3\pi^2} \tag{19.3}$$

(density of electrons)

Estimations:

$$\frac{N}{V} \sim 1/\mathring{A}^3 \ , \quad K_F \sim 1\mathring{A}^{-1}$$

$$v_F \sim \frac{p_F}{m} = \frac{\hbar K_F}{m} \sim 10^6 \ m/s$$

$$\epsilon_F = \frac{\hbar^2 K_F^2}{2m} \sim 1.5 - 15 \ eV$$

$$T_F \equiv \epsilon_F/k_B \sim 10^4 \ - \ 10^5 \ {}^oK$$

HW: *Find* ϵ_F , K_F , v_F , T_F *for Ag*

with

$$a_0 = \hbar^2/mk_e e^2 = 0.529 \cdot 10^{-8} \ cm$$

and

$$r_s = \left(\frac{3V}{4\pi N}\right)^{1/3}$$

$$K_F = 3.63 \left(\frac{a_0}{r_s}\right) \ \mathring{A}^{-1}$$

$$\epsilon_F = 50.1 \left(\frac{a_0}{r_s}\right)^2 \ eV$$

$$v_F = 4.20 \cdot 10^8 \left(\frac{a_0}{r_s}\right) \ cm/s$$

HW: *show this*

Energy :

$$E(0) = RV \int_0^{\epsilon_F} d\epsilon\, \epsilon^{3/2} = \frac{3}{5} N \epsilon_F \tag{19.4}$$

Pressure: for any gas with $\epsilon = p^2/2m$ one has [see eq.(14.30)]

$$PV = 2E/3$$

Thus,

$$P_F = \frac{2N}{5V}\epsilon_F \sim \left(\frac{N}{V}\right)^{5/3} \frac{\hbar^2}{m} \tag{19.5}$$

HW: *estimate the number - should be large*

HW: *Consider an ultra-relativistic gas with $\epsilon = cp$. Find ϵ_F (Hint: no changes in k-space). Estimate the numbers for density of $\sim 10^{30}\, cm^{-3}$ (apparently, the density in a white dwarf star, about 10^7 that of Sun). Find T_F and compare to $T \sim 10^7\, {}^oK$ at the center of Sun and any other star. T_F should be much larger, implying a high degeneration of the gas.*

Chapter 20

$T > 0$, contribution to specific heat

20.1 Fermi distribution

$$f(\epsilon) = \frac{1}{\exp\left\{\frac{\epsilon-\mu}{k_B T}\right\} + 1} \tag{20.1}$$

see Fig. 20.1.
HW: *plot $f(\epsilon)$ with ϵ in eV for silver at $T = 200\,^oK$ and $T = 600\,^oK$*
Derivative:

$$f'(\epsilon) = \frac{1}{kT}\frac{1}{4\cosh^2(x/2)} \ , \quad x = (\epsilon - \mu)/kT$$

[Note: $\mu(T)$ in x, not $\epsilon_F \equiv \mu(0)$].

20.2 Transformation of integrals

Let $h(\epsilon)$ be a smooth function of a power-law type. One has

$$I \equiv \int_0^\infty d\epsilon\, h(\epsilon) f(\epsilon) = -\int_0^\infty d\epsilon\, f'(\epsilon)\left(\int_0^\epsilon d\epsilon\, h\right)$$

Or,

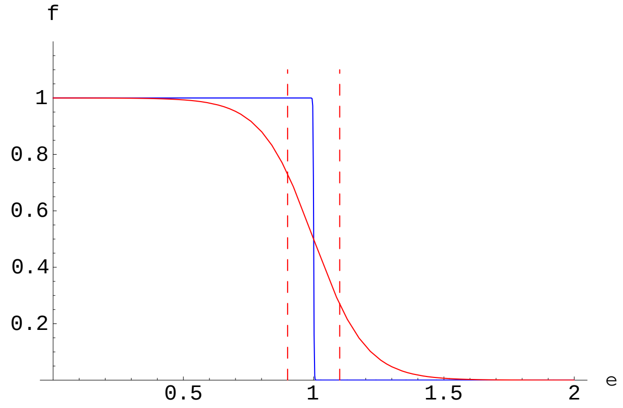

Figure 20.1: Fermi distribution: occupation of energy levels at $T = 0$ (blue line) and $T = 0.1\,\mu$ (red line); reduced energy ϵ/μ, μ being the chemical potential (the "Fermi energy") is used. The distance between the dashed vertical lines is of the order $k_B T$ in non-reduced units; only electrons within this domain contribute to specific heat.

$$I \simeq \int_0^\mu d\epsilon\, h + \frac{1}{2!}\,(k_B T)^2 \left(\frac{dh}{d\epsilon}\right)_{\epsilon=\mu} l_2 + \ldots \tag{20.2}$$

with

$$l_j = \int_{-\infty}^{\infty} \frac{dx\, x^j}{4\cosh^2(x/2)} \tag{20.3}$$

For example

$$l_2 = \frac{\pi^2}{3}$$

(see *fermi.nb*)
HW: *find l_4 and further correction in the expansion for I*

20.3 The chemical potential

The scaled density of particles is given by

$$\frac{N}{RV} = \int_0^\infty d\epsilon\, \epsilon^{1/2} f(\epsilon) \tag{20.4}$$

This is an equation for $\mu(N,V,T)$. Now one has

$$h = \sqrt{\epsilon}$$

Using the above expansion for I and solving the resulting equation iteratively, one obtains

$$\frac{2}{3}\epsilon_F^{3/2} \equiv \frac{N}{RV} \simeq \frac{2}{3}\mu^{3/2} + \frac{1}{2}(kT)^2\frac{1}{2\sqrt{\mu}}\frac{\pi^2}{3} + \dots$$

$$\mu = \epsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_BT}{\epsilon_F}\right)^2\right] \tag{20.5}$$

HW: *verify the above*

20.4 Energy

Here

$$h = \epsilon^{3/2}$$

and

$$E = \frac{2}{5}\mu^{5/2} + \frac{1}{2}\frac{3}{2}\sqrt{\mu}(kT)^2\frac{\pi^2}{3} + \dots \simeq E(0)\left(\frac{\mu}{\epsilon_F}\right)^{5/2}\left[1 + \frac{5\pi^2}{8}\left(\frac{kT}{\epsilon_F}\right)^2\right]$$

$$E(T) = E(0)\left[1 + \frac{5\pi^2}{12}\left(\frac{k_BT}{\epsilon_F}\right)^2\right] \tag{20.6}$$

HW: *verify the above*

20.5 Specific heat

Use

$$C_V = \frac{dE}{dT}$$

Thus,

$$C_V = \frac{\pi^2}{2}Nk_B\frac{T}{T_F} \tag{20.7}$$

HW: *Express C_V as a function of N/V; find the temperature when equal to phonon contribution; estimate for Ag; compare with Fig. 18.3*

The total specific heat at low T thus contains a linear term due to electrons and a cubic term due to phonons - see Fig. 20.2.

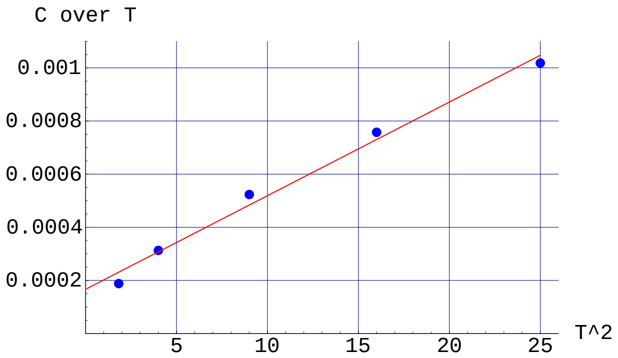

Figure 20.2: Low-temperature reduced specific heat of Ag, $C_V/(NK_BT)$ (in $^oK^{-1}$) as a function of T^2 (in $^oK^2$). The data can be used to estimate both the Fermi energy and the Debye temperature.

HW: **Important:** *Use Fig. 20.2 to estimate both the Fermi energy and the Debye temperature*

Chapter 21

Magnetism of electron gas

21.1 Paramagnetism: Boltzmann gas

Energy in magnetic field B

$$U = \mp\mu_B\, B\ , \quad \mu_B = \frac{e\hbar}{2m_e} \simeq 9.274 \cdot 10^{-24}\, \frac{\mathrm{J}}{\mathrm{T}} \simeq 5.788 \cdot 10^{-5}\, \frac{\mathrm{eV}}{\mathrm{T}} \tag{21.1}$$

where μ_B is Bohr magneton. Correction factor to partition function

$$q_H = 2\cosh x\ , \quad x = \mu_B B/kT \tag{21.2}$$

Magnetic moment (magnetization)

$$\mathcal{M} = -\frac{\partial}{\partial B}F = NkT\frac{\partial}{\partial B}\ln q_H = N\mu_B \tanh x \tag{21.3}$$

For $x \to 0$ (high T or small B)

$$\mathcal{M} = \frac{N\mu_B^2}{kT} \cdot B \tag{21.4}$$

which determines the small-field susceptibility.

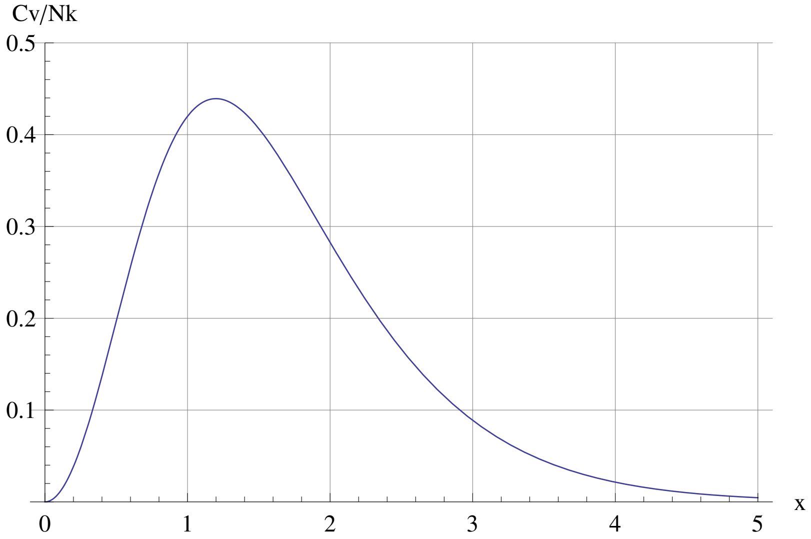

Figure 21.1: Magnetic contribution to specific heat in a dilute (Boltzmann) electron gas.

21.1.1 Correction to specific heat

With correction to energy

$$\delta E = -N\frac{\partial}{\partial\beta}\ln q_H = -\mu_B BN\tanh x = -\mathcal{M}\cdot B \tag{21.5}$$

one has correction to specific heat

$$\delta Cv = \frac{dE}{dT} = Nk\frac{x^2}{\cosh^2 x} \tag{21.6}$$

see Fig. 21.1

21.2 Paramagnetism: quantum

All formulas for densities of levels as before, only ϵ has meaning of "kinetic energy", without interaction with field. On the other hand, f, the occupation number for a level, depends on the full energy $\epsilon \pm \mu_B B$. The numbers of spins are now given by

$$N_\pm = \frac{1}{2}RV\int_0^\infty \epsilon^{1/2}\, d\epsilon\, f\left(\epsilon \pm \mu_B B\right) \tag{21.7}$$

For $\mu_B B \ll \epsilon_F$ one obtains

$$\mathcal{M} = \mu_B \left(N_+ - N_-\right) \simeq \frac{1}{2} RV\mu_B^2 B \int_0^\infty \epsilon^{1/2}\, d\epsilon\, 2\frac{\partial}{\partial\epsilon} f \simeq RV\mu_B B\epsilon_F^{1/2} \tag{21.8}$$

From

$$N = \frac{2}{3} RV\epsilon_F^{3/2}$$

one gets (*Pauli*):

$$\mathcal{M} = \frac{3}{2}\frac{\mu_B^2 N}{\epsilon_F} \cdot B \tag{21.9}$$

HW: *get a 2D version of Pauli's formula*

21.3 Landau diamagnetism for a 2-D gas

Consider field $\vec{B}$ in the z direction and particles confined to xy plane. They will move in circles with variable radii $r = mv/|e|B$ but identical frequency

$$\omega = \frac{|e|B}{m} \tag{21.10}$$

This frequency implies oscillator-like levels

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = (2n+1)\mu_B B \tag{21.11}$$

(Note: the 2d part is specific for electrons; also is specific that when spin is included E_n changes exactly by $\pm\mu_B B$, leading to extra degeneracy).

Unlike oscillator, however, levels are extremely degenerate. For an elementary estimation of degeneracy g one can use the magnetic flux quantisation condition

$$|e|B \cdot A = ih\,,\ i = 1, 2, \ldots \tag{21.12}$$

where A is the area enclosed by the orbit [1] Identifying the maximum area with the area of the sample, one gets

$$g = 2i_{\max} = \frac{2|e|BA}{h} \tag{21.13}$$

(where the 2 is for two values of spin).

In principle, knowing the structure of energy levels allows to consider arbitrary T - see **LL**. Here we consider only $T \to 0$ (i.e., $kT \ll \mu_B B \ll \epsilon_F$). Introduce

$$x = \frac{N}{g} + 1 \tag{21.14}$$

and

$$[x]\ ,\ \ \{x\} = x - [x]$$

[1] this follows from the standard

$$\oint p\,dx = ih\,,\ i = 1, 2, \ldots$$

but in magnetic field one needs to replace $\vec{p}$ by $\vec{p} - e\vec{\mathcal{A}}$, the vector potential, with $\vec{B} = -\nabla \times \mathcal{A}$ - see, e.g. the book by Kittel.

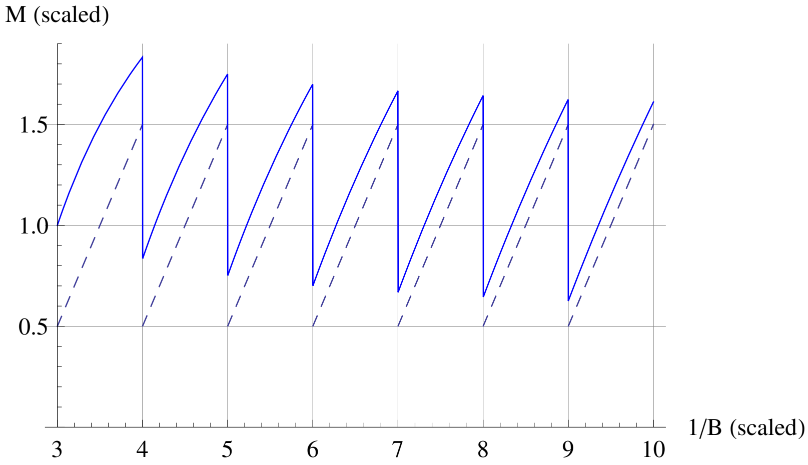

Figure 21.2: Magnetization per electron in units of μ_B as a function of $x \propto 1/B$, eq. (21.16). Dashed line is the large-x asymptote.

for integer and fractional parts, respectively. Then, electrons occupy $[N/g]$ filled n-levels (each having degeneracy g) and one partially filled n-level with $g\{N/g\}$ electrons on that level. The energy is given by

$$E = g \sum_{n=0}^{[x]-1} E_n + g\{x\}E_{[x]} = \frac{\pi\hbar^2}{mA} g^2 \left(\frac{1}{2}[x]^2 + \{x\}([x] + \frac{1}{2}) \right) \qquad (21.15)$$

Note

$$\frac{\partial}{\partial B} = \frac{2A|e|}{h} \frac{\partial}{\partial g} = -\frac{N}{g^2} \frac{2A|e|}{h} \frac{\partial}{\partial x}$$

Thus, for $\mathcal{M} = -\frac{\partial}{\partial B} E$ at $T = 0$ one has

$$\frac{\mathcal{M}}{N} = -\mu_B \, (x-1)^2 \, \frac{\partial}{\partial x} \frac{\frac{1}{2}[x]^2 + \{x\}([x] + \frac{1}{2})}{(x-1)^2} \to \mu_B \left(\{x\} + \frac{1}{2} \right) \qquad (21.16)$$

for $x \gg 1$ - see Fig. 21.2.

Part VI

Appendix

Chapter 22

Notations

Notations are consistent throughout each chapter of the course. Some of the key symbols, e.g. S for entropy are use in the entire text. For dummy variables (e.g., for change of variables in integration) I often use x, y, z, or w, and the variables with only "local" values will not be listed below.

The thermodynamic variables for a large system will be denoted by capital letters, S, E, etc. and used globally. Reduced values per particle will be denoted by a corresponding lower-case letter, s, but will be mostly used locally.

22.1 Specific symbols

A - not used (used for free energy in *Huang, McQuarrie* etc, equivalent to our F)
a - lattice constant
C_v , C_p - specific heat
c - speed of light
E - energy
F - Helmholtz free energy
F_i - force on a particle (in Chapter on phonons)
g - degeneracy associated with the spin
$h = 2\pi\hbar$
$k_B = 1.38 \cdot 10^{-23} J/^oK$ (occasionally, just k is used when no confusion can happen)

$\vec{k}$, $\vec{K}$ - wave vector
LL - *Statistical Physics* by L. Landau and I. Lifshits
Li - polylogarithm (special function)
m, M - masses of particles; m_n - mass of a neutron
N - number of particles
$\bar{n}$ - occupation number
P - pressure
p - probability (only in Chapter I); otherwise absolute value of momentum
$\vec{p}$ - momentum
Q - canonical partition function
q - "partition function" of a single molecule in an ideal gas
R - a constant (with dimension!) in quantum gas description, eq. (289)
S - entropy
T - absolute temperature
T_c - temperature of Bose-Einstein condensation
u - displacement(in Chapter on phonons)
V - volume
v - speed of sound (in Chapter on phonons).
α - Lagrange multiplier
$\beta = 1/k_B T$
Γ - volume of phase space
ϵ - energies of individual particles in ideal gas
μ - chemical potential
ρ - density; linear density (in Chapter on phonons)
κ - elastic constant (in Chapter on phonons)
ω - angular frequency
ω_D - Debye frequency
Θ_D - Debye temperature