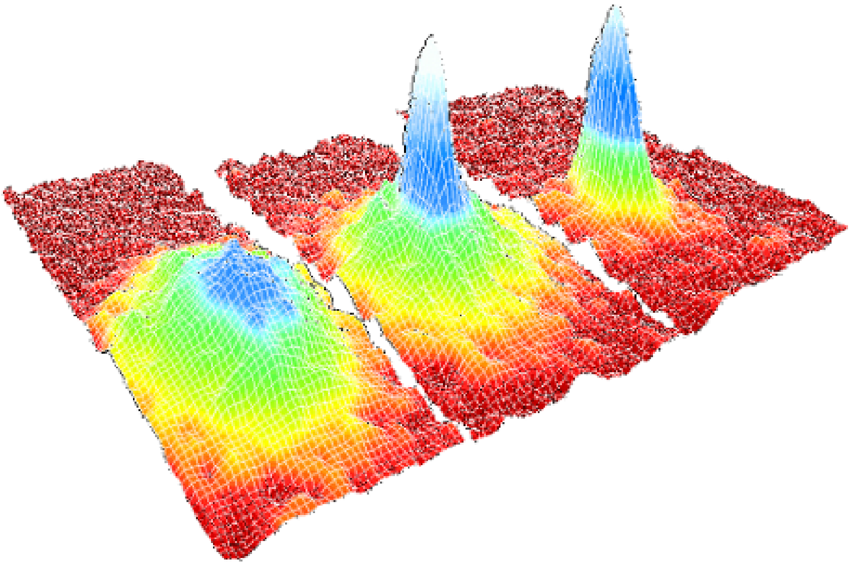

Quantum statistics

Notes of the lecture from
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Contents

1 Concepts of probability

In the *theory of common sense* we have a

- fair coin with 2 possible outcomes head (H) and tail (T) and a
- fair die (pl. dice) with outcomes from 1 to 6.

In this context fair means unbiased.

1.1 Random numbers, probabilities, simple rules

Definition 1.1.1 *A sequence $x_1, x_2, ..., x_N$ of numbers is called random, if the probability for x_{N+1} to have a value of x does not depend on the previous numbers.*

An example: Sequences like *HTHTHTHT* or *HHHHHHH* let us think that the next event must be H in both cases. This is *common sense* and not a good random sequence. When there's a pattern it's not a random sequence.

In reality we can never be sure if the sequence is random. A truly random sequence is infinite. In computers we have *quasi random* numbers. This means they are random FAPP (for all pratical purposes).

Assigning probabiliy We have to distinguish between

- Trial, process:
  - Tossing (flipping) a coin or
  - throwing a dice.
- Outcome of a trial:

  - H, T,
  - $1, 2, 3, 4, 5, 6$ or
  - all so called *microstates*.
- Sample space (which is the set of all outcomes):
  - $\{H, T\}$,
  - $\{1, 2, 3, 4, 5, 6\}$ or
  - all so called *phase space*.

For a fair coin we obtain

- $p(H)$ the probability of outcome H,
- $p(T)$ the probability of outcome T,
- $p(H) = p(T) = \frac{1}{2}$.

Similar for a fair die:

$$p(1) = p(2) = p(3) = p(4) = p(5) = p(6) = \frac{1}{6}.$$

In general for a probability we require that

$$p(\text{outcome } i) = p_i \geq 0.$$

As boundary condition we have

$$\sum_{\text{outcomes } i} p_i = 1 \quad \text{(something always happens)}.$$

For continuous outcomes $x \in \mathbb{R}$ we find that

$$p_i \to p(x)dx$$

is the possibility to find the outcome in $[x, x + dx]$. While p_i is dimensionless, $p(x)$ is a probability density (think of $|\psi(x)|^2$). So we have to normalize it. The normalization of the continuous distribution is

$$\int_{-\infty}^{\infty} p(x)dx = 1.$$

The simplest example for this would be

$$p(x) = \begin{cases} \frac{1}{b-a}, & x \in [a,b], \\ 0, & \text{else.} \end{cases}.$$

Addition rule The probability that two independent outcomes i or j occur is

$$p(i \text{ or } j) = p(i) + p(j).$$

Example: The probability that a die gives 1 or 3 is

$$p(1 \text{ or } 3) = p(1) + p(3) = \frac{1}{6} + \frac{1}{6} = \frac{1}{3}.$$

Multiplication rule The probability that two independent outcomes i and j occur is

$$p(i \text{ and } j) = p(i) \cdot p(j).$$

Example: The probability that a die gives 1 and (then) 3 is

$$p(1 \text{ and } 3) = p(1) \cdot p(3) = \frac{1}{6}\frac{1}{6} = \frac{1}{36}.$$

Example: Suppose a DNA evidence is likely with probability $1 - 10^{-6}$. The chances are $10^6 : 1$ that the defendant is guilty. The systematic error in collecting, analysing, handling, reporting DNA evidence is $\approx 1\%$.

Question: What is the probability that the defendant is guilty?

1.2 Mean values, standard deviations

- The mean value or average of x is defined as

$$\overline{x} = \langle x \rangle = \sum_i x_i p(i) = \int_{-\infty}^{\infty} dx x p(x).$$

- The mean square of x is defined as

$$\overline{x^2} = \langle x^2 \rangle = \sum_i x_i^2 p(i) = \int_{-\infty}^{\infty} dx x^2 p(x).$$

- The variance or dispersion of x is defined as

$$\sigma_x^2 = \overline{x^2} - \overline{x}^2 = \overline{(x-\overline{x})^2}.$$

- The standard deviation or r.m.s. (root mean square) of x is defined as

$$\sigma_x \equiv +\sqrt{\sigma_x^2}.$$

As an example we consider a coin with $H = 1$ and $T = 0$. We obtain

$$\begin{aligned}
\overline{x} &= 1 \cdot p(H) + 0 \cdot p(T) = \frac{1}{2}, \\
\overline{x^2} &= 1^2 \cdot p(H) + 0^2 \cdot p(T) = \frac{1}{2}, \\
\sigma_x^2 &= \overline{x^2} - \overline{x}^2 = \frac{1}{2} - \frac{1}{4} = \frac{1}{4}, \\
\sigma_x &= \sqrt{\sigma_x^2} = \frac{1}{2}.
\end{aligned}$$

This means that the actual values of the outcome are likely in the interval $[\overline{x} - \sigma_x, \overline{x} + \sigma_x]$. For the coin we found $\frac{1}{2} \pm \frac{1}{2}$.

1.3 Uncertainty, disorder, entropy

Shannon did some research in the 1940's. He found that that a system is in order when not much (the least) information (knowledge) about a system is required in order to describe it, while a system is in disorder when a lot of (more than the least) information is required in order to reconstruct it.

Example: A child in a house with n rooms. We bring the child in the morning to the house. We then come back in the evening to see in which room the child is.

Task: Calculcate the probability ($p(i)$) for the child being in room i. We already know that there are two main cases in this scenario.

1. A certain (well-behaved) child: We have full knowledge of it. So the probability will be

   $$p(i) = \delta_{i,i_0},$$

   where i_0 is the room in which the child stays all the time.

2. An *uncertain* child (this one is running around): We have the least knowledge of where he or she is. We probability will be

   $$p(i) = \frac{1}{n}.$$

Our task is now to find a function of $p(i)$ which cover our main cases. In the case of minimum uncertainty we have to obtain a minimum of $p(i)$ while in the case of maximum uncertainity we have to obtain a maximum. In addition we require that the function is additive.

Example: Two children and two houses. We then get for our function S that

$$S = S_1 + S_2,$$

where S_1 is the function for the first child in the first house and S_2 is the function for the second child in the second house. So we have to obtain

$$p(1, 2) = p(1) \cdot p(2).$$

Satz 1.3.1 (Shannon) *There is only one such function:*

$$S = -k \sum_i p_i \ln p_i = -k\overline{\ln p}, \tag{1.1}$$

where $p_i \equiv p(i)$ and k is some constant. This function is called Shannon's (information) entropy.

Example: If $p(i) = \delta_{i,i_0}$ we get $S = -k1 \ln 1 = 0$. If $p(i) = \frac{1}{n}$ we obtain that $S = k \ln n$.

1.4 Maximum uncertainty distribution

Task: Find p_i such that S has a maximum and the average value of a quantity A_i,

$$\overline{A} = \sum_i p_i A_i,$$

is fixed. This is an optimization problem with Lagrange multipliers. The function to be maximized is

$$S = -k \sum_i p_i \ln p_i,$$

with the constraints that

$$\sum_i p_i = 1 \quad \text{and} \quad \sum_i p_i A_i = \overline{A}.$$

Calculating we obtain

$$\begin{aligned}
0 &\overset{!}{=} \delta\left[S - \lambda_1(\sum_i p_i - 1) - \lambda_2(\sum_i p_i A_i - \overline{A})\right], \\
\delta S &= -k \sum_i \left(\delta p_i \ln p_i + p_i \frac{1}{p_i}\delta p_i\right) = \\
&= -k \sum_i (\ln p_i + 1)\delta p_i. \\
\Rightarrow 0 &= -k \sum_i (\ln p_i + 1)\delta p_i - \lambda_1 \sum_i \delta p_i - \lambda_2 \sum_i A_i \delta p_i = \\
&= -k \sum_i (\ln p_i + 1) - \lambda_1 \sum_i 1 - \lambda_2 \sum_i A_i = \\
&= \sum_i \left(\ln p_i + 1 + \frac{\lambda_1}{k} + \frac{\lambda_2}{k} A_i\right).
\end{aligned}$$

Finally we get individually

$$\ln p_i + 1 + \frac{\lambda_1}{k} + \frac{\lambda_2}{k} A_i = 0,$$

which gives us

$$p_i = \exp\left(-\left(1 + \frac{\lambda_1}{k} + \frac{\lambda_2}{k} A_i\right)\right).$$

The coefficients λ_1 and λ_2 can be determined by the constraints above. We can simplify the solution for p_i in order to get

$$p_i = \frac{1}{Z} \exp\left(-\frac{\lambda_2}{k} A_i\right), \qquad Z = \sum_i \exp\left(-\frac{\lambda_2}{k} A_i\right). \tag{1.2}$$

1.5 Useful probability distributions and central limit theorem

1.5.1 Binomical distribution

Suppose an event A can occur with probability p. Then, out of N trials, the event A will be found exactly k times with the probability

$$p_k^{(N)} = \begin{pmatrix} N \\ k \end{pmatrix} p^k (1-p)^{N-k}. \tag{1.3}$$

In this formula we have

- $\begin{pmatrix} N \\ k \end{pmatrix}$ the combinatorial factor, read 'N choose k' which is $\frac{N!}{(N-k)!k!}$. That is the number of ways to choose k objects out of N.
- p^k the probability to find k events A.
- $(1-p)^{N-k}$ the probability that the remaining $N-k$ events are <u>not</u> A.

Example: Suppose I flip a coin 100 times. What is the probability that H comes 20 times?

$$\Rightarrow \quad p_{20}^{(100)} = \begin{pmatrix} 100 \\ 20 \end{pmatrix} \frac{1}{2^{20}} \frac{1}{2^{80}} = 4.22 \cdot 10^{-10}.$$

Example: Suppose you play darts (L little squares). You can shoot (throw) N times. What is the probability to hit the same (pre-determined) little square 2 times when $p = \frac{1}{L}$?

$$\Rightarrow \quad p_2^{(N)} = \begin{pmatrix} N \\ 2 \end{pmatrix} \frac{1}{L^2}\left(1-\frac{1}{L}\right)^{N-2}.$$

Question: What is the probability that in the first two throws I hit the same little square? It is $\frac{1}{L^2}$.

Another question: What is the probability that in the first two throws $\overline{\text{only}}$ I hit the same little square? In all other throws I do not hit it. It is $\frac{1}{L^2}\left(1-\frac{1}{L}\right)^{N-2}$.

Let us calculate the average value of k and variance σ_k^2.

- For the mean value we calculate:

$$\begin{aligned} \overline{k} &= \sum_{k=0}^{N} kP_k^{(N)} = \sum_{k=0}^{N} k \begin{pmatrix} N \\ k \end{pmatrix} p^k (\underbrace{1-p}_{\equiv q})^{N-k} = \\ &= \sum_{k=0}^{N} k\frac{N!}{(N-k)!k!}p^k q^{N-k} = p\frac{\partial}{\partial p}\sum_{k=0}^{N}\frac{N!}{(N-k)!k!}p^k q^{N-k} = \\ &= p\frac{\partial}{\partial p}(p+q)^N = pN(\underbrace{p+q}_{=1})^{N-1} = pN, \end{aligned}$$

  which is the result we expected.

- Now we do the same for $\overline{k^2}$:

$$\begin{aligned} \overline{k^2} &= \sum_{k=0}^{N} k^2 P_k^{(N)} = \left(p\frac{\partial}{\partial p}\right)^2 (p+q)^N = p\frac{\partial}{\partial p}\left(Np(p+q)^{N-1}\right) = \\ &= Np\left((p+q)^{N-1} + (N-1)p(p+q)^{N-2}\right) = Np(1+pN-p). \end{aligned}$$

- So we get for the variance

$$\sigma_k^2 = \overline{k^2} - \overline{k}^2 = Np(1+pN-p) - p^2N^2 = Np(1-p).$$

- Finally we have the standard deviation as

$$\sigma_k = \sqrt{Np(1-p)}, \qquad \Rightarrow \quad \frac{\sigma_k}{\overline{k}} = \sqrt{\frac{1-p}{p}\frac{1}{\sqrt{N}}}.$$

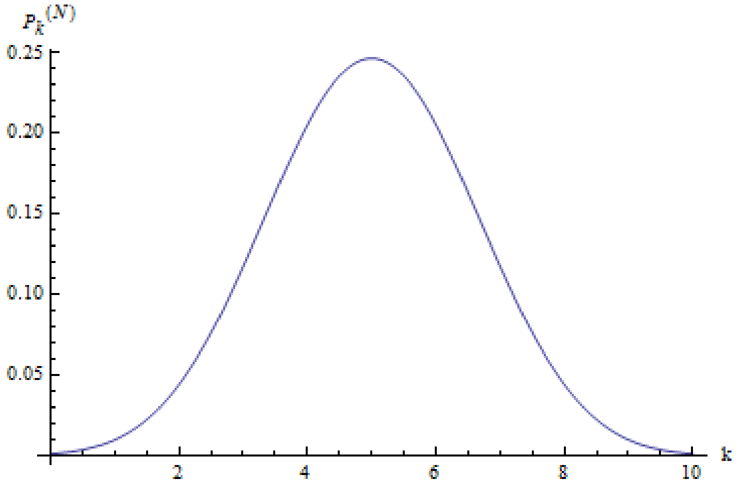


Figure 1.1: Plot of a binomical distribution with FWHM $2\sqrt{Np(1-p)}$ for $p = \frac{1}{2}$ and $N = 10$.

1.5.2 Poisson distribution

The Poisson distribution is given as

$$P_k = \frac{\lambda^k}{k!}\exp(-\lambda), \qquad k = 0, 1, 2, ..., \infty, \tag{1.4}$$

where λ is the parameter of the distribution. Let us now calculate the average $\overline{k}$ and variance σ_k^2.

- For the average value we get

$$\begin{aligned}\overline{k} &= \sum_{k=0}^{\infty} k\left(\frac{\lambda^k}{k!}\right)\exp(-\lambda) = \exp(-\lambda)\sum_{k=1}^{\infty}\frac{\lambda^k}{(k-1)!} = \\ &= \lambda\exp(-\lambda)\sum_{k=1}^{\infty}\frac{\lambda^{k-1}}{(k-1)!} = \lambda\exp(-\lambda)\underbrace{\sum_{k=0}^{\infty}\frac{\lambda^k}{k!}}_{\exp(\lambda)} = \lambda.\end{aligned}$$

- By exactly the same we get

$$
\begin{aligned}
\overline{k^2} &= \sum_{k=0}^{\infty} k^2 \left(\frac{\lambda^k}{k!}\right)\exp(-\lambda) = \exp(-\lambda)\sum_{k=1}^{\infty} k\frac{\lambda^k}{(k-1)!} = \\
&= \exp(-\lambda)\lambda\sum_{k=0}^{\infty}(k+1)\frac{\lambda^k}{k!} = \exp(-\lambda)\lambda\left(\sum_{k=0}^{\infty} k\frac{\lambda^k}{k!} + \sum_{k=0}^{\infty}\frac{\lambda^k}{k!}\right) = \\
&= \lambda^2 + \lambda.
\end{aligned}
$$

- For the variance we get

$$\sigma_k^2 = \overline{k^2} - \overline{k}^2 = \lambda^2 - \lambda^2 + \lambda = \lambda.$$

- So we found the standard deviation which is $\sqrt{\lambda}$. The relative error is

$$\frac{\sigma_k}{\overline{k}} = \frac{1}{\sqrt{\lambda}}.$$

We will show that the poisson distribution is a limiting case of the binomical one as $N \to \infty$ (many experiments) and $p \to 0$ (small probability).

$$
\begin{aligned}
p_k^{(N)} &= \frac{N!}{(N-k)!k!}p^k(1-p)^{N-k} \overset{\lambda=pN}{=} \frac{N!}{(N-k)!k!}\left(\frac{\lambda}{N}\right)^k\left(1-\frac{\lambda}{N}\right)^{N-k} = \\
&= \underbrace{\frac{N\cdot(N-1)\cdots(N-k+1)}{N^k}}_{\approx 1}\frac{\lambda^k}{k!}\underbrace{\left(\left(1-\frac{\lambda}{N}\right)^{\frac{N}{\lambda}}\right)^{\lambda}}_{\approx\exp(-1)^{\lambda}=\exp(-\lambda)}\underbrace{\left(1-\frac{\lambda}{N}\right)^{-k}}_{\approx 1} = \\
&= \frac{\lambda^k}{k!}\exp(-\lambda).
\end{aligned}
$$

1.5.3 Normal (Gaussian) distribution

It is a continuous distribution for a variable x:

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{(x-a)^2}{2\sigma^2}\right). \tag{1.5}$$

Let us calculate the average and variance.

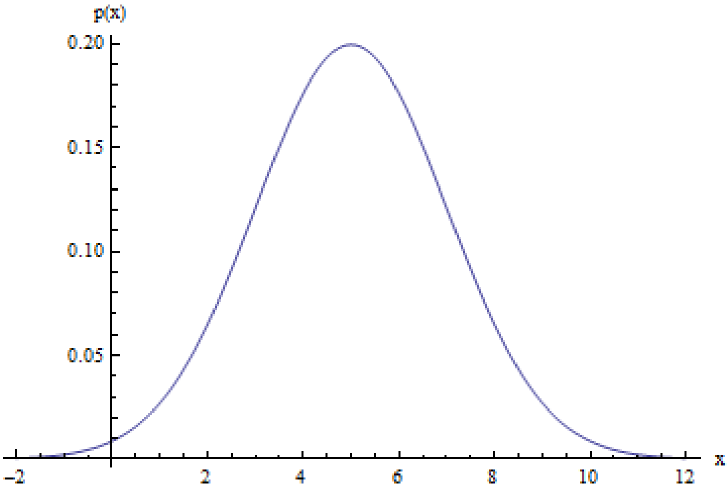


Figure 1.2: Plot of a Gaussian distribution with FWHM $2\sigma_x$ for $a = 5$ and $\sigma_x = 2$.

- For the mean value we calculate, that

$$\begin{aligned} \overline{x} &= \int_{-\infty}^{\infty} dx x p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx x \exp\left(-\frac{1}{2}\frac{(x-a)^2}{\sigma^2}\right) = \\ &= \frac{1}{\sqrt{2\pi\sigma^2}} \underbrace{\int_{-\infty}^{\infty} dx(x-a) \exp\left(-\frac{1}{2}\frac{(x-a)^2}{\sigma^2}\right)}_{=0} + \\ &+ \frac{1}{\sqrt{2\pi\sigma^2}} a \underbrace{\int_{-\infty}^{\infty} dx \exp\left(-\frac{1}{2}\frac{(x-a)^2}{\sigma^2}\right)}_{=a} = a. \end{aligned}$$

- In the next step we get

$$\begin{aligned} \overline{x^2} &= \frac{1}{\sqrt{2\pi\sigma^2}\int_{-\infty}^{\infty}} dx x^2 \exp\left(-\frac{1}{2}\frac{(x-a)^2}{\sigma^2}\right) = \\ &= \sigma^2 + a^2. \end{aligned}$$

- So we get what we expected:

$$\begin{aligned} \sigma_x^2 &= \overline{x^2} - \overline{x}^2 = \sigma^2 + a^2 - a^2 = \sigma^2, \\ \sigma_x &= \sigma. \end{aligned}$$

The normal distribution also follows from the binomical one, in the limit of $N \to \infty$ and taking $k \to x$, centered at $\bar{k} \approx a$, and considering expansion around $\bar{k}$. See Gold and Tobachnik for a proof.

1.5.4 Central limit theorem

Suppose $x_1, x_2, x_3, ...x_N$ are distributed according to some distribution $p(x)$. The average of x is $\bar{x}$ and variance of the distrubtion, σ_x^2, exists (not infite). Then the average

$$y_N = \frac{1}{N} \sum_{i=1}^{N} x_i,$$

are distributed according to

$$P(y_N) = \frac{1}{\sqrt{2\pi\sigma_y^2}} \exp\left(-\frac{1}{2}\frac{(y_N - \bar{x})^2}{\sigma_y^2}\right),$$

and $\sigma_y = \frac{\sigma_x}{\sqrt{N}}$. For a proof see Gold and Tobachnik.

Alternativly for the sums

$$S_N = \sum_{i=1}^{N} x_i$$

the distribution is

$$p(S_N) = \frac{1}{\sqrt{2\pi\sigma_S^2}} \exp\left(-\frac{1}{2}\frac{(S_N - N\bar{x})}{\sigma_S^2}\right).$$

So the standard deviation is

$$\sigma_S = \sigma_x \sqrt{N}.$$

The relative error is again $\frac{\sigma_x \sqrt{N}}{\bar{x} N} \propto \frac{1}{\sqrt{N}}$.

Example: Shopping in a supermarket. Typical price is approximently $\bar{x} = 2$ €. Buy $N \approx 20$ items. Guess the total price. What is the total error when $\sigma_x = 0.5$ €. The average sum is $N\bar{x}$ which is 40 €. The total error is $\sqrt{20}0.5 \approx 2$ €. So we have (40 ± 2) €.

2 Classical and quantum microstates

2.1 Configuration, momentum and phase space

The from the classical probability theory known systems coin or dice now go over to more complicated systems like gas, solids, etc.

We need to find the sample space for the generic physical system. We first discuss the classical systems. Consider a collection of N particles. Assume that the particles cannot escape from the box. We say they are confined. Assume also, that the total energy is preserved, i.e. particles do not give away energy to the walls of the box.

$\Rightarrow (N, V, E)$ are fixed.

- The collection of the positions of particles is

  $$Q = (\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = (x_1, y_1, z_1, ..., x_N, y_N, z_N),$$

  which forms the configuration space. This space is $3N$ dimensional.
- The collection of the momenta of the particles is

  $$P = (\vec{p}_1, \vec{p}_2, ..., \vec{p}_N),$$

  which forms the momentum space. This space is again $3N$ dimensional.
- The state of the system of N particles is uniquely defined / determined by the collection (Q, P). We call this collection the phase space. It has $3N + 3N = 6N$ dimensions. It is huge!

The important question is: How big is the phase space? We will argue that the phase space is the sample space. A leap in thinking brought us to the conclusion that...

the only preserved quantity, constraining the phase space (in addition to V, N) is the energy! Large systems 'forget' their initial conditions, i.e. all other integrals of motions are 'forgotten'.

2.2 Phase space volume, density of states

We introduce 3 measures for the phase-space volume, Γ, g and Ω.

- First of all we introduce

  $$\Gamma(E) = \int \frac{dQdP}{h^{3n}} \Theta(E - H(Q,P)) = \int_{H(Q,P)\leq E} \frac{dQdP}{h^{3n}}, \tag{2.1}$$

  with the step function

  $$\Theta(x) = \begin{cases} 1, & x \geq 0, \\ 0, & x < 0. \end{cases}$$

  $H(Q,P)$ is the Hamiltonian of the system. So $\Gamma(E)$ tells us the volume of the phase space up to the energy E. This brings us to h which is the yet to be determined constant (which will be the Planck constant), of dimension $[xp]$ =kgm^{2}s^{-1}, introduced to make Γ dimensionless.

- Second we introduce the density of state

  $$g(E) = \frac{d\Gamma(E)}{dE} = \int \frac{dQdP}{h^{3N}} \delta(E - H(Q,P)). \tag{2.2}$$

  The dimension of $g(E)$ is $[\frac{1}{E}]$=J^{-1}.

- Finally we introduce the number of states

  $$\Omega(E) = g(E)\delta E. \tag{2.3}$$

  This is again dimensionless and gives us the number of states in the interval $[E, E + \delta E]$.

Example: **1-dimensional linear harmonic oscillator**

We set our $Q = x$ and $P = p$. We already know that

$$H = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 x^2.$$

The 'surface' of the equal energy is

$$H(Q,P) = E \quad \Rightarrow \quad \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 x^2 = E \quad \Rightarrow \quad \frac{p^2}{2mE} + \frac{x^2}{\frac{2E}{m\omega^2}} = 1.$$

To calculate the volume we use

$$\Gamma(E) = \frac{\text{area of ellipse}}{h} = \frac{\pi ab}{h} = \frac{\pi\sqrt{2mE}\sqrt{\frac{2E}{m\omega^2}}}{h} = \frac{E}{\hbar\omega}.$$

So we get

$$g(E) = \frac{d\Omega}{dE} = \frac{1}{\hbar\omega} \text{ and } \Omega(E) = g(E)\delta E = \frac{\delta E}{\hbar\omega}.$$

Important example: **Phase space volume of classical ideal gas**

We have N particles in an 'ideal' gas (no/weak interacting particles) with no potential energy, i.e.

$$H = \frac{\vec{P}^2}{2m} = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}.$$

Our task is now to calculate $\Gamma(E)$, which is an integral

$$\Gamma(E) = \int_{H(Q,P)\leq E} \frac{dQdP}{h^{3N}} = \frac{1}{h^{3N}} \int dQ \int_{\sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} \leq E} d^3p_1 d^3p_2 \cdots d^3p_N.$$

We already know that

$$\int dQ = V^N.$$

The remaining momentum integral is the volume of a sphere in $3N$ dimensions of radius $\sqrt{2mE}$. Generally we have

$$\vec{p}_1^2 + ... + \vec{p}_N^2 = p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + ... + p_{Nx}^2 + p_{Ny}^2 + p_{Nz}^2 \leq (\sqrt{2mE})^2.$$

This is a mathematical problem. The solution is discussed in appendix 8.1. We now know that

$$R = \sqrt{2mE}, \quad n = 3N, \qquad \Rightarrow \int_{P^2 \leq 2mE} dP = \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} (2m)^{\frac{3N}{2}} E^{\frac{3N}{2}} = \frac{(2\pi m E)^{\frac{3N}{2}}}{(\frac{3N}{2})!}.$$

The measures

$$\begin{aligned} \Gamma(E) &= \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{\frac{3N}{2}}}{(\frac{3N}{2})!} \propto E^{\frac{3N}{2}}, \\ g(E) &= \frac{d\Gamma}{dE} = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{\frac{3N}{2}}}{(\frac{3N}{2})!} \frac{3N}{2E} = \frac{\Gamma(E)}{\frac{2}{3}(\frac{E}{N})}, \\ \Omega(E) &= \Gamma(E) \frac{\delta E}{\frac{2}{3}(\frac{E}{N})}. \end{aligned}$$

All thermodynamics of classical gases follows from here!

Important remark The phase-space volume change $\overline{\text{very very}}$ fast with E. Suppose there are $N = 10^{23}$ particles. If you change E by $\delta E \approx \left(\frac{E}{N}\right)\frac{2}{3}$, which is the energy of just one particle, the volume of Γ increases twice:

$$\Omega(E) \approx \Gamma(E)!$$

2.3 The ergodic hypothesis

We consider a coin with $H = 0$ and $T = 1$. We can now calculate the average value:

1. By flipping the coin many times: $HHTHTT$ and so on we get

$$\begin{aligned}
\text{avg} &= \frac{0+0+1+0+1+1}{6} = \frac{\text{flip}(t=1)+\text{flip}(t=2)+\ldots+\text{flip}(t=6)}{\text{number of flips}} = \\
&= \frac{[\text{flip}(t=1)+\text{flip}(t=2)+\ldots+\text{flip}(t=6)]\,\Delta t}{\text{number of flips}\cdot\Delta t} = \\
&= \left.\begin{array}{l} \frac{1}{T}\sum_i \text{flip}(t_i)\Delta t \\ \frac{1}{T}\int dt\text{flip}(t) \end{array}\right\}\text{time average, i.e. average over time,}
\end{aligned}$$

where Δt is the difference in time between the flips and T is the total time.

2. Guess the answer by finding the sample space and the probabilities for the events. So we have a guess, like

$$p_{H=0} = \frac{1}{2}, \qquad p_{T=1} = \frac{1}{2}.$$

The average is then

$$\text{avg} = 0\cdot p_H + 1\cdot p_T = \sum_{i=H,T} i\cdot p_i \rightarrow \int dx x p(x) = \frac{1}{2}.$$

This is the *ensemble* average - an ensemble is the sample space. In this case it would be (H, T).

The ergodic hypthesis then states that *time average* ($T \rightarrow \infty$) *is equal to the ensemble average*. Flipping a coin is an ergodic process as long as the flipper explores the whole ensemble.

Example for a non-ergodic-process: An ant cannot flip the coin due to the energy barrier. So the time-average is $H = 0 \neq \frac{1}{2}$.

Important: H, T need to have the same (gravitational) energy - but in this scenario there is an energy barrier.

Example: Glass (amorpheous material) has also energy barriers which prevent the material to be in a crystal formation.

Also in an experiment we measure the time averages

$$\overline{A}_{\text{time}} = \frac{1}{T}\int_0^T dtA(t).$$

In theory due to the high number of particles (10^{23}) we have

$$\overline{A}_{\text{ensemble}} = \int_{\text{phase space}} dQdPA(Q,P)\varrho(Q,P),$$

where $\varrho(Q,P)$ is a probability density in phase space. The ergodic hypothesis now states, that

$$\overline{A}_{\text{time}}\Big|_{T\to\infty} = \overline{A}_{\text{ensemble}}. \tag{2.4}$$

2.4 Phase-space invariance and Liouville's theorem

We already know that phase-space trajectories cannot cross because if they would cross, the system would have two futures. The question now is (for a phase-space volume): how much does the volume of a phase-space region change in time?

The answer is that it does not change! We are now going to proof this.

Proof Denote q_α as coordinates and p_α as momenta with $\alpha = 1,2,...,3N$. So we have

$$\begin{aligned}(q_1,q_2,...,q_{3N}) &= (x_1,y_1,z_1,x_2,y_2,z_2,...,x_N,y_N,z_N),\\ (p_1,p_2,...,p_{3N}) &= (p_{x_1},P_{y_1},p_{z_1},p_{x_2},p_{y_2},p_{z_2},...,p_{x_N},p_{y_N},p_{z_N}).\end{aligned}$$

A general point (Q,P) evolves in time to (Q',P') according to

$$\begin{aligned}q'_\alpha &= q_\alpha + \dot{q}_\alpha\delta t = q'_\alpha(q_\alpha,\dot{q}_\alpha),\\ p'_\alpha &= p_\alpha + \dot{p}_\alpha\delta t = p'_\alpha(p_\alpha,\dot{p}_\alpha).\end{aligned}$$

So we can say that it is

$$(Q,P) \to (Q',P'), \qquad Q' \equiv Q'(Q,P),\ P' \equiv P'(Q,P).$$

Remark $\dot{q}_\alpha$ and $\dot{p}_\alpha$ are functions of q_α, p_α. So the volume at a time $t > 0$ is equal to the trajectory times the volume at time $t = 0$,

$$dQ'dP' = JdQdP, \quad J = \left|\frac{\partial(Q',P')}{\partial(Q,P)}\right| = \begin{vmatrix} \frac{\partial q_1'}{\partial q_1} & \cdots & \frac{\partial q_1'}{\partial p_{3N}} \\ \vdots & \ddots & \vdots \\ \frac{\partial p_{3N}'}{\partial q_1} & \cdots & \frac{\partial p_{3N}'}{\partial p_{3N}} \end{vmatrix}.$$

So to get a feeling for this formula we first consider a simple one-dimensional case with 1 particle, i.e.

$$q' = q + \dot{q}\delta t, \qquad p' = p + \dot{p}\delta t.$$

Now we calculate the Jacobian:

$$\begin{aligned} \frac{\partial q'}{\partial q} &= 1 + \frac{\partial \dot{q}}{\partial q}\delta t, \qquad \frac{\partial p'}{\partial p} = 1 + \frac{\partial \dot{p}}{\partial p}\delta t, \\ \frac{\partial q'}{\partial p} &= \frac{\partial \dot{q}}{\partial p}\delta t, \qquad \frac{\partial p'}{\partial q} = \frac{\partial \dot{p}}{\partial q}\delta t, \\ \Rightarrow J &= \begin{vmatrix} \frac{\partial q'}{\partial q} & \frac{\partial q'}{\partial p} \\ \frac{\partial p}{\partial q} & \frac{\partial p}{\partial p} \end{vmatrix} = \begin{vmatrix} 1 + \frac{\partial \dot{q}}{\partial q}\delta t & \frac{\partial \dot{q}}{\partial p}\delta t \\ \frac{\partial \dot{p}}{\partial q}\delta t & 1 + \frac{\partial \dot{p}}{\partial p}\delta t \end{vmatrix} = \\ &= \left(1 + \frac{\partial \dot{q}}{\partial q}\delta t\right)\left(1 + \frac{\partial \dot{p}}{\partial p}\delta t\right) - \frac{\partial \dot{q}}{\partial p}\delta t \frac{\partial \dot{p}}{\partial q}\delta t = \\ &= 1 + \left(\frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p}\right)\delta t + \mathcal{O}(\delta t^2). \end{aligned}$$

δt^2 and higher can be neglected because our taylor expansion was also just to order δt^2. We already know the Hamilton equations,

$$\dot{q} = \frac{\partial \mathcal{H}}{\partial p}, \qquad \dot{p} = -\frac{\partial \mathcal{H}}{\partial q}.$$

Inserting them we obtain

$$\Rightarrow \left(\frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p}\right) = \left(\frac{\partial^2 \mathcal{H}}{\partial p \partial q} - \frac{\partial^2 \mathcal{H}}{\partial q \partial p}\right) = 0.$$

Therefore we get that $J = 1$! The same proof can be done for more particles in more dimensions, then

$$J = 1 + \sum_{\alpha=1}^{3N} \underbrace{\left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right)}_{=0} \delta t + O(\delta t^2).$$

Thus it is proofen. We now go one step further. Since the volume does not change it is like an incompressable liquid, where the shape changes but the area is preserved. We are now going to introduce the phase-space density of states $\varrho(Q, P)$,

$$\int_{\text{all phase-space}} dQdP \varrho(Q, P) = 1. \tag{2.5}$$

Consider a volume V in the phase-space (not in the real-space - V is not the box volume!). Suppose we have n ensemble members (points) total. The number of ensemble points in volume V is then

$$n_v = n \int_V dQdP \varrho(Q, P).$$

We consider time evolution. The net increase of the number of points inside V is then given through

$$-\frac{dn_v}{dt} = -\frac{d}{dt} n \int_V dQdP \varrho(Q, P) = -n \int_V dQdP \frac{\partial \varrho(Q, P)}{\partial t}.$$

The net decrease is accompanied by the flow through the surface of the volume,

$$-\frac{dn_v}{dt} = \oint_{\partial V} d\vec{S} \vec{j}, \qquad \vec{j} = n \varrho \vec{v},$$

where $d\vec{S}$ is an infinitesimal surface element, $\vec{v}$ the velocity ($6N$ dimensional vector, $(\dot{Q}, \dot{P})$) and $n\varrho$ the number of points (density) at (Q, P). By using Gauss' theorem we obtain

$$-\frac{dn_v}{dt} = -n \int_V dQdP \frac{\partial \varrho}{\partial t} = \oint_{\partial V} d\vec{S} \vec{j} = \int_V dQdP \nabla \vec{j} = n \int_V dQdP \nabla(\varrho \vec{v}).$$

So we found another continuity equation in form of

$$\frac{\partial \varrho}{\partial t} + \nabla(\varrho \vec{v}) = 0. \tag{2.6}$$

By using

$$\mathrm{div}(\varrho\vec{v}) = \sum_{\alpha=1}^{3N}\left(\frac{\partial\varrho\dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial\varrho\dot{p}_\alpha}{\partial p_\alpha}\right) = \sum_{\alpha}\left(\frac{\partial\varrho}{\partial q_\alpha}\dot{q}_\alpha + \frac{\partial\varrho}{\partial p_\alpha}\dot{p}_\alpha\right)$$

we find Liouville's equation,

$$\frac{\partial\varrho}{\partial t} + \sum_{\alpha}\left(\frac{\partial\varrho}{\partial q_\alpha}\dot{q}_\alpha + \frac{\partial\varrho}{\partial p_\alpha}\dot{p}_\alpha\right) \equiv \frac{d\varrho}{dt} = 0. \tag{2.7}$$

Conclusions We can directly make two statements:

1. We see that $\frac{d\varrho}{dt} = 0$, where $\frac{d\varrho}{dt}$ is a full derivative, i.e. the observer moves with the flow, while $\frac{\partial\varrho}{\partial t}$ is the stationary observer case.
2. If $\frac{\partial\varrho}{\partial t} = 0$ then $\varrho = \varrho(E)$ only. So the energy is conserved.

2.5 Microstates in quantum mechanics, the density matrix/operator

We already know the Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \ldots + \nabla_N^2),$$

where

$\psi = \psi(\vec{r}_1, \ldots, \vec{r}_N)$: wave function

N : Number of particles

$\left|\psi\right|^2 d^3\vec{r}$: probability to find particle(s) in a small neighorhood of volume $d^3\vec{r}$ arround $\vec{r}$,

$\psi(\vec{r}_1, \ldots \vec{r}_N)$: defines the microsopie state = microstate. (2.8)

Stationary states ϕ_n have

$$\hat{H}\phi_n = E_n\phi_n.$$

Any wavefunction can be expanded as

$$\psi = \sum_n c_n \phi_n.$$

Normalization requires that

$$\sum_n |c_n|^2 = 1.$$

The average value of a physical observable A, to which there is a hermitian operator $\hat{A}$, is given by

$$\langle A \rangle = \int dQ \psi^* \hat{A} \psi = \left\langle \psi | \hat{A} | \psi \right\rangle,$$

where $\langle A \rangle$ is the expectation value of A. We continue,

$$\langle A \rangle = \int dQ \sum_{nn'} c_n^* c_n' \phi_n^* \hat{A} \phi_n = \sum_{nn'} c_n^* c_n' \int dQ \underbrace{\phi_n^* \hat{A} \phi_n}_{A_{nn'}} = \sum_{nn'} c_n^* c_n' A_{nn'}.$$

We now introduce $\underbrace{\varrho_{nn'}}_{\text{density matrix}} \equiv c_n^* c_n',$

$$\rightarrow \langle A \rangle = \sum_{nn'} \varrho_{nn'} A_{nn'} = \mathrm{tr} \hat{\varrho} \hat{A}.$$

In operator notation we have $\hat{\varrho} = |\psi\rangle\langle\psi|$.

- $\langle \phi_n | \hat{\varrho} | \phi_{n'} \rangle = \overbrace{\langle \phi_n | \psi \rangle}^{c_n} \underbrace{\langle \psi | \phi_{n'} \rangle}_{c_{n'}^*} = c_{n'}^* c_n = \varrho_{nn'}.$
- Diagonal elements, $\varrho_{nn'} = |c_n|^2$, are called probabilities. Off-diagonal elements, are called coherences.
- $\mathrm{tr} \varrho = \sum_n |c_n|^2 = 1$
  $\hat{\varrho}^2 = \hat{\varrho}\hat{\varrho} = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi| = \hat{\varrho}$
  $\hat{\varrho}$: Complete description of the quantum mechanical state. Up to now, considering only pure states, it is a redundant description.

- The motion of mixed states (Schrödinger′s cat). Mixed state: there is a probability p_α, that the system is in state ψ_α.
- I cannot write a wave function for such a mixed state. Average Value of A is

$$\bar{A} = \sum_\alpha \overbrace{p_\alpha}^{\text{statistical average}} \underbrace{\langle A\rangle_\alpha}_{\text{QM average}}$$

$$\langle A_\alpha\rangle = \int dQ \psi_\alpha^* \hat{a} \psi_a .$$

Let us rewrite:

$$\begin{aligned} \bar{A} &= \sum_\alpha p_\alpha \langle\psi_\alpha|\hat{A}|\psi_\alpha\rangle = \sum_\alpha \sum_{nn'} p_\alpha c_n^{\alpha *} c_n^{\prime\alpha} \int dQ \phi_n^* \hat{A} \phi_{n'} = \sum_\alpha \sum_{nn'} p_\alpha c_n^{\alpha *} c_n^{\prime\alpha} A_{nn'} = \\ &= \sum_\alpha \sum_{nn'} p_\alpha \varrho_{nn'} A_{nn'} = \mathrm{tr}(\hat{\varrho}\hat{A}) \end{aligned}$$

- $\varrho_{nn'} = \sum_\alpha p_\alpha c_n^{\alpha *} c_n^{\prime\alpha}$,
  $\hat{\varrho} = \sum_\alpha p_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|$: describes mixed states
- $\mathrm{tr}(\hat{\varrho}) = \sum_\alpha p_\alpha \sum_n |c_n|^2 = \sum_\alpha p_\alpha = 1$,
  $\hat{\varrho}^2 \neq \varrho$! Signature of mixed states!

Summary:

	pure states	mixed states
$\hat{\varrho}$	$\|\psi\rangle\langle\psi\|$	$\sum_\alpha p_\alpha \|\psi_\alpha\rangle\langle\psi_\alpha\|$, $\sum_\alpha p_\alpha = 1$
tr$\hat{\varrho}$	1	1
$\hat{\varrho}^2$	$= \hat{\varrho}$	$\neq \hat{\varrho}$
$\overline{A}$	$\mathrm{tr}\left[\hat{\varrho}\hat{A}\right]$	$\mathrm{tr}\left[\hat{\varrho}\hat{A}\right]$

2.6 Quantum Liouvilles theorem

$$\begin{aligned}
\frac{\partial}{\partial t} &= \sum_\alpha \frac{\partial}{\partial t}\left(p_\alpha|\psi_\alpha >< \psi_\alpha|\right) = \sum_\alpha p_\alpha \underbrace{\left(\frac{\partial|\psi_\alpha >}{\partial t}\langle\psi_\alpha| + |\psi_\alpha\rangle\frac{\partial\langle\psi_\alpha|}{\partial t}\right) =}_{\text{SGL}} \\
&= \sum_\alpha p_\alpha\left(\frac{1}{i\hbar}\hat{H}|\psi_\alpha\rangle\langle\psi_\alpha| - \frac{1}{i\hbar}\psi_\alpha\rangle\langle\psi_\alpha|\hat{H}\right) = \frac{1}{i\hbar}\left(\hat{H}\hat{\varrho} - \hat{\varrho}\hat{H}\right) = \\
&= \frac{1}{i\hbar}\left[\hat{H},\hat{\varrho}\right].
\end{aligned}$$

The Von Neumann's equation is

$$\frac{\partial\varrho}{\partial t} = \frac{1}{i\hbar}\left[\hat{H},\hat{\varrho}\right].$$

In QM we learned that the time evolution of an operator $\hat{A}$ is

$$\frac{d}{dt}\hat{A} = \frac{\partial\hat{A}}{\partial t} + \frac{1}{i\hbar}\left[\hat{A},\hat{H}\right].$$

By using this we obtain

$$\begin{aligned}
\rightarrow \frac{d}{dt}\hat{\varrho} &= \frac{1}{i\hbar}[\hat{H},\hat{\varrho}] + \frac{1}{i\hbar}[\hat{\varrho},\hat{H}] = 0, \\
\rightarrow \frac{d}{dt}\hat{\varrho} &= 0 \text{ Quantum Liouvilles theorem.}
\end{aligned}$$

- For time independent $\hat{\varrho}$:

$$\frac{\partial\varrho}{\partial t} = 0 \qquad \rightarrow \qquad [\hat{\varrho},\hat{H}] = 0.$$

- $\hat{\varrho}$: integral of motion, conserved quantity.

Definition 2.6.1 *Energy is the only integral of motion left, (quantum chaos)*

$$\hat{\varrho} \equiv \hat{\varrho}(E).$$

- It is then natural to take ϕ_n as stationary states, $\hat{H}\phi_n = E_n\phi_n$, and $\varrho_{nn'} = \varrho(E_n)\delta_{nn'}$, Diagonal in the basis of stationary states,

$$\varrho(E_n) = |c_n|^2 = p_n.$$

Is the probaility to find the system in a microstate (state) of energy E_n. ($\neq$ the probability that the system has energy E_n).

- What happens if there are degenerate states (having the same energy E_n)?

$$\varrho_{nn'} = p_n(E_n)\delta_{nn'} = \begin{pmatrix} p_n(E_n) & 0 & 0 \\ 0 & p_n(E_n) & 0 \\ 0 & 0 & p_n(E_n) \end{pmatrix}.$$

For degenerate states, the coherences $\rho_{n\neq n'}$ are also zero. This is called the random phase assumption or a priori equal probabilities.

- We see that

$$\begin{aligned} \bar{A} &= \sum_n p_n(E_n)A_n = \sum_n p_n A_n, \\ A_n &= \langle\phi_n|\hat{A}|\phi_n\rangle. \end{aligned}$$

The task of statistical physics is to find $p(E_n)$ or p_n.

2.7 Counting quantum states

In analogy with classical physics, define

- Number of states below E,

$$\Gamma(E) = \sum_n \Theta(E - E_n).$$

- The density of states,

$$g(E) = \frac{d\Gamma}{dE} = \sum_n \delta(E - E_n).$$

- And the number of states in $[E, E + dE]$,

$$\Omega(E) = g(E)dE.$$

Important example: Single-particle states. Consider one particle in a box of linear dimension L, with periodic boundary conditions (see QM lecture). We calculate

$$\begin{aligned}
\hat{H} &= -\frac{\hbar^2}{2m}\vec{\nabla}^2, \\
\psi(\vec{r}+L\vec{m}) &= \psi(\vec{r}) \text{ with an integer vector } \vec{m}.
\end{aligned}$$

Therefore we can calculate the spectrum (eigenstates and eigenenergies),

$$\begin{aligned}
\psi_{\vec{k}} &= \frac{1}{\sqrt{V}}e^{i\vec{k}\vec{r}}, \\
\varepsilon_{\vec{k}} &= \frac{\hbar^2\vec{k}^2}{2m}, \\
\vec{k} &= \frac{2\pi}{L}\vec{n} \; \vec{n}\text{: integer vector.}
\end{aligned}$$

Trick: from discrete sums to integrals:

$$\begin{aligned}
\sum_{\vec{k}} f(\vec{k}) &= \sum_{n_x}\sum_{n_y}\sum_{n_z} f(\vec{k}) = \sum_{n_x}\sum_{n_y}\sum_{n_z} f(\vec{k}) \underbrace{\Delta n_x}_{1}\underbrace{\Delta n_y}_{1}\underbrace{\Delta n_z}_{1} = \\
&= \sum_{n_x}\sum_{n_y}\sum_{n_z} f(\vec{k})\left(\frac{2\pi}{L}\right)^3 \Delta k_x \Delta k_y \Delta k_z = \left(\frac{2\pi}{L}\right)^3 \sum_{\vec{k}_x}\sum_{\vec{k}_y}\sum_{\vec{k}_z} \Delta\vec{k}^3, \\
\Rightarrow &\underbrace{\longrightarrow}_{\text{continuum}} \left(\frac{2\pi}{L}\right)^3 \int d^3\vec{k} f(\vec{k}).
\end{aligned}$$

Back to our example:

$$\begin{aligned}
\Gamma(E) &= \sum_{\text{states}} \Theta(E - E_{\text{states}}) = \sum_{\vec{k}} \Theta(E - E_{\vec{k}}), \\
&\underbrace{\longrightarrow}_{\text{continuum}} \left(\frac{2\pi}{L}\right)^3 \int d^3\vec{k}\Theta(E - \frac{\hbar^2\vec{k}^2}{2m}) = \left(\frac{2\pi}{L}\right)^3 \int_{\vec{k}\le\frac{2mE}{\hbar^2}} d^3\vec{k} = \frac{V}{(2\pi)^3}\frac{4\pi}{3}\left(\frac{2mE}{\hbar^2}\right)^{\frac{3}{2}}.
\end{aligned}$$

Recall the classical result ($N = 1$), which was

$$\Gamma(E)_{cl} = \frac{V}{h^3}\frac{4\pi}{3}(2mE)^{\frac{3}{2}}.$$

This becomes the quantum result, if we identify $h = \hbar 2\pi$. Classical-quantum corespondence fixes the value of h to be Planck's constant.

3 Classical Ensembles

- Classical physics

$$
\begin{aligned}
\{Q,P\} &\equiv \text{microstate} \\
\varrho(Q,P) &\equiv \text{probability density} \\
\int dQdP\varrho(Q,P) &= 1 \\
\overline{A} &= \int dQdPA(Q,P)\varrho(Q,P).
\end{aligned}
$$

- Quantum physics

$$
\begin{aligned}
n \leftrightarrow \varphi_n &\equiv \text{microstate} \\
p_n &\equiv \text{probability to be in } n \\
\hat{\varrho} &\equiv \text{density operator} \\
\sum_n p_n &= 1 \\
\overline{A} &= \sum_n p_n A_n = \mathrm{tr}\left[\hat{\varrho}\hat{A}\right], \\
A_n &= \langle n|\hat{A}|n\rangle.
\end{aligned}
$$

3.1 Microcanonical ensemble

We consider a system which is totally closed. We have only 3 parameters, the total energy E, the volume V and the number of particles N. These parameters are fixed and describe a macrostate.

We need to find the probability that, given the macrostate (E, V, N), the system is in a specified microstate. In equilibrium (things do not change with time) we can guess: a priori equal probabilities,

$$p_{\text{microstate}} = \left.\frac{1}{\text{nr. of microstates}}\right|_{E,V,N}.$$

1. **classical physics**

$$\varrho(Q, P) = \frac{1}{h^{3N}} \frac{1}{g(E)} \delta \left[E - H(Q, P)\right].$$

2. **quantum physics**

$$\begin{aligned} p_n &= \frac{1}{\Omega(E)}, \text{ if } E \leq E_n \leq E + \delta E \\ &= 0, \text{ else.} \\ \hat{\varrho} &= \frac{1}{\Omega(E)} \sum_{n, E \leq E_n \leq E+\delta E} |\varphi_n\rangle\langle\varphi_n|. \end{aligned}$$

3. **entropy** We know $S = S(E, V, N)$. From the first chapter we still know

$$S = -k_B \sum_n p_n \ln(p_n) = k_B \ln \Omega(E).$$

So we identify

$$S(E, V, N) = k_B \ln \Omega(E, V, N), \tag{3.1}$$

with the Boltzmann constant $k_B = 1.38 \cdot 10^{-23}$ J/K. This constant connects statistics with thermodynamics.

Important remark: As $N \to \infty$ we see that

$$S = k_B \ln \Omega = k_B \ln \Gamma = k_B \ln(g\delta E),$$

up to negligable constants.

4. **temperature**

   For this we consider a system which we devide into two parts. This system can exchange energy. In this system we see that

$$\begin{aligned} E &= E_A + E_B, \\ V &= V_A + V_B, \\ N &= N_A + N_B, \end{aligned}$$

   are fixed and

$$E'_A = E_A + \Delta E,$$
$$E'_B = E_B - \Delta E,$$
$$E'_A + E'_B = E_A + E_B = E.$$

   In equilibrium the enrgy is distributed (on average) such, that $S = S_A + S_B$ will have a maximum

$$\Delta S = 0, \quad \Delta S = \frac{\partial S_A}{\partial E_A}\Delta E - \frac{\partial S_B}{\partial E_B}\Delta E = 0.$$

   So we conclude for every division, that

$$\frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B}. \tag{3.2}$$

   It is useful to introduce a name for this derivative, the thermodynamic temperature T or

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}. \tag{3.3}$$

   This is the partial derivative of S with respect to E, keeping V and N fixed.

5. **pressure and chemical portential**

   By doing the same as before we obtain (by changing the volume) the pressure over the temperature

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}. \tag{3.4}$$

And if we allow particles N to be exchanged we get the negative chemical potential over the temperature

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V}. \tag{3.5}$$

Summary

macrostate	p_n	thermodynamic potential	thermodynamics
E, V, N	$\frac{1}{\Omega(E,V,N)}$	$S = k_B \ln \Omega$ $dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$	$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$ $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}$ $\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}$

3.2 Microcanonical ideal gas, Gibbs paradox, indistinguished particles

Thermodynamics of an ideal gas (weakly interacting particles) using microcanonical ensemble.

- We will use

  $$S = k_B \ln \Gamma.$$

  We calculated Γ in chapter 2.2,

  $$\Gamma(E, V, N) = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{\frac{3N}{2}}}{(3N/2)!}.$$

  Therefore we get

  $$S = k_B \ln \Gamma = k_B \left(N \ln V + \frac{3N}{2} \ln(2\pi m E) - \ln \frac{3N}{2}! - 3N \ln h \right).$$

  We can easily see that for the temperature we obtain

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3N}{2}\frac{1}{E}k_B.$$

This leads to the well known equation

$$E = \frac{3}{2}Nk_BT. \tag{3.6}$$

We say that k_BT is the thermal energy. The equipartitian theorem says that for every (quadratic) degree of freedom there is, in equilibrium, the energy $\frac{1}{2}k_BT$ for a particle. This is classical physics. In an ideal gas we have three degrees of freedom. They are quadratic since

$$H \propto \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}.$$

- We can also calculate the pressure over the temperature,

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = k_BN\frac{1}{V} \quad \Rightarrow \quad PV = Nk_BT.$$

This is also well known as the equation of state of an ideal gas.

1. **Gibbs paradox** Striling's formula (Appendix) is given by

$$\lim_{N\to\infty} \ln N! \approx N\ln N - N.$$

Therefore we see that

$$\ln\left(\frac{3N}{2}\right)! \approx \frac{3N}{2}\ln\frac{3N}{2} - \frac{3N}{2}.$$

The entropy then changes to

$$S \approx k_BN\ln\left[V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right] + \frac{3}{2}k_BN.$$

This is a problem, cause V should be $\frac{V}{N}$. We will see this by considering 2 gases, where $T_1 = T_2$ and $P_1 = P_2$. Therefore we get

$$\frac{E_1}{N_1} = \frac{E_2}{N_2}, \qquad \frac{N_1}{V_1} = \frac{N_2}{V_2}.$$

Suppose we remove the partition between the two gases and let the gases mix. We can calculate

$$\Delta S = S - \underbrace{(S_1 + S_2)}_{\text{mixing entropy}} \ .$$

As we see we find

$$\Delta S = k_B N_1 \ln \frac{V}{V_1} + k_B N_2 \ln \frac{V}{V_2}.$$

Example: $N_1 = N_2 = \frac{N}{2}$, $V_1 = V_2 = \frac{V}{2}$. So we get

$$\Delta S = k_B N \ln 2 > 0.$$

This is a <u>paradox</u>, because if we take the *same* gas left and right we see that ΔS is still greater than zero. So the entropy increases - that makes it ill defined. The formula must be wrong since

$$\Delta S_{\text{expect}} = 0.$$

The solution by Gibbs was to devide the phase-space volume(s) by $N!$. So we get

$$\Gamma(E) \rightarrow \frac{\Gamma(E)}{N!} = \frac{V^N}{h^{3N} N!} \frac{(2\pi m E)^{\frac{3N}{2}}}{(3N/2)!}.$$

Then, we see that the V problem in S is fixed,

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

Now we get $\Delta S = 0$ for the same gases.

2. **Undistinguished particles**

   In quantum mechanics two particles are indistinguishable in principle.

   Example: two particles in three states. We have $3! = 6$ possible states of the system. These are called 6 microstates. If the particles are undistinguished we have only

$$3 = \frac{3!}{2!}$$

states, where $\frac{1}{N!}$ removes the degeneracy due to undistinguished particles.

3. **Correct classical phase space measures**

$$\begin{aligned}
\Gamma(E) &= \int \frac{dQdP}{h^{3N}N!}\Theta(E - H(Q,P)),\\
g(E) &= \frac{d\Gamma}{dE},\\
\Omega(E) &= g(E)\delta E.
\end{aligned}$$

If there are two types of particles we have to use

$$\frac{1}{N!} \to \frac{1}{N_1!}\frac{1}{N_2!}, \cdots$$

3.3 Canonical ensemble (T, V, N)

Canonical ensemble in a set of microstates of a system (A) in contact with thermal bath (B). We say that a thermal bath is a *reservoir*. The system itself can be very small (even 1 particle). The reservoir is to be very large and is not changing due to the contact with the system. We exchange energy between the reservoir and the system. We propose

$$E = E_A + E_B = \text{const.},$$

where E is the total system energy. Thus the total system is isolated. A and B can exchange energy.

- **Question** What is the probability to find system A in microstate n of energy E_n?

  Answer We will show that

$$\begin{aligned}
p_n &= \frac{1}{Z}\exp(-\beta E_n),\\
\beta &= \frac{1}{k_B T}.
\end{aligned}$$

The number of microstates corresponding to a fixed energy E_A is

$$\Omega_A(E_A) \cdot \Omega_B(\underbrace{E - E_A}_{=E_B}),$$

with the number of microstates of A of energy E_A, Ω_A, and the number of microstates of B of energy E_B, Ω_B.

- The number of microstates available is

$$\sum_{E_A} \Omega_A(E_A) \cdot \Omega_B(E - E_A).$$

- **Question** What is the probability to find A with energy E_A?

  Answer We know that this is given by

$$p(E_A) = \frac{\Omega_A(E_A) \cdot \Omega_B(E - E_A)}{\sum_{E_A} \Omega_A(E_A) \cdot \Omega_B(E - E_A)}.$$

- **Question** What is the probability to find A in a microstate n of energy $E_n = E_A$?

$$p_n = p_n(E_n = E_A) = \frac{\Omega_B(E - E_A)}{\sum_{E_A} \Omega_A(E_A) \cdot \Omega_B(E - E_A)}.$$

  This probability is given mainly by $\Omega_B(E - E_A)$, the number of microstates of the reservoir! We know that

$$\Omega_B(E_B) = \exp\left(\frac{1}{k_B} S_B(E_B)\right),$$

  with the entropy S_B of B. So $\Omega_B(E_B)$ is a steep function of E_B. Therefore it is the best to deal with $\ln \Omega = \frac{1}{k_B} S$, when we do a Taylor expansion.

- In equilibrium, A will have average (most probable) energy $\overline{E}_A$. We expand $\Omega_B(E - E_A)$ around $\overline{E}_A$. We calculate

$$
\begin{aligned}
S_B(E-E_A) &\approx S_B(E-\overline{E}_A) + \left.\frac{\partial S_B}{\partial E_A}\right|_{E_A=\overline{E}_A}(E_A-\overline{E}_A) + \ldots, \\
&\approx S_B(E-\overline{E}_A) - \left.\frac{\partial S_B}{\partial E_B}\right|_{E_B=E-\overline{E}_A}(E_A-\overline{E}_A) + \ldots = \\
&= S_B(E-\overline{E}_A) - \frac{1}{T}(E_A-\overline{E}_A) + \ldots
\end{aligned}
$$

- Neglecting higher order terms ($\partial^2 S/\partial E^2$) means that we assume $T = \text{const}$. So we calculate

$$
\begin{aligned}
\Rightarrow \Omega_B(E-\overline{E}_A) &\approx \exp\left(\frac{1}{k_B}S(E-\overline{E}_A)\right)\exp\left(\frac{1}{k_BT}(E_A-\overline{E}_A)\right), \\
\Rightarrow p_n &= \frac{\Omega_B(E-E_A)}{\sum_{E_A}\Omega_A(E_A)\cdot\Omega_B(E-E_A)} = \\
&= \frac{\Omega_B(E-\overline{E}_A)\exp\left(\frac{\overline{E}_A}{k_BT}\right)\exp\left(-\frac{E_A}{k_BT}\right)}{\Omega_B(E-\overline{E}_A)\exp\left(\frac{\overline{E}_A}{k_BT}\right)\sum_{E_A}\Omega_A(E_A)\exp\left(-\frac{E_A}{k_BT}\right)} = \\
&= \frac{\exp(-E_A/k_BT)}{\sum_{E_A}\Omega_A(E_A)\exp(-E_A/k_BT)} = \left| E_A = E_n, \quad \sum_{E_A}\Omega = \sum_n \cdot \right| = \\
&= \frac{\exp(-E_n/k_BT)}{\sum_n \exp(-E_n/k_BT)}.
\end{aligned}
$$

Thus we found the *Boltzmann probability* with the partition function Z,

$$
\begin{aligned}
p_n &= \frac{1}{Z}\exp(-\beta E_n), \\
\beta &= 1/k_BT, \\
Z &= \sum_n \exp(-\beta E_n).
\end{aligned}
\tag{3.7}
$$

1. Classical physics

   We see that

$$
\begin{aligned}
\varrho(Q,P) &= \frac{1}{Z}\frac{1}{N!}\frac{1}{h^{3N}}\exp(-\beta H(Q,P)), \\
Z &= \int \frac{dQdP}{h^{3N}N!}\exp(-\beta H(Q,P)).
\end{aligned}
$$

2. Quantum physics

   Again we observe that

$$\begin{aligned}\varrho_{nn} &= p_n = \frac{1}{Z}\exp(-\beta E_n),\\ Z &= \sum_n \exp(-\beta E_n),\\ \hat{\varrho} &= \frac{1}{Z}\exp(-\beta \hat{H}).\end{aligned}$$

3. Maximum uncertainty principle

   In chapter 1.4 we found that if we fix the average of an observable A,

$$\overline{A} = \sum_n p_n A_n,$$

   then the probability that maximum uncertainity is

$$p_n = \frac{1}{Z}\exp(-\overline{\lambda}_2 A_n).$$

   Thus the canonical ensemble is such that the uncertainty is maximized and

$$\begin{aligned}\overline{E} &= \sum_n p_n E_n = const.,\\ \overline{\lambda}_2 &= \frac{1}{k_B T} = \beta.\end{aligned}$$

4. Internal energy $\overline{E}$ (or just E) and specific heat C

   We know that

$$\overline{E} = \sum_n p_n E_n = \frac{1}{Z}\sum_n E_n \exp(-\beta E_n) = -\frac{\partial \ln Z}{\partial \beta}.$$

   This is called the *internal energy*. For the specific heat or *heat capacity* we calculate

$$\begin{aligned}
c_v &= \left(\frac{\partial \overline{E}}{\partial T}\right)_V = \frac{\partial \beta}{\partial T}\frac{\partial \overline{E}}{\partial \beta} = \\
&= \frac{1}{k_B T^2}\left(\frac{\partial}{\partial \beta}\frac{1}{Z}\frac{\partial z}{\partial \beta}\right) = \frac{1}{k_B T^2}\left[-\frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}\right] = \\
&= \frac{1}{k_B T^2}\left(\overline{E^2} - \overline{E}^2\right).
\end{aligned}$$

Here we must know that

$$\begin{aligned}
\overline{E^2} &= \sum_n p_n E_n^2 = \frac{1}{Z}\sum_n \exp(-\beta E_n) E_n^2 = \\
&= \frac{1}{Z}\frac{\partial^2}{\partial \beta^2}\sum_n \exp(-\beta E_n) = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}, \\
c_v &= \frac{1}{k_B T^2}\left[\overline{E^2} - \overline{E}^2\right] = \frac{\sigma_E^2}{k_B T^2}.
\end{aligned}$$

This forumla is important, since it shows that

a) c_v is proportional to the energy fluctuation (σ_E^2).

b) c_v is greater than 0 !

c) c_v is proportional to N due to $(\partial E/\partial T)_V$. Therefore we calculate

$$\sigma_E^2 \propto N \quad \Rightarrow \quad \sigma_E \propto \sqrt{N}.$$

The relative error in measuring the energy is thus given by

$$\frac{\sigma_E}{E} \propto \frac{\sqrt{N}}{N} \propto \frac{1}{\sqrt{N}} \to 0,$$

for $N \to \infty$.

In the *thermodynamic limit*, i.e. $N \to \infty$, $V \to \infty$ and thus $N/V = \text{const}$ the average energy will be

$$\overline{E} \to E \qquad \text{fixed!}$$

Thus it is very important to see that in the thermodynamic limit the canonical ensemble is equivalent to the microcanonical ensemble!

5. Entropy and free energy F

   We see that

$$\begin{aligned} S &= -k_B \sum_n p_n \ln p_n = -k_B \sum_n \frac{1}{Z} \exp(-\beta E_n) \ln \left[\frac{1}{Z} \exp(-\beta E_n)\right] = \\ &= -k_B \frac{1}{Z} \sum_n \exp(-\beta E_n)(-\ln Z - \beta E_n) = \\ &= k_B \frac{1}{Z} \ln Z \left[\sum_n \exp(-\beta E_n)\right] + k_B \frac{\beta}{Z} \sum_n E_n \exp(-\beta E_n) = \\ &= k_B \ln Z + \frac{1}{T} \overline{E}. \end{aligned}$$

   We call

$$F = -k_B T \ln Z = \overline{E} - TS, \tag{3.8}$$

   the (Helmholz) *free energy*. It is the thermodynamic potential, $F \equiv F(T, V, N)$ for the canonical ensemble.

6. Thermodynamics

   We will now calculate some of the thermodynamic quantities. We see that

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -k_B \ln Z - k_B T \frac{d\beta}{T} \frac{\partial \ln Z}{\partial \beta} = \frac{F}{T} + \frac{k_B T}{k_B T^2}(-\overline{E}) = -S.$$

   Therefore we have

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}. \tag{3.9}$$

   Similarly we introduce two other thermodynamic quantities. We have the pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N},$$

   and the chemical potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} .$$

Summary

macrostate	p_n	thermodynamic potential	thermodynamics
T, V, N	$\frac{1}{Z}\exp(-\beta E_n)$	$F \equiv F(T, V, N)$	$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$
	$Z = \sum_n \exp(-\beta E_n)$	$F = -k_B T \ln Z$	$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$
		$dF = -SdT - PdV + \mu dN$	$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

3.4 Grand canonical ensemble (T, V, μ)

Again our system A can be small, even 1 particle. The heat reservoir B is very very large and $E_A + E_B = E$, $N_A + N_B = N$, as well as V_A and V_B are fixed. The system A can exchange energy and particles with the reservoir.

- **Question** What is the probability to find system A in a (one) microstate n corresponding to the energy E_n and number of particles N_n?

  Answer We will show that

$$\begin{aligned} p_n &= \frac{1}{Z_G} \exp(-\beta(E_n - \mu N_n)), \\ Z_G &= \sum_n \exp(-\beta(E_n - \mu N_n)). \end{aligned}$$

  Z_G is called the grand partition function (sometimes also written as Z). The number of microstates of the total isolated system $A + B$ corresponding to a fixed energy E_A and a fixed number of particles N_A is

$$\Omega_A(E_A, N_A) \cdot \Omega_B(E - E_A, N - N_A),$$

  with the number of microstates of A of energy E_A and particles N_A, Ω_A, and the number of microstates of B of energy E_B and particles N_B, Ω_B.

- The number of microstates available is

$$\sum_{E_A,N_A} \Omega_A(E_A,N_A)\cdot\Omega_B(E-E_A,N-N_A).$$

- **Question** What is the probability to find A with energy E_A and particles N_A?

  Answer We know that this is given by

$$p(E_A,N_A)=\frac{\Omega_A(E_A,N_A)\cdot\Omega_B(E-E_A,N-N_A)}{\sum_{E_A,N_A}\Omega_A(E_A,N_A)\cdot\Omega_B(E-E_A,N-N_A)}.$$

- **Question** What is the probability to find A in a (one) microstate n of energy $E_n=E_A$ and number of particles $N_n=N_A$?

$$p_n=p_n(E_n=E_A,N_n=N_A)=\frac{\Omega_B(E-E_A,N-N_A)}{\sum_{E_A,N_A}\Omega_A(E_A,N_A)\cdot\Omega_B(E-E_A,N-N_A)}.$$

  This probability is given mainly by $\Omega_B(E-E_A,N-N_A)$, the number of microstates of the reservoir!

- Assuming that $E_B\gg E_A$, $N_B\gg N_A$ we can do the mathematics of large numbers.
- In equilibrium, A will have average (most probable) energy $\overline{E}_A$ and number of particles $\overline{N}_A$ that corresponds to the maximum of $S_A+S_B=S_{A+B}$. Then we can expand $\Omega_B(E-E_A,N-N_A)$ around $\overline{E}_A$ in E_A and $\overline{N}_A$ in N_A. We calculate

$$\begin{aligned}
S_B(E-E_A,N-N_A) &\approx S_B(E-\overline{E}_A,N-\overline{N}_A)+\left.\frac{\partial S_B}{\partial E_A}\right|_{E_A=\overline{E}_A}(E_A-\overline{E}_A)+\\
&+\left.\frac{\partial S_B}{\partial N_A}\right|_{N_A=\overline{N}_A}(N_A-\overline{N}_A)+\ldots,\\
&\approx S_B(E-\overline{E}_A,N-\overline{N}_A)-\left.\frac{\partial S_B}{\partial E_B}\right|_{E_B=E-\overline{E}_A}(E_A-\overline{E}_A)-\\
&-\left.\frac{\partial S_B}{\partial N_B}\right|_{N_B=N-\overline{N}_A}(N_A-\overline{N}_A)+\ldots=\\
&=\left|\left.\frac{\partial S_B}{\partial E_B}\right|_{E_B=E-\overline{E}_A}=\frac{1}{T},\qquad \left.\frac{\partial S_B}{\partial N_B}\right|_{N_B=N-\overline{N}_A}=-\frac{\mu}{T}\right|=\\
&=S_B(E-\overline{E}_A,N-\overline{N}_A)-\frac{1}{T}(E_A-\overline{E}_A)+\frac{\mu}{T}(N_A-\overline{N}_A)+\ldots
\end{aligned}$$

- Neglecting higher order terms ($\partial^2 S/\partial E^2$) means that we assume T = const, because B is very very big, so that

  $$\frac{\partial T}{\partial E_A}, \quad \frac{\partial \mu}{\partial N_A} \approx 0.$$

  So we calculate

  $$\begin{aligned} p_n &= \frac{\Omega_B(E-E_A, N-N_A)}{\sum_{E_A,N_A} \Omega_A(E_A,N_A)\cdot\Omega_B(E-E_A,N-N_A)} = \\ &= \frac{\Omega_B(E-\overline{E}_A, N-\overline{N}_A)\exp\left(\frac{\overline{E}_A}{k_BT}\right)\exp\left(-\frac{E_A}{k_BT}\right)\exp\left(-\mu\frac{\overline{N}_A}{k_BT}\right)\exp\left(\mu\frac{N_A}{k_BT}\right)}{\Omega_B(E-\overline{E}_A, N-\overline{N}_A)\exp\left(\frac{\overline{E}_A-\mu\overline{N}_A}{k_BT}\right)\sum_{E_A,N_A}\Omega_A(E_A,N_A)\exp\left(-\frac{E_A-\mu N_A}{k_BT}\right)} = \\ &= \frac{\exp(-\beta(E_NA-\mu N_A))}{\sum_n \exp(-\beta(E_n-\mu N_n))}. \end{aligned}$$

- We call the $Z = \exp(\beta\mu)$ fugacity, which means tendency to escape. Overall we found

$$\begin{aligned} Z_N &= \sum_n \exp(-\beta E_n(N)), \quad Z_G = \sum_{N=0}^{\infty} Z^n Z_N, \\ Z &= \exp(\beta\mu). \end{aligned} \tag{3.10}$$

1. classical physics

   We see that

   $$\begin{aligned} Z_G &= \sum_{N=0}^{\infty} Z^N \int \frac{dQdP}{h^{3N}N!}\exp(-\beta H(Q,P)), \\ \varrho(Q,P) &= \frac{1}{Z_G}\sum_{N=0}^{\infty} Z^N \frac{1}{h^{3N}N!}\exp(-\beta H(Q,P,N)). \end{aligned}$$

2. Quantum physics

   Here it is

$$
\begin{aligned}
p_n &= \frac{1}{Z_G}\exp(-\beta(E_n(N_n)-\mu N_n)),\\
\hat{\varrho} &= \frac{1}{Z_G}\exp(-\beta(\hat{H}-\mu\hat{N})), \qquad \hat{N}|n\rangle = N|n\rangle,\\
Z_G &= \mathrm{tr}\left[\exp(-\beta(\hat{H}-\mu\hat{N}))\right].
\end{aligned}
$$

Note: The trace means $\sum_{N=0}^{\infty}\sum_{n(N)}$.

3. Information theory point of view The grand canonical ensemble is the one which maximizes uncertainty given the constraints

$$\overline{E} = \sum_n p_n E_n, \qquad \overline{N} = \sum_n p_n N_n,$$

where T, μ are the Lagrange multipliers in that case.

4. Particle number fluctuations Let us calculate $\partial\overline{N}/\partial\mu$.

$$
\begin{aligned}
\frac{\partial\overline{N}}{\partial\mu} &= \frac{\partial}{\partial\mu}\frac{1}{Z_G}\sum_n N_n\exp(-\beta(E_n-\mu N_n)) =\\
&= \underbrace{-\frac{1}{Z_G^2}\frac{\partial Z_G}{\partial\mu}\sum_n N_n\exp(-\beta(E_n-\mu N_n))}_{=-\overline{N}^2\beta} + \underbrace{\frac{1}{Z}\beta\sum_n N_n^2\exp(-\beta(E_n-\mu N_n))}_{=\overline{N^2}\beta} =\\
&= \frac{\overline{N^2}-\overline{N}^2}{k_BT} = \frac{\sigma_N^2}{k_BT}.
\end{aligned}
$$

This result is important since

a) This means that $\partial\overline{N}/\partial\mu > 0$!

b) The error in N is $\sigma_N/\overline{N}$ which is proportional to $1/\sqrt{\overline{N}}$. This goes to zero when $\overline{N}$ goes to infinity. We also see

$$\sigma_N^2 \propto \frac{\partial\overline{N}}{\partial\mu} \propto \overline{N}.$$

So the average number of particles $\overline{N}$ is very well defined (small σ_N) in the thermodynamic limit. This can be considered as fixed. Therefore in the thernodynamic limit with $N, V \to \infty$ and N/V = const. the microcanonical, canonical and grandcanonical ensembles are equivalent! The reason is that

$$\overline{E} \to \text{fixed} \quad \left(\frac{\sigma_E}{\overline{E}} \to 0\right), \quad \overline{N} \to \text{fixed} \quad \left(\frac{\sigma_N}{\overline{N}} \to 0\right).$$

5. Grand free energy $\Phi(T, V, \mu)$

   We now introduce another potential,

   $$\Phi(T, V, \mu) = -k_B T \ln Z_G.$$

   Remark The notation in the literature is $\Omega, L, \Psi, G,...$ Let us calculate the entropy,

   $$\begin{aligned} S &= -k_B \sum_N p_n \ln p_n = \\ &= -k_B \sum_n \frac{1}{Z_G} \exp(-\beta E_n + \beta\mu N_n) \ln\left[\frac{1}{Z_G} \exp(-\beta E_n + \beta\mu N_n)\right] = \\ &= -k_B \frac{1}{Z_G}(-\ln Z_G) \sum_n \exp(-\beta E_n + \mu\beta N_n) + \\ &+ k_B \frac{\beta}{Z_G} \sum_n (E_n - \mu N_n) \exp(-\eta E_n + \mu\beta N_n) = \\ &= k_B \ln Z_G + \frac{1}{T}(\overline{E} - \mu\overline{N}) = -\frac{\Phi}{T} + \frac{\overline{E} - \mu\overline{N}}{T}. \end{aligned}$$

   Therefore we see that

   $$\Phi = \overline{E} - ST - \mu\overline{N}. \tag{3.11}$$

   In thermodynamics we see that $\overline{E} \to E$ and $\overline{N} \to N$.

6. Thermodynamics We now calculate some relations.

$$
\begin{aligned}
\frac{\partial \Phi}{\partial \mu} &= -k_B T \frac{\partial}{\partial \mu} \ln Z_G = -k_B T \frac{1}{Z_G} \frac{\partial Z_G}{\partial \mu} = \\
&= -k_B T \frac{1}{Z_G} \sum_n \beta N_n \exp(-\beta(E_n - \mu N_n)) = -\overline{N}, \\
\frac{\partial \Phi}{\partial T} &= -k_B \ln Z_G - k_B \frac{d\beta}{dT} \frac{\partial \ln Z_G}{\partial \beta} = \\
&= \frac{\Phi}{T} + \frac{1}{T} \sum_n -(E_n - \mu N_n) \exp(-\beta(E_n - \mu N_n)) = \\
&= \frac{\Phi}{T} - \frac{1}{T}(\overline{E} - \mu \overline{N}) = -S.
\end{aligned}
$$

We will see later that

$$\frac{\partial \Phi}{\partial V} = -P.$$

Summary

macrostate	p_n	thermodynamic potential	thermodynamics
T, V, μ	$\frac{1}{Z_G} \exp(-\beta(E_n - \mu N_n))$	$\Phi \equiv \Phi(T, V, \mu)$	$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}$
	$Z_G = \sum_n \exp(-\beta(E_n - \mu N_n))$	$\Phi = -k_B T \ln Z_G$	$P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}$
		$d\Phi = -SdT - PdV - Nd\mu$	$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$

4 Ideal classical, bose and fermi gas

- **classical gas**

  non-interacting classical particles, low occupation probabilities.

- **bose gas**

  non-interacting bosons (integer spin), photons, phonons, integer-spin atoms, cooper pairs, ... with no restriction on the occupation of states.

- **fermi gas**

  non-interacting fermions (half-integer spin), electrons, protons, neutrons, up to one particle in 1 state (Pauli exclusion principle).

- In the limit of $T \to \infty$ all the gases are equivalent.

4.1 Ideal classical gas

In chapter 3.2 we found that

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

in the microcanonical ensemble.

1. <u>Canonical treatment</u>
    - We know that

      $$H(Q,P) = \frac{\vec{P}^2}{2m} = \frac{\vec{p}_1^2}{2m} + ... \frac{\vec{p}_N^2}{2m}.$$

      We need to calculate

$$Z \equiv Z(T,V,N) = \int \frac{dQdP}{h^{3N}N!}\exp(-\beta H(Q,P)).$$

- We need to calculate the partition function

$$\begin{aligned} Z &= \frac{1}{h^{3N}N!}\int dQ \int d^3\vec{p}_1 d^3\vec{p}_2 \cdots d^3\vec{p}_N \exp(-\beta\vec{p}_1^2/2m)\cdots\exp(-\beta\vec{p}_N^2/2m) = \\ &= \frac{V^N}{h^{3N}N!}\left[\int d^3\vec{p}\exp\left(\beta\frac{\vec{p}^2}{2m}\right)\right]^N = \frac{Z_1^N}{N!}. \end{aligned}$$

- In the factorization we used the one particle partition function which is

$$\begin{aligned} Z_1 &= \frac{V}{h^3}\left[\int_{-\infty}^{\infty} dp_x \exp(-\beta p_x^2/2m)\int_{-\infty}^{\infty} dp_y \exp(-\beta p_y^2/2m)\int_{-\infty}^{\infty} dp_z \exp(-\beta p_z^2/2m)\right] = \\ &= \frac{V}{h^3}\left(\sqrt{\pi 2 m k_B T}\right)^3 = \frac{V}{\left(\frac{h}{\sqrt{2\pi m k_B T}}\right)^3} = \frac{V}{\lambda^3}, \\ \lambda &= \sqrt{\frac{h^2}{2\pi m k_B T}} = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}. \end{aligned}$$

  This thermal-de-Broglie-wavelength is equivalent to the de-Broglie-wavelength (h/momentum) of a particle of energy $\approx k_B T$.

- Question Why can Z be factorized into the product of Z_1?

  Answer Each particle interacts (exchanges energy) independently with the reservoir. This leads to

$$Z = \frac{1}{N!}\frac{V^N}{h^{3N}}(2\pi m k_B T)^{3N/2} = \frac{1}{N!}\frac{V^N}{\lambda^{3N}}.$$

- The free energy is $F = -k_B T \ln Z$. Therefore we calculate

$$\begin{aligned} F &= -k_B T \ln\left[\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\right] = k_B T \ln N! - k_B T N \ln\left(\frac{V}{\lambda^3}\right) = \\ &= |\ln N! \approx N\ln N - N| = k_B T N \ln\left[\frac{N}{V}\lambda^3\right] - k_B T N = \\ &= k_B T N\left(\ln\left[\frac{N}{V}\lambda^3\right] - 1\right) \propto N. \end{aligned}$$

- The entropy is $S = -(\partial F/\partial T)_{V,N}$. So we calculate

$$\begin{aligned} S &= -k_B N\left(\ln\left[\frac{N}{V}\lambda^3\right] - 1\right) - k_B T N \frac{\partial}{\partial T}\ln\lambda^3 = \\ &= -k_B N \ln\left(\frac{N}{V}\lambda^3\right) + \frac{5}{2}k_B N. \end{aligned}$$

  Remark We see that

$$T\frac{\partial}{\partial T}\ln\lambda^3 = T\frac{\partial}{\partial T}3\ln\lambda = 3T\frac{1}{\lambda}\frac{d\lambda}{dT} = -\frac{3}{2}.$$

  Therefore we have found the *Sackur-Tetrole equation*,

$$S \equiv S(T,V,N) = -k_B N \ln\left[\frac{N}{V}\lambda^3\right] + \frac{5}{2}k_B N. \tag{4.1}$$

- The internal energy $\overline{E} = F + TS$,

$$\overline{E} = \frac{3}{2}k_B T N \quad \to \quad S = k_B N \ln\left[\frac{V}{N}\left(\frac{4\pi m\overline{E}}{3Nh^2}\right)^{3/2}\right] + \frac{5}{2}k_B N,$$

  as in the microcanonical treatment ($\overline{E} \to E$).

2. Grandcanonical treatment

   We calculate

$$\begin{aligned} z &= \exp(\beta\mu), \\ Z_G &= \sum_{N=0}^{\infty} z^N Z_N = \sum_{N=0}^{\infty}\exp(\beta\mu N)\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N = \sum_{N=0}^{\infty}\frac{1}{N!}\left(\exp(\beta\mu)\frac{V}{\lambda^3}\right)^N = \\ &= \exp\left(\exp(\beta\mu)\frac{V}{\lambda^3}\right). \end{aligned}$$

- The grand canonical potential $\Phi = -k_B T \ln Z_G$ is

$$\Phi = -k_B T\left(\frac{V}{\lambda^3}\right)\exp(\beta\mu).$$

- The average particle number $\overline{N} = -(\partial\Phi/\partial\mu)_{T,V}$ is

$$\overline{N} = k_B T\left(\frac{V}{\lambda^3}\right)\beta\exp(\beta\mu) = -\beta\Phi \quad\Rightarrow\quad \Phi = -k_B T\overline{N}.$$

- Chemical potential

$$\mu = k_B T\ln\left(\frac{\overline{N}}{V}\lambda^3\right).$$

Remark If $\overline{N} \ll V/\lambda^3$ we see that $\mu \to -\infty$. This is the case when the distance between the particles is much greater than λ or when there are much more boxes than particles.

- The entropy is $S = -(\partial\Phi/\partial T)_{V,\mu}$. We see

$$\begin{aligned} S &= k_B\left(\frac{V}{\lambda^3}\right)\exp(\beta\mu) + k_B T V\left(-\frac{3}{\lambda^4}\frac{d\lambda}{dT}\right)\exp(\beta\mu) + k_B T\left(\frac{V}{\lambda^3}\right)\frac{d\beta}{dT}\mu\exp(\beta\mu) = \\ &= -\frac{\Phi}{T} - \frac{3}{2}\frac{\Phi}{T} + \frac{\mu}{k_B T}\frac{\Phi}{T} = -\frac{5}{2}k_B\overline{N} - \overline{N}\frac{\mu}{T} = \\ &= -k_B\overline{N}\ln\left[\frac{\overline{N}}{V}\lambda^3\right] + \frac{5}{2}k_B\overline{N}. \end{aligned}$$

This is the same as in the canonical treatment in the thermodynamic limit ($\overline{N} \to N$).

- The internal energy is $\overline{E} = \Phi + TS + \mu\overline{N}$. We see

$$\overline{E} = -k_B T\overline{N} - T\overline{N}\frac{\mu}{T} + \frac{5}{2}k_B T\overline{N} + \mu\overline{N} = \frac{3}{2}k_B T\overline{N}.$$

Again in agreement with the equipartition theorem.

4.2 Maxwell-Boltzmann probability distribution

Question What is the probability to find a given one particle in a state of momentum $\vec{p}$?

Answer We know that

$$\varrho_1(\vec{p}) = (2\pi m k_B T)^{-3/2} \exp\left(-\frac{\vec{p}^2}{2mk_BT}\right).$$

We now want to calculate

$$\varrho_1(\vec{r}_1, \vec{p}_1) = \frac{1}{Zh^3} \exp(-\beta H(\vec{r}_1, \vec{p}_1)), \quad Z = \int d^3\vec{r}_1 d^3\vec{p}_1 \frac{1}{h^3} \exp(-\beta H(\vec{r}_1, \vec{p}_1)).$$

This is the canonical ensemble for one particle! So we see that

$$\begin{aligned}
\varrho_1(\vec{r}_1, \vec{p}_1) &= \exp\left(-\frac{\vec{p}_1^2}{2mk_BT}\right) \frac{1}{h^3 \int \frac{d^3\vec{r}_1}{h^3} \int d^3\vec{p}_1 \exp\left(-\frac{\vec{p}_1^2}{2mk_BT}\right)} = \\
&= \frac{1}{V} \frac{\exp(-\vec{p}_1^2/2mk_BT)}{(2\pi m k_B T)^{3/2}}, \\
\Rightarrow \varrho_1(\vec{p}_1) &= \int d^3\vec{r}_1 \varrho_1(\vec{p}_1, \vec{r}_1) = V \varrho_1(\vec{r}_1, \vec{p}_1), \\
\Rightarrow \varrho_1(\vec{p} - 1) &= (2\pi m k_B T)^{-3/2} \exp\left(\frac{-\vec{p}^2}{2mk_BT}\right).
\end{aligned}$$

Question Suppose the particle is in an external potential $U(\vec{r})$. What is $\varrho_1(\vec{p})$?

Answer It is the same because we also devide through the potential term. Thus we do not have any space dependence! This is very important.

The velocity distribution

$$\begin{aligned}
\varrho_1(\vec{p}) d^3p = \varrho_1(\vec{p}) 4\pi p^2 dp \equiv \varrho_1(p = |\vec{p}|) dp, \\
\Rightarrow \varrho_1(p) &= 4\pi p^2 (2mk_BT)^{-3/2} \exp(-p^2/2mk_BT), \\
\varrho_1(p) dp = \varrho_1(v) dv = \varrho_1(v) \frac{1}{m} dp, \\
\Rightarrow \varrho_1(v) &= 4\pi (vm)^2 m (2\pi m k_B T)^{-3/2} \exp\left(-\frac{mv^2}{2k_BT}\right).
\end{aligned}$$

So we found the Maxwell distribution

$$\varrho_1(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_BT}\right). \tag{4.2}$$

We see that we get

$$v_{\max} = \sqrt{\frac{2k_BT}{m}}, \qquad \overline{v} = \sqrt{\frac{8k_BT}{\pi m}}.$$

The distribution is shown in figure (4.1).

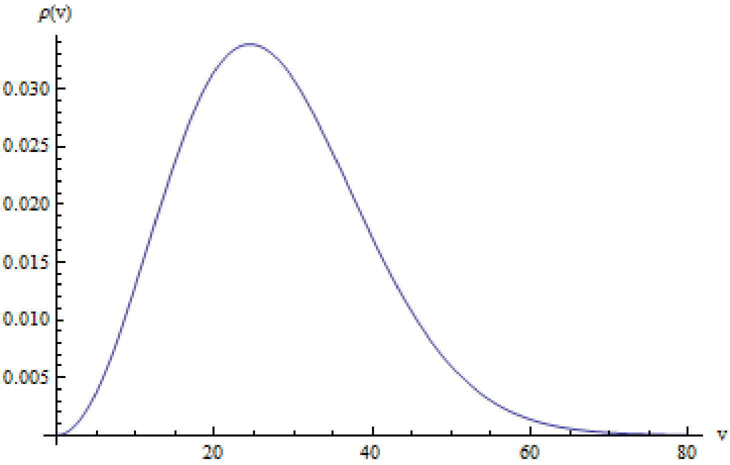


Figure 4.1: Plot of the Maxwell distribution with $k_B = m = 1$ at $T = 300$.

4.3 Ideal bose and fermi gases; occupation numbers

Consider N identical (nondistinguishable) particles. The system is described by a wavefunction

$$\psi = \psi(\vec{r}_1, ..., \vec{r}_N).$$

- bosons The wavefunction is symmetric with respect to the exchange (swap) of particles

  $$\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \psi(\vec{r}_2, \vec{r}_1, ..., \vec{r}_N) = \psi(\vec{r}_{p_1}, ..., \vec{r}_{p_N}),$$

  with p_i the permuations of particle i, e.g.

  $$(1, 2, 3) \xrightarrow{P} (2, 3, 1) = (p_1, p_2, p_3) \Rightarrow \sigma(P) = +1.$$

  Here $\sigma(P)$ is the sign of the permutation P, defined

$$\sigma(P) = (-1)^{\text{number of permutations}}.$$

- If $\sigma(P) = +1$ we have an even number of permutations, while with $\sigma(P) = -1$ we have an odd number of permutations.
- <u>fermions</u> The wavefunction is antisymmetric with respect to the exchange of two fermions,

$$\psi(\vec{r}_1, ..., \vec{r}_N) = -\psi(\vec{r}_2, \vec{r}_1, ..., \vec{r}_N) = \sigma(P)\psi(\vec{r}_{p_1}, ..., \vec{r}_{p_N}).$$

- <u>algorithm</u>
  - Write down the Hamiltonian for N particles,

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}(\nabla_1^2 + ... + \nabla_N^2)}_{\text{kinetic}} + \underbrace{u(\vec{r}_1, ..., \vec{r}_N)}_{\text{potential}}.$$

  - Solve to get eigenstates ψ_N and energies E_n,

$$\hat{H}\psi_n = E_n\psi_n.$$

  - Symmetrize (antisymmetrize) to get bosonic (fermionic) states.

$$\begin{aligned}\psi_{n,\text{bosons}} &= c_b \sum_P \psi_n(\vec{r}_{p_1}, ..., \vec{r}_{p_N}),\\ \psi_{n,\text{fermions}} &= c_f \sum_P \sigma(P)\psi_n(\vec{r}_{p_1}, ..., \vec{r}_{p_N}).\end{aligned}$$

    The bosonic and fermionic states n have energy E_n. It can happen that $\psi_{n,\text{fermions}} = 0$. Then the corresponding state n does not exist and E_n is absent in the spectrum.

- Now consider ideal bose and fermi gases, in which the particles do *not* interact, $u = 0$,

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + ... + \nabla_N^2).$$

Let $\psi_k(\vec{r})$ be the single-particle wave function,

$$-\frac{\hbar^2}{2m}\nabla^2\psi_k(\vec{r}) = E_k\psi_k(\vec{r}),$$

obtained by solving the single-particle hamiltonian. The *single-particle* energy is ε_k. The quantum numbers of the single particle states are k. A generic N-particle wavefunction (eigenstate of H) can be written as

$$\psi(\vec{r}_1, ..., \vec{r}_N) = \prod_i \psi_{k_i}(\vec{r}_i).$$

The corresponding energy is

$$E = \sum_i \varepsilon_{k_i}.$$

The *boson* wavefunction is

$$\psi_{\text{boson}}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = c_b \sum_P \prod_{i=1}^{N} \psi_{k_i}(\vec{r}_{p_i}).$$

The *fermion* wavefunction is

$$\psi_{\text{fermion}}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = c_f \sum_P \sigma(P) \prod_{i=1}^{N} \psi_{k_i}(\vec{r}_{p_i}).$$

Therefore we can rewrite this with the help of the so called Slater-Determinate,

$$\psi_{\text{fermion}}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(\vec{r}_1) & \dots & \psi_{k_1}(\vec{r}_N) \\ \vdots & \ddots & \vdots \\ \psi_{k_N}(\vec{r}_1) & \dots & \psi_{k_N}(\vec{r}_N) \end{vmatrix}.$$

Example The Pauli-exclusion principle follows directly from this. Consider a single-particle state k and two particles.

$$\begin{aligned} \psi_{k,\text{boson}} &= \psi_k(\vec{r}_1)\psi_k(\vec{r}_2), \quad E = 2\varepsilon_k, \\ \psi_{k,\text{fermion}} &= \frac{1}{\sqrt{2!}}\left(\psi_k(r_1)\psi_k(r_2) - \psi_k(r_2)\psi_k(r_1)\right) = 0. \end{aligned}$$

The state in which two fermions (or more) occupy a single state, does not exist. This is the Pauli-exclusion principle.

Remark The distinction between bosons and fermions is important as long as the single-particle wavefunction overlap. For non-interacting particles, the state is uniquely given by the set of occupation numbers n_k (number of particles occupying the single particle state k),

$$E = \sum_k n_k \varepsilon_k.$$

We have the constraint $N = \sum_k n_k$.

- Grand canonical ensemble treatment. We have

$$\text{bosons } n_k = 0, 1, 2, ..., N, \qquad \text{fermions } n_k = 0, 1.$$

The grand partition function is then

$$Z_G = \sum_{N=0}^{\infty} \sum_{\text{states}} \exp(-\beta E_{\text{state}}(N) + \beta\mu N).$$

With $E_{\text{state}}(N) = \sum_k n_k \varepsilon_k$ we can rewrite this to

$$Z_G = \sum_{N=0}^{\infty} \sum_{\{n_k\}, \sum_k n_k = N} \exp\left(-\beta \sum_k n_k \varepsilon_k + \beta\mu \sum_k n_k\right).$$

Therefore we find that

$$\begin{aligned}
Z_G &= \sum_{N=0}^{\infty} \sum_{\{n_k\},\sum_k n_k=N} \exp\left(-\beta \sum_k (\varepsilon_k - \mu) n_k\right) = \\
&= \sum_{N=0}^{\infty} \sum_{\{n_k\}} \exp\left(-\beta \sum_k (\varepsilon_k - \mu) n_k\right) \delta_{\sum_k n_k, N} = \\
&= \sum_{\{n_k\}} \exp(-\beta \sum_k (\varepsilon_k - \mu) n_k) \underbrace{\sum_{N=0}^{\infty} \delta_{\sum_k n_k, N}}_{=1} = \\
&= \sum_{n_1} \exp(-\beta(\varepsilon_1 - \mu) n_1) \sum_{n_2} \exp(-\beta(\varepsilon_2 - \mu) n_2) \cdots = \prod_k Z_k, \\
Z_k &= \sum_{n_k} \exp(-\beta(\varepsilon_k - \mu) n_k).
\end{aligned}$$

We call Z_k the single-state k grand canonical function.

- Bose-Einstein-statistics Since we have $n_k = 0, 1, 2, \ldots\infty$, we can see by using the geometric series for $\mu < \varepsilon_k$ that we have

  $$Z_k = \sum_{n_k=0}^{\infty} \exp(-\beta(\varepsilon_k - \mu) n_k) = \frac{1}{1 - \exp(-\beta(\varepsilon_k - \mu))}.$$

  So we obtain

  $$Z_G = \prod_k Z_k = \prod_k \frac{1}{1 - \exp(-\beta(\varepsilon_k - \mu))}.$$

  The grand free energy is

  $$\Phi = -k_B T \ln Z_G = k_B T \sum_k \ln(1 - \exp(-\beta(\varepsilon_k - \mu))).$$

  The average number of particles is

  $$\overline{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = \sum_k \frac{1}{\exp(\beta(\varepsilon_k - \mu)) - 1} = \sum_k \overline{n}_k.$$

  Therefore we got the *Bose-Einstein statistics*

$$\overline{n}_k = \frac{1}{\exp(\beta(\varepsilon_k - \mu)) - 1} \equiv n(\varepsilon_k). \tag{4.3}$$

The average occupation of single-particle state k.

- Fermi-Dirac-statistics Here we have $n_k = 0, 1$ which gives us

  $$Z_k = 1 + \exp(-\beta(\varepsilon_k - \mu)).$$

  So the grand canonical function is

  $$Z_G = \prod_k Z_k = \prod_k (1 + \exp(-\beta(\varepsilon_k - \mu))).$$

  The grand free energy is

  $$\Phi = -k_B T \ln Z_G = -kBT \sum_k \ln(1 + \exp(-\beta(\varepsilon_k - \mu))).$$

  The average number of particles is

  $$\overline{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = \sum_k \frac{1}{\exp(\beta(\varepsilon_k - \mu)) + 1} = \sum_k \overline{n}_k.$$

  Therefore we got the *Fermi-Dirac statistics*

  $$\overline{n}_k = \frac{1}{\exp(\beta(\varepsilon_k - \mu)) + 1} \equiv f(\varepsilon_k). \tag{4.4}$$

  The average number of fermions in a single-particle state k is described by this.

4.4 Quantum gases at high temperatures - the classical limit

From the last section we know that

$$n_k = \frac{1}{\exp(\beta(\varepsilon_k - \mu)) \mp 1},$$

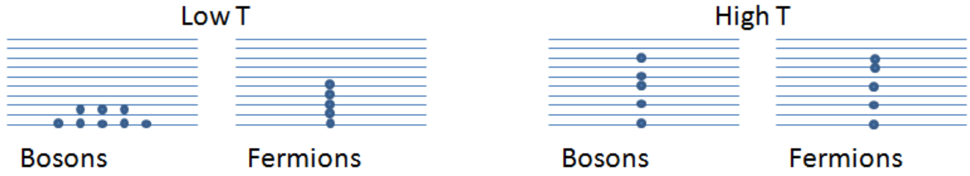


Figure 4.2: Comparison of fermions and bosons at low and high temperatures

with $-$ for bosons and $+$ for fermions. This results in figure 4.2.

We get $n_k \ll 1$ if $\exp(\beta(\varepsilon_k - \mu)) \gg 1$. In this limit we have

$$n_k \approx \exp(-\beta(\varepsilon_k - \mu)). \tag{4.5}$$

This is called the Maxwell-Boltzmann statistics. This is used to describe classical gases. For the average particle number we get

$$\overline{N} = \sum_k n_k = \exp(\beta\mu) \sum_k \exp(-\beta\varepsilon_k) = \exp(\beta\mu) Z_1 \quad \Rightarrow \quad \exp(\beta\mu) = \frac{\overline{N}}{Z_1}.$$

Overall we found that

$$n_k = \overline{N} \frac{1}{Z_1} \exp(-\beta\varepsilon_k).$$

Thus the probability that a single-particle energy level ε_k is occupied is given by

$$p_k = \frac{n_k}{\overline{N}} = \frac{1}{Z_1} \exp(-\beta\varepsilon_k). \tag{4.6}$$

Remark Compare this with

$$p_n = \frac{1}{Z} \exp(-\beta E_n).$$

The difference is that the one above is *always* valid and refers to the probability to find the (whole) system in *many particle* state of energy E_n while the one we found only describes one particle states and is only valid in the classical limit.

Question At which physical conditions is the classical limit realized? What is '∞' in $T \to \infty$?

Answer For $n_k \ll 1 \; \forall \varepsilon_k$ we get that

$$\frac{\mu}{k_B T} = \beta\mu \to -\infty.$$

In chapter 4.2 we found for a classical gas

$$\mu = k_B T \ln\left(\frac{\overline{N}}{V}\lambda^3\right).$$

We see that $\mu/k_B T \to -\infty$ if $\lambda^3 \overline{N}/V \ll 1$. Therefore we see that

$$\left(\frac{V}{\overline{N}}\right)^{1/3} \gg \lambda.$$

This can be interpreted when we see that V/N is the volume available for one particle. The classical limit is reduced when the distance between particles is much greater than the thermal de-Broglie wavelength λ. We should note that $\lambda = \lambda(T) \propto 1/\sqrt{T}$.

The summary is shown in a graph, figure 4.3.

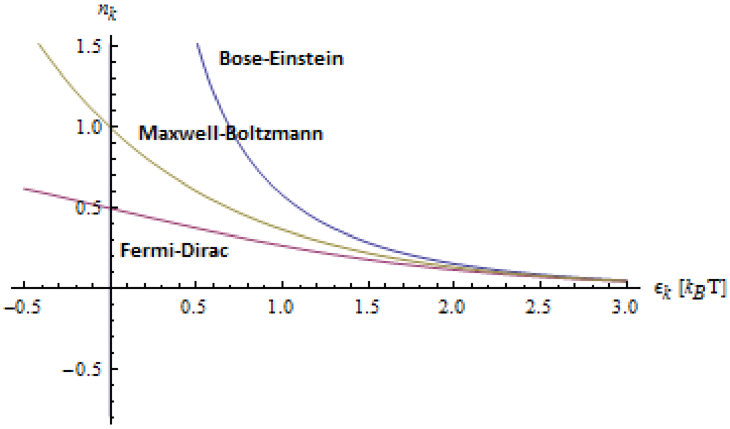


Figure 4.3: Comparison of the most important statistics

4.5 Ideal quantum gases and the maaximum uncertainty principle

Consider levels i of energy ε_i, each g_i degenerate. Let n_i be the occupation number of (all degenerate) levels of energy ε_i. We will now investigate using

$$N = \sum_{\varepsilon_i} n_i, \qquad E = \sum_{\varepsilon_i} \varepsilon_i n_i.$$

1. **Bosons**

   Question In how many ways can we distribute n_i Bosons in g_i states?

   We see that we have n Bosons and $g-1$ seperating walls. Thus we have total $n+g-1$ circles. This results in

   $$\Omega_i = \begin{pmatrix} n_i + g_i - 1 \\ n_i \end{pmatrix}.$$

   This is the number of ways to distribute n_i Bosons in g_i states. For all energy levels we have

   $$\Omega = \prod_{\varepsilon_i} \Omega_i = \prod_{\varepsilon_i} \begin{pmatrix} n_i + g_i - 1 \\ n_i \end{pmatrix}.$$

2. **Fermions**

   Here we have

   $$\Omega_i = \begin{pmatrix} g_i \\ n_i \end{pmatrix}.$$

   Therefore we find for all energy levels

   $$\Omega = \prod_{\varepsilon_i} \begin{pmatrix} g_i \\ n_i \end{pmatrix}.$$

3. **Maxwell-Boltzmann particles**

   Classical, indistinguished particles. There is no correlation between particle occupation.

   - Distinguished particles,

     $$\Omega_i = g_i^{n_i}.$$

- Undistinguished particles,

$$\Omega_i = \frac{g_i^{n_i}}{n_i!} \quad \Rightarrow \quad \Omega = \prod_{\varepsilon_i} \frac{g_i^{n_i}}{n_i!}.$$

4. **Maximum uncertainty principle**

   We will now do the basic calculation for the Bose-Einstein statistics. The calculation for the Fermi-Dirac and Maxwell-Boltzmann statistics is nearly the same.

   Question What is n_i if the entropy should be a maximum, given the two constraints

$$E = \sum_{\varepsilon_i} \varepsilon_i n_i, \qquad N = \sum_{\varepsilon_i} n_i ?$$

   Answer We can do the calculation with the method of Lagrange-multipliers and

$$S = k \ln \Omega.$$

   A variation of this results in

$$\delta\left(S - \lambda_1 \sum_{\varepsilon_i} n_i - \lambda_2 \sum_{\varepsilon_i} \varepsilon_i n_i \right) = 0.$$

   By using $\delta g_i = 0$ (g_i is a constant) and Stirling's approximation we calculate

$$\begin{aligned}
S &= k \ln \Omega = k \ln \prod_{\varepsilon_i} \ln \begin{pmatrix} n_i + g_i - 1 \\ n_i \end{pmatrix} = k \sum_{\varepsilon_i} \ln \begin{pmatrix} n_i + g_i - 1 \\ n_i \end{pmatrix} = \\
&= k \sum_{\varepsilon_i} \left[\ln(n_i + g_i - 1)! - \ln n_i! - \ln(g_i - 1)! \right], \\
\frac{\delta S}{k} &= \sum_{\varepsilon_i} \left(\delta \ln(n_i + g_i - 1)! - \delta \ln n_i! \right) = \\
&= \sum_{\varepsilon_i} \left(\delta((n_i + g_i) \ln(n_i + g_i) - \ln(n_i + g_i)) - \delta(n_i \ln(n_i) - n_i) \right) = \\
&= \sum_{\varepsilon_i} \left(\delta n_i \ln(n_i + g_i) + (n_i + g_i) \frac{n_i + g_i}{\delta} n_i - \delta n_i \right) - \left(\delta n_i \ln n_i + n_i \frac{1}{n_i} \delta n_i - \delta n_i \right) = \\
&= \sum_{\varepsilon_i} \delta n_i \left(\ln(n_i + g_i) - \ln n_i \right) = \sum_{\varepsilon_i} \delta n_i \ln\left(\frac{n_i + g_i}{n_i} \right).
\end{aligned}$$

The extremum problem

$$\begin{aligned} 0 &\overset{!}{=} \delta S - \lambda_1 \sum_{\varepsilon_i} \delta n_i - \lambda_2 \sum_{\varepsilon_i} \varepsilon_i \delta n_i = \\ &= k \sum_{\varepsilon_i} \delta n_i \left(\ln\left(\frac{n_i + g_i}{n_i} \right) - \frac{\lambda_1}{k} - \frac{\lambda_2}{k} \varepsilon_i \right), \end{aligned}$$

can then be solved with the knowledge of

$$\lambda_2 / k = \beta, \qquad \lambda_1 / k = -\beta\mu.$$

Overall we get

$$n_i = g_i \frac{1}{\exp(\varepsilon_i \lambda_2 / k + \lambda_1 / k) - 1} = g_i \frac{1}{\exp(\beta(\varepsilon - \mu)) - 1}.$$

To get the occupation of one of the states g_i divide by g_i. Therefore we found the Bose-Einstein statistics,

$$n_{\text{state of energy } \varepsilon_i} = \frac{1}{\exp(\beta(\varepsilon_i - \mu)) - 1}.$$

4.6 Blackbody radiation

We already know that photons have a wave vector $\vec{k}$ and a polarization λ. We also know that there are two independent polarization states. The photon energy is given by

$$\hbar\omega = \hbar\omega_k = \hbar k c,$$

with the speed of light c.

- Photons are bosons (with spin 1), so they obay the Bose-Einstein statistics.
- The chemical potential of photons is zero ($\mu_\gamma = 0$). The reason for this is the creation and annihilation of photons. Their number is *not* fixed. The average number of photons is determined by T, V. Then we see that

$$F \equiv F(T, V) \quad \Rightarrow \quad \mu = \left(\frac{\partial F}{\partial N}\right) = 0.$$

Another (alternative) explenation will be given in the recitation class.

- Photon-statistics:

$$n_k = \sum_{\lambda} \frac{1}{\exp(\beta\hbar\omega_k) - 1} = \frac{2}{\exp(\beta\hbar\omega_k) - 1}.$$

Question How many photons there are at given frequency ω?

Answer The photon spectral density is

$$\begin{aligned} n(\omega) &= \sum_k n_k \delta(\omega - ck) = \frac{V}{(2\pi)^3} \int d^3k \frac{2}{\exp(\beta\hbar\omega_k) - 1} \delta(\omega - ck) = \\ &= \frac{2V}{(2\pi)^3} 4\pi \int dk k^2 \frac{1}{\exp(\beta\hbar\omega_k) - 1} \frac{1}{c} \delta\left(\frac{\omega}{c} - k\right) = \\ &= \frac{V}{\pi^2 c^3} \frac{\omega^2}{\exp(\beta\hbar\omega) - 1}. \end{aligned}$$

So we get the number of photons of frequencies in $[\omega, \omega + d\omega]$ in a box of volume V,

$$n(\omega) d\omega = \frac{V}{\pi^2 c^3} \frac{\omega^2}{\exp(\beta\hbar\omega) - 1} d\omega.$$

- Historically important is the spectral energy density, $u(\omega)$ per unit volume, defined as

$$V u(\omega) d\omega = \hbar\omega n(\omega) d\omega.$$

This is the equation known as Planck's law,

$$u(\omega) = \frac{1}{\pi^2 c^3} \frac{\hbar\omega^3}{\exp(\hbar\omega / k_B T) - 1}. \tag{4.7}$$

Therefore the shape of $u(\omega)$ depends only on T! This is a way to measure T very precise. The general shape is shown in figure 4.4.

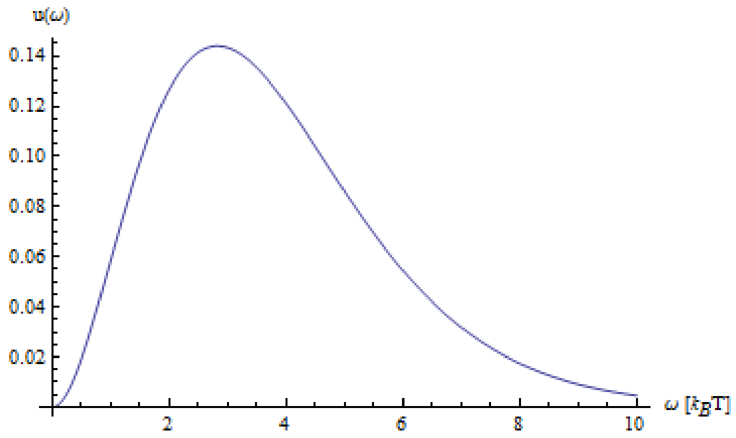


Figure 4.4: Planck's law for $c = \hbar = 1$ with ω in units for $k_B T$

- A black body absorbs all radiation and emits according to Planck's law.
- The number of photons is calculated by

$$\begin{aligned}
\overline{N} &= \int_0^\infty n(\omega) d\omega = \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\omega^2}{\exp(\beta\hbar\omega) - 1} d\omega = \\
&= \left| \begin{array}{c} x = \beta\hbar\omega \\ dx = \beta\hbar d\omega \end{array} \right| = \frac{V}{\pi^2 c^3} \frac{1}{(\beta\hbar)^3} \underbrace{\int_0^\infty \frac{x^2 dx}{\exp(x) - 1}}_{\approx 2.404} = \\
&= 2.404 \frac{V}{\pi^2} \left(\frac{k_B T}{c\hbar} \right)^3 \propto T^3.
\end{aligned}$$

- Total radiated energy is then

$$\begin{aligned}
E &= \int_0^\infty V u(\omega) d\omega = \frac{V}{\pi^2 c^3} \hbar \int_0^\infty \frac{\omega^3}{\exp(\beta\hbar\omega) - 1} d\omega = |x = \beta\hbar\omega| = \\
&= \frac{V\hbar}{\pi^2 c^3} \frac{1}{(\beta\hbar)^4} \underbrace{\int_0^\infty dx \frac{x^3}{\exp(x) - 1}}_{= \pi^4/14} = \frac{V\hbar}{\pi^2 c^3} \frac{(k_B T)^4}{\hbar^4} \frac{\pi^4}{15} = \\
&= \frac{4}{c} \sigma V T^4 \propto T^4, \\
\sigma &= \frac{c}{4} \frac{1}{\hbar^3} \frac{1}{\pi^2 c^3} k_B^4 \frac{\pi^4}{15} = \frac{1}{60} \frac{\pi^2 k_B^4}{\hbar^3 c^2}.
\end{aligned}$$

We call σ the Stefan-Boltzmann constant.

4.7 Bose-Einstein condensation (BEC)

Consider bosons of mass m (real atoms) of energy $\varepsilon_k = \hbar^2 k^2/2m$. The number of bosons is given by

$$N = \sum_k \frac{1}{\exp(\beta(\varepsilon_k - \mu)) - 1}.$$

Remark We can calculate

$$\sum_k f(\varepsilon_k) \to \frac{V}{(2\pi)^3}\int d^3k f(\varepsilon_k) = \frac{V}{(2\pi)^3}\int d\varepsilon \int d^3k \delta(\varepsilon - \varepsilon_k).$$

So we see that this is

$$\int d\varepsilon g(\varepsilon) f(\varepsilon), \quad g(\varepsilon) = \frac{V}{(2\pi)^3}\int d^3k\delta(\varepsilon - \varepsilon_k) = \frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\sqrt{\varepsilon}.$$

Then we get

$$N = \sum_k n_k = \int_0^\infty d\varepsilon n(\varepsilon) g(\varepsilon) = \frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{\exp(\beta(\varepsilon - \mu)) - 1}.$$

We get $\mu < 0$ because μ has to be smaller than the smallest ε, which is $\varepsilon = 0$.

- The maximum number of bosons corresponds to $\mu = 0$. We calculate

$$\begin{aligned} N_{\text{max}}^{\text{cont}} &= \frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{\exp(\beta\varepsilon) - 1} = |\beta\varepsilon = x| = \\ &= V\left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^3 \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\sqrt{x}}{\exp(x) - 1}dx = \\ &= \left(\frac{V}{\lambda^3}\right)\frac{2}{\sqrt{\pi}}\underbrace{\int_0^\infty \frac{\sqrt{x}}{\exp(x) - 1}}_{=\zeta(3/2)\Gamma(3/2)} \approx 2.612\left(\frac{V}{\lambda^3}\right). \end{aligned}$$

  Here we have a problem by using the integral instead of the sum. We forget about the first (ground) state. We get $g(0) = 0$ - but we know that there is 1 state. We can fix this problem by using

$$N = N_{\varepsilon=0} + N^{\text{cont}}.$$

So this one is fixed at T, μ. $N_{\varepsilon=0}$ is the number of bosons at the lowest energy state, $k = 0$ and $\varepsilon = 0$. We see that

$$\frac{N^{\text{cont}}_{\text{max}}}{V} = \frac{2.612 \text{ particles}}{\text{thermal de-Broglie value}}.$$

The temperature at which the lowest state is populated is called T_C, critical temperature. We see that

$$\begin{aligned} N^{\text{cont}}_{\text{max}}(T_C) &= N, \\ \Rightarrow 2.612 \cdot \left(\frac{V}{\lambda^3}\right) &= N \quad \Rightarrow \quad k_B T_C = \frac{\hbar^2}{2\pi m}\left(\frac{N}{2.612 V}\right)^{2/3}. \end{aligned}$$

At $T = T_C$ we speak of the BEC.

Question What is the number of atoms in $\varepsilon = 0$ level?

Answer We see that

$$\frac{N^{\text{cont}}_{\text{max}}}{V} = \frac{N_{\varepsilon>0}}{V} = \frac{N}{V}\left(\frac{T}{T_C}\right)^{3/2}.$$

Therefore we can calculate that

$$\frac{N_{\varepsilon=0}}{V} = \frac{N}{V}\left(1 - \left(\frac{T}{T_C}\right)^{3/2}\right).$$

The relative number of particles is illustrated in figure 4.5.

4.8 Vibrations in solids (phonon gas)

1. **Einstein's model**

   Atoms are connected to a spring of frequency ω. The energy of the spring is given by

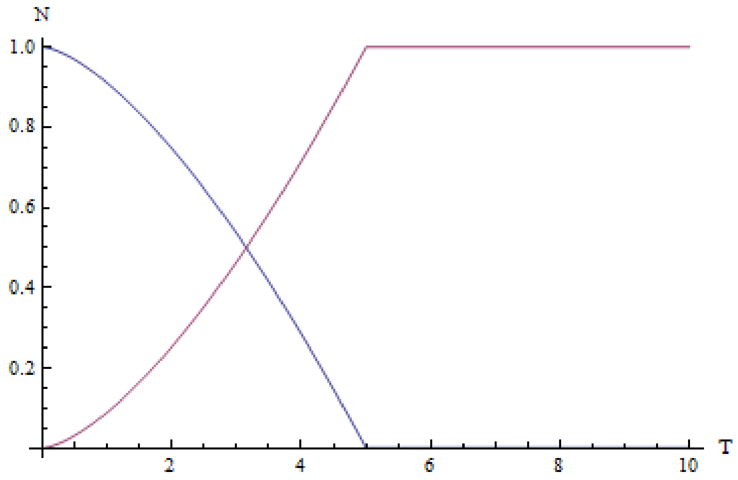


Figure 4.5: The relative number of particles for $N_{\varepsilon=0}$ (blue) and $N_{\varepsilon>0}$ (red)

$$\varepsilon = \hbar\omega\left(n + \frac{1}{2}\right).$$

The average energy for one such oscillator is

$$\overline{\varepsilon} = \hbar\omega\left(\overline{n} + \frac{1}{2}\right), \qquad \overline{n} = \frac{1}{\exp(\beta\hbar\omega) - 1},$$

given by the Bose-Einstein statistics for quantized vibrations. Atomic vibrations are bosons with $\mu = 0$.

- There are N atoms. There are then $3N$ independent oscillators. The internal energy of Einstein's solid is

$$\overline{E} = 3N\hbar\omega\left[\frac{1}{\exp(\beta\hbar\omega) - 1} + \frac{1}{2}\right].$$

- The heat capacity is

$$c_V = \left(\frac{\partial\overline{E}}{\partial T}\right)_V = \frac{\partial\beta}{\partial T}\frac{\partial\overline{E}}{\partial\beta} = 3N\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp(\beta\hbar\omega)}{(\exp(\beta\hbar\omega) - 1)^2} k_B.$$

- For large T with $k_B T \gg \hbar\omega$ we get that

$$c_V = 3Nk_B = 6\frac{1}{2}k_B N.$$

Therefore $6N$ times equipartition theorem value. So 6 quadratic degrees of freedom. This is the classical result.

- For low T with $k_B T \ll \hbar\omega$ we get that

$$c_V = 3Nk_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \exp(-\beta\hbar\omega) \rightarrow_{T\to 0} 0.$$

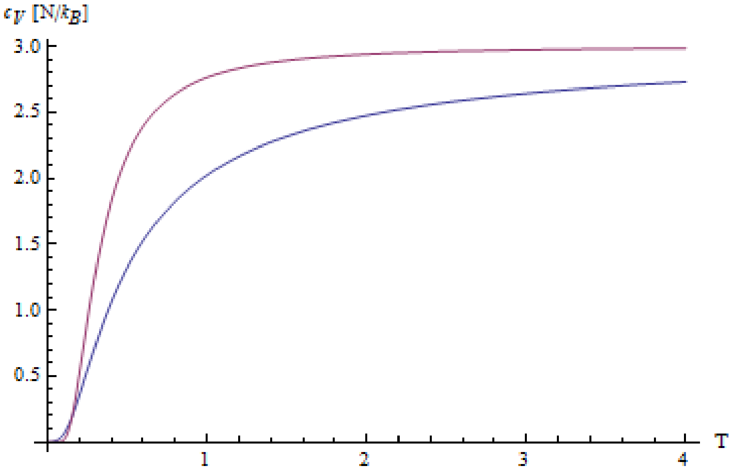


Figure 4.6: Einstein's model (red) in comparison to experiment to a.u. (blue)

Remark If there are conduction electrons present in a solid at a very low T, we have $c_V \propto T$. For insulators we have $c_V \propto T^3$ for low T.

2. **Debye model**

   The atoms are connected by springs. The dynamics decomposes to that of $3N$ normal modes (phonons), plane waves. These are characterized by momentum $\vec{k}$ and polarization λ. There are 3 polarizations: 2 transversal and 1 longitudinal.

   - The spectrum is given by

$$\omega_{k\lambda} = v_\lambda k \quad \Rightarrow \quad \begin{cases} \omega_{kt} &= v_t k \\ \omega_{kl} &= v_l k \end{cases} .$$

   Typically we have $v_l > v_t$ with $v \approx 10^3 - 0^4$ m/s.

   - The density of states is

$$\begin{aligned}
g(\omega) &= \sum_{k,\lambda} \delta(\omega - \omega_{k\lambda}) = \frac{V}{(2\pi)^3} \sum_{\lambda} \int d^3\vec{k}\delta(\omega - v_\lambda k) = \\
&= \frac{V}{(2\pi)^3} \sum_{\lambda} 4\pi \int_0^\infty dk k^2 \frac{1}{v_\lambda} \delta\left(\frac{\omega}{v_\lambda} - k\right) = \\
&= \frac{V}{2\pi^2} \sum_{\lambda} \frac{\omega^2}{v_\lambda^3} = \frac{V\omega^2}{2\pi^2} \underbrace{\left(\frac{1}{v_t^3} + \frac{1}{v_t^3} + \frac{1}{v_l^3}\right)}_{\equiv 3/v_s^3} = \frac{V\omega^2}{2\pi^2} \frac{3}{v_s^3}.
\end{aligned}$$

So we found that

$$g(\omega) \propto \omega^2. \tag{4.8}$$

- The total number of phonons is given by

$$3N = \int_0^{\omega_D} d\omega g(\omega) = \frac{V}{2\pi^2} \frac{3}{v_s^3} \int_0^{\omega_D} \omega^2 d\omega, \qquad \omega_D = \left(6\pi^2 \frac{N}{V} v_s^3\right)^{1/3},$$

with the Debye frequency ω_D, which is the maximum allowed frequency.

- The internal energy is

$$\begin{aligned}
\overline{E} &= \int_0^{\omega_D} d\omega \frac{\omega^3}{\exp(\beta\hbar\omega) - 1} = \left| \begin{array}{l} \beta\hbar\omega = x \\ d\omega = \frac{dx}{\beta\hbar} \end{array} \right| = \\
&= \frac{V}{2\pi^2} \frac{3\hbar}{v_s^3} \left(\frac{1}{\beta\hbar}\right)^4 \int_0^{\beta\hbar\omega_D} dx \frac{x^3}{\exp(x) - 1} = \\
&= \left| v_s^3 = \frac{V}{3N} \frac{1}{2\pi^2} \omega_D^3 \right| = 9Nk_BT \left(\frac{k_BT}{\hbar\omega_D}\right)^3 \int_0^{\frac{\hbar\omega_D}{k_BT}} dx \frac{x^3}{\exp(x) - 1} = \\
&= \left| T_D = \frac{\hbar\omega_D}{k_B} \right| = 9Nk_BT \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} dx \frac{x^3}{\exp(x) - 1}.
\end{aligned}$$

We call T_D the Debye temperature.

- For high temperatures $T \gg T_D$ we get

$$\int_0^{T_D/T \ll 1} dx \frac{x^3}{\exp(x) - 1} \approx \int_0^{T_D/T} dx \frac{x^3}{x} = \frac{1}{3} \left(\frac{T_D}{T}\right)^3.$$

Therefore we calculate that $\overline{E} \approx 3Nk_BT$ and thus $c_V \approx 3Nk_B$.

- For low temperatures $T \ll T_D$ we calculate

$$\int_0^{T_D/T \gg 1} dx \frac{x^3}{\exp(x)-1} \approx \int_0^{\infty} dx \frac{x^3}{\exp(x)-1} = \frac{\pi^4}{15}.$$

Therefore we calculate that

$$\begin{aligned} \overline{E}(T \ll T_D) &\approx 3Nk_BT\left(\frac{T}{T_D}\right)^3 \frac{\pi^4}{5} \propto T^4, \\ c_V(T \ll T_D) &\approx \frac{12\pi^4}{5} Nk_B \left(\frac{T}{T_D}\right)^3 \propto T^3. \end{aligned}$$

This is in agreement with the experiment.

4.9 Equipartition theorem, virial theorem, thermodynamics of diatomic gases

1. Equipartition theorem

   Let q_i be generalized coordinates and p_i be generalized momenta. Thermal averages (classical physics only)

$$\overline{q_i \frac{\partial H}{\partial q_i}} = \overline{p_i \frac{\partial H}{\partial p_i}} = k_BT.$$

   Proof on the web of the lecture.

2. Virial theorem

   This follows directly from the equipartition theorem,

$$\dot{q}_i = -\frac{\partial H}{\partial q_i} \quad \Rightarrow \quad \sum_{i=1}^{3N} \overline{q_i \dot{p}_i} = -3Nk_BT.$$

3. Thermodynamics of ideal diatomic gases (H_2, HCl, N_2) at high temperatures

   This is an application of the equipartition theorem. We calculate

$$H = \sum_{i=1}^{3N} a_i p_i^2 + \sum_{i=1}^{3N} b_i q_i^2.$$

Therefore we see that

$$\sum_{i=1}^{3N} p_i \frac{\partial H}{\partial p_i} + q_i \frac{\partial H}{\partial q_i} = 2\sum_{i=1}^{3N} a_i p_i^2 + 2\sum_{i=1}^{3N} b_i q_i^2 = 2H.$$

So overall we have

$$2\overline{H} = 3Nk_BT + 3Nk_BT \quad \Rightarrow \quad \overline{H} = (3N + 3N) \cdot \frac{1}{2} k_B T.$$

For the heat capacity we derive

$$c_V = (3N + 3N) \cdot \frac{1}{2} k_B.$$

Per *quadratic* degree of freedom the heat capacity is $\frac{1}{2}k_B$.

a) Translation: 3,

$$\frac{c_{v,\text{trans}}}{N} = 3 \cdot \frac{1}{2} k_B.$$

b) Rotation: 2,

$$\frac{c_{v,\text{rot}}}{N} = 2 \cdot \frac{1}{2} k_B.$$

The energy of the rotation is given by

$$\varepsilon = \frac{\hbar^2}{2I} l(l+1), \qquad H = \frac{1}{2I}\vec{L}^2,$$

with the moment of inertia I and the orbital momentum quantum number l. Only two rotation freedoms, because in the 3rd one, I is very small. Therefore $\hbar^2/2I \gg$ the disocciation energy. Effectivly two rotational degrees of freedom.

c) Vibrations: 2 (momentum and position),

$$\frac{c_{v,\text{vib}}}{N} = 2 \cdot \frac{1}{2} k_B.$$

The energy of the vibrations are given by

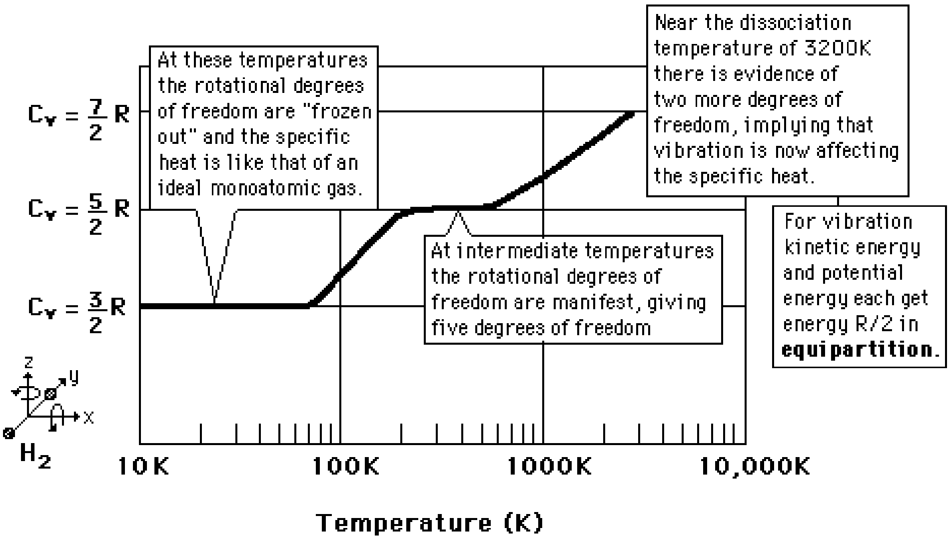
$$\varepsilon = \hbar\omega\left(n + \frac{1}{2}\right).$$

At very very large T we have

$$\frac{c_V}{N} = (3+3+2)\cdot\frac{1}{2}k_B = \frac{7}{2}k_B.$$

Typically vibrations are excited only at very large T, so usually we observe only translation and rotation,

$$\frac{c_V}{N} = \frac{5}{2}k_B. \tag{4.9}$$



At these temperatures the rotational degrees of freedom are "frozen out" and the specific heat is like that of an ideal monoatomic gas.

At intermediate temperatures the rotational degrees of freedom are manifest, giving five degrees of freedom

Near the dissociation temperature of 3200K there is evidence of two more degrees of freedom, implying that vibration is now affecting the specific heat.

For vibration kinetic energy and potential energy each get energy R/2 in **equipartition.**

Figure 4.7: The addition of degrees of freedom with increasing temperatures

4.10 Degenerate Fermi Gas

Electrons in metals, white dwarfs, ^3He, ... We know that ε_F is the largest occupied level at zero temperature and is called Fermi energy. We thus can define T_F, the Fermi temperature through

$$k_B T_F = \varepsilon_F. \tag{4.10}$$

We can analyse three special limits.

1. For $T = 0$ we get

$$f(\varepsilon) = \Theta(\mu - \varepsilon).$$

2. For $T \ll T_F$ with $T > 0$ we get

$$f(\varepsilon) = \frac{1}{\exp(\beta(\varepsilon - \mu)) + 1}.$$

3. For $T \gg T_F$ we see that $\mu \to -\infty$ which leads to

$$f(\varepsilon) \approx \exp(-\beta(\varepsilon - \mu)) \ll 1, \qquad \beta(\varepsilon - \mu) \gg 1.$$

We can see the plots to these limits in figure 4.7. The case of $T \ll T_F$ is the case of degenerate Fermi gas.

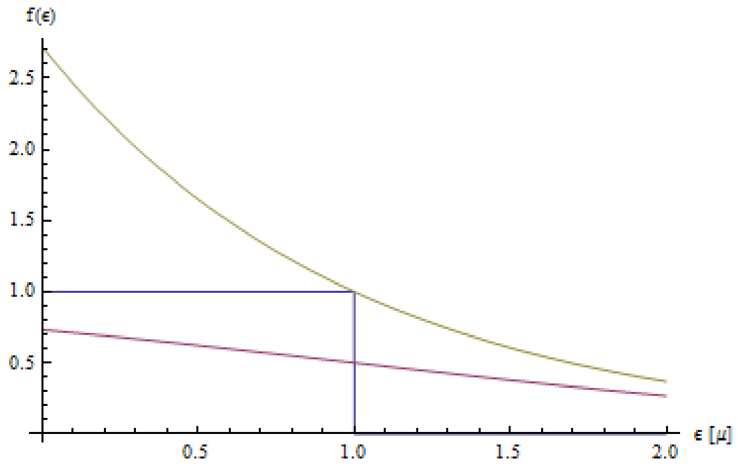


Figure 4.8: $T = 0$ (blue) vs. $T \ll T_F$ (red) vs. $T \gg T_F$ (gold) with $\beta = 1$

Example Electrons in metal have $E_F \approx 10$ eV. Therefore we calculate that

$$T_F = E_F / k_B = 10^5 \text{ K}.$$

So electrons in metals are degenerate fermions. In this section wie deal with degenerate electron gases.

1. **The density of states $g(\varepsilon)$**

   We have $\varepsilon = \hbar^2 k^2/2m$ with a spin degeneracy of $g = 2$. We know that

   $$g(\varepsilon) = 2\frac{V}{(2\pi)^3}\int d^3k\delta(\varepsilon - \varepsilon_k) = 2\frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\sqrt{\varepsilon} \propto \sqrt{\varepsilon}.$$

2. **The chemical potential**

   First we calculate the number of particles with a factor 2 due to the spin degeneracy,

   $$N = 2\sum_k \overline{n}_k = 2\frac{V}{(2\pi)^3}\int d^3k f(\varepsilon_k) = \int_0^\infty d\varepsilon g(\varepsilon) f(\varepsilon).$$

   This equation defines our μ! So we just have to calculate it - which gives us

   $$N = 2\frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\int_0^\infty d\varepsilon\,\sqrt{\varepsilon}\frac{1}{\exp(\beta(\varepsilon-\mu))+1} = 2\frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}I(\mu).$$

   So we can determine the chemical potential using

   $$I(\mu) = \int_0^\infty d\varepsilon\,\sqrt{\varepsilon}\frac{1}{\exp(\beta(\varepsilon-\mu))+1},$$

   and Sommerfeld's expansion (see appendix). We get

   $$I(\mu) \approx \frac{2}{3}\mu^{3/2} + \frac{\pi^2}{6}(k_BT)^2\frac{1}{2}\frac{1}{\sqrt{\mu}} + ...$$

   By inserting this into the number of particles equation we get

   $$N = 2\frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\left[\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{12}(k_BT)^2\frac{1}{\sqrt{\mu}} + ...\right]. \tag{4.11}$$

   For the special case $T = 0$ we get

   $$N = 2\frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\frac{2}{3}(\underbrace{\mu(0)}_{=\varepsilon_F})^{3/2} = 2\frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\frac{2}{3}\varepsilon_F^{3/2}. \tag{4.12}$$

By dividing equation 4.11 through equation 4.12 we obtain

$$1 = \left(\frac{\mu}{\varepsilon_F}\right)^{3/2} + \frac{\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2 \frac{1}{(\mu/E_F)^{1/2}} + ...$$

We can solve this for $\mu = \mu(T)$ by iteration. The lowest order os $\mu \approx \varepsilon_F$. This solution is inserted into the second term on the right. So we get

$$1 = \left(\frac{\mu}{\varepsilon_F}\right)^{3/2} + \frac{\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + ... \quad \Rightarrow \quad \left(\frac{\mu}{\varepsilon_F}\right)^{3/2} = 1 - \frac{\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2.$$

By using $(1+x)^n \approx 1 + nx$ for small x we get that

$$\mu \approx \varepsilon_F \left(1 - \frac{\pi^2}{8}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right)^{2/3} \approx \varepsilon_F \left(1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2\right) < \varepsilon_F.$$

Two other important identites are

$$\begin{aligned} \Gamma(\varepsilon) &= \frac{V}{2(\pi)^3}\frac{4}{3}\pi\left(\frac{2mE}{\hbar^2}\right)^{3/2}, \\ g(\varepsilon) &= \frac{d\Gamma}{d\varepsilon} = \frac{V}{(2\pi)^3}\frac{4}{3}\pi\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}. \end{aligned}$$

3. **Internal energy $\overline{E}$**

   We see that

$$\overline{E} = \int_0^\infty d\varepsilon \varepsilon g(\varepsilon) f(\varepsilon) \approx \frac{3}{5}\left(\frac{\mu}{\varepsilon_F}\right)^{3/2} N\mu \left[1 + \frac{5\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2 + ...\right].$$

   By substituting $\mu = \mu(T)$ from the last subsection we get

$$\overline{E} = \frac{3}{5}N\varepsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + ...\right].$$

   At $T = 0$ we see that $\overline{E}_{T=0} = \frac{3}{5}N\varepsilon_F$.

4. **Heat capacity**

   We calculate

$$c_V = \left(\frac{d\overline{E}}{dT}\right)_V = \frac{3}{5}N\varepsilon_F\frac{5\pi^2}{12}\frac{2k_B^2T}{\varepsilon_F^2} = \frac{\pi^2}{2}Nk_B\left(\frac{k_BT}{\varepsilon_F}\right).$$

Therefore we found that

$$c_V \propto T. \tag{4.13}$$

This is important since phonons are $\propto T^3$ for instance.

1st Remark The Fermi momentum $\hbar k_F$

We can calculate the radius of the Fermi sphere in momentum space and obtain

$$k_F = \left(3\pi^2\frac{N}{V}\right)^{1/3}, \qquad \varepsilon_F = \frac{\hbar^2k_F^2}{2m},$$

where $\hbar k_F$ is the highest momentum of an electron at $T = 0$. We found that

$$\varepsilon_F = \mu(T=0) = \left[\left(\frac{N}{V}\frac{1}{2}\frac{\sqrt{2}\pi^2\hbar^3}{m^{3/2}}\frac{3}{2}\right)^{1/3}\right]^2.$$

Typically $k_F \sim 1/\text{Å}$. Therefore $\lambda_F \sim$ Å.

2nd Remark Physics behind $c_V \propto T$

Many energy levels. With $T \ll T_F$ we have all levels occupied till ε_F. Since k_BT is the thermal energy per particle and the Pauli-exclusion principle does not allow lower electrons to go up with their energy because the upper states are occupied, only electrons of energies k_BT below ε_F can be thermally excited. So

$$N_{\text{excited electrons}} \propto T.$$

The energy of the excited electrons is k_BT/electron. Thus the total change in energy (compared to $T = 0$) is

$$\Delta E \propto T \cdot T = T^2,$$

because the number of electrons is also proportional to T. So overall we found that

$$c_V = \frac{d\Delta E}{dT} \propto T.$$

5 Non-ideal gas

5.1 Virial expansion

We consider a non-ideal, which is an interacting gas.

- Assume pairwise interaction,

$$u_{ij}(\vec{r}) = u(|\vec{r}_i - \vec{r}_j|),$$

  with the distance between i and j being $|\vec{r}_i - \vec{r}_j|$.

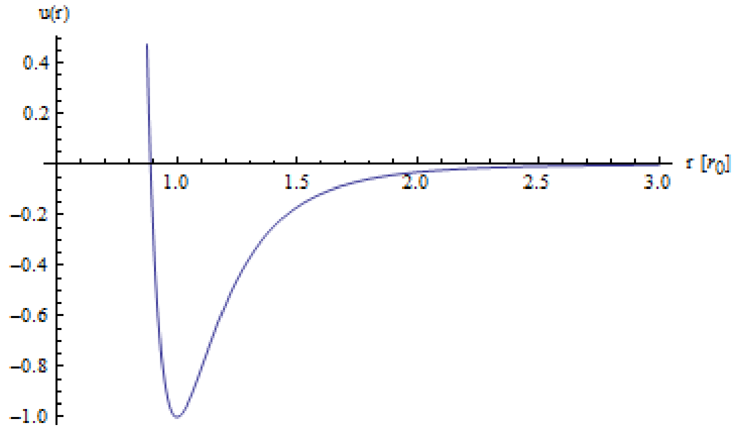


Figure 5.1: Typical potential with a strong repulsion at the beginning and weak attraction in r_0

  We consider weakly interacting systems, *dilute* gases (low density), so that u(typical distance) is much smaller than $k_B T$.

- Note At room temperature $k_B T$ = 25 meV. The total potential energy is

$$U = \sum_{i<j} u_{ij}.$$

The total energy is then

$$H = \frac{p^2}{2m} + U, \qquad p^2 = \vec{p}_1^{\,2} + \vec{p}_2^{\,2} + ... + \vec{p}_N^{\,2}.$$

<u>Task</u> Calculate (as well as possible) Z. We see that

$$\begin{aligned} Z &= \int \frac{dQdP}{h^{3N}N!} \exp(-\beta H) = \int \frac{dQdP}{h^{3N}N!} \exp(-\beta p^2/2m) \exp(-\beta u) = \\ &= \underbrace{V^N \int \frac{dP}{h^{3N}N!} \exp(-\beta p^2/2m)}_{\equiv Z_{id}} \int \frac{dQ}{V^N} \exp(-\beta u) = Z_{id} \int \frac{dQ}{V^N} \exp(-\beta u), \\ Z_{id} &= \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N. \end{aligned}$$

- We need to calculate the exponential function,

$$\begin{aligned} \exp(-\beta U) &= \exp(-\beta \sum_{i<j} u_{ij}) = \prod_{i<j} \exp(-\beta u_{ij}) = \\ &= \prod_{i<j} (1 + \underbrace{\exp(-\beta u_{ij}) - 1}_{\equiv f_{ij} \ll 1}) = \prod_{i<j} (1 + f_{ij}). \end{aligned}$$

We call f_{ij} the Mayer f-function.

- We expand

$$\exp(-\beta u) = (1 + f_{12})(1 + f_{13}) \cdots (1 + f_{N-1,N}) = 1 + \sum_{i<j} f_{ij} + \sum_{i<j} \sum_{k<l} f_{ij} f_{kl} + ...,$$

and continue evalulating

$$Z = Z_{id} \cdot \mathcal{Z} = Z^{(0)} + Z^{(1)} + Z^{(2)} + ... \,.$$

- We see directly that $Z^{(0)} = Z_{id}$. For the first order term we obtain that

$$\begin{aligned} Z^{(1)} &= Z_{id} \int \frac{dQ}{V^N} \sum_{i<j} f_{ij} = Z_{id} \frac{1}{V^N} \frac{N(N-1)}{2} \int d^3\vec{r}_1 d^3\vec{r}_2 \cdots d^3\vec{r}_N f(|\vec{r}_1 - \vec{r}_2|) = \\ &= |N \gg 1| = Z_{id} \frac{1}{V^2} \frac{N^2}{2} \int d^3\vec{r}_1 d^3\vec{r}_2 f(|\vec{r}_1 - \vec{r}_2|) = \\ &= \left|\vec{r} = \vec{r}_1 - \vec{r}_2\right| = Z_{id} \frac{1}{V^2} \frac{N^2}{2} \int d^3\vec{r}_1 \int d^3\vec{r} f(r) = \\ &= Z_{id} \frac{1}{V} \frac{N^2}{2} 4\pi \int dr r^2 f(r). \end{aligned}$$

- If we neglect higher-order terms ($f^2, f^3, ...$) we get

$$Z \approx Z^{(0)} + Z^{(1)} = Z_{id} + Z_{id} \frac{N}{V} 2\pi N \int dr r^2 f(r),$$

or

$$\frac{Z}{Z_{id}} \approx 1 - NnB_2, \qquad B_2 = -2\pi \int dr r^2 f(r),$$

with $n = N/V$ and the second virial coefficient B_2. We call $Z = Z^{(0)} + Z^{(1)} + ...$ the virial expansion.

1. Cluster expansion

   Remark We see that Z/Z_{id} is $1 - NnB_2$. We expected something to be to the power of N - not linear in N. This is a problem, because we want something to be $F \propto \ln Z \propto N$.

   Let us go back:

$$\int \frac{dQ}{V^N} \sum_{i<j} f_{ij} = \frac{1}{2} \frac{N(N-1)}{V^2} \int d^3\vec{r}_1 d^3\vec{r}_2 f_{12}.$$

   Denote this as symbol . The diagrammatic rules to calculate Z/Z_{id} are

   - Number the dots from 1 to n, .

   - For each dot i write

$$\frac{1}{V}\int d^3\vec{r}_i.$$

- Give a factor of $N, N-1, N-2, \ldots$ for dots $1, 2, 3, \ldots$ corresponding.
- Finally divide by the symmetry factor, which is the number of permutations of the diagram leaving the product $f_{ij}f_{kl}$ (or the diagram) unchanged.

Let us look at $O(f^2)$ terms,

$$\int \frac{dQ}{V^N}\sum_{i<j}\sum_{k<l} f_{ij}f_{kl}.$$

There are 2 ways to make the diagrams with 2 links: connected or disconnected.

a) *connected*

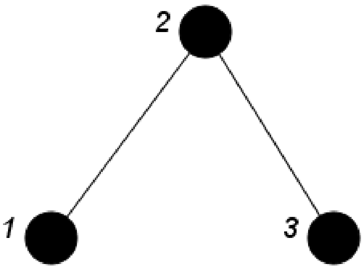


Figure 5.2: The diagram for two connected links

The symmetry factor is 2 because we can only change 1 → 3 in order to get the same diagram again. The integral is then

$$\frac{N(N-1)(N-2)}{2V^3}\int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 f(|\vec{r}_1-\vec{r}_2|)f(|\vec{r}_2-\vec{r}_3|).$$

b) *disconnected*

The symmetry factor is 8 because we can change 1 → 2, 3 → 4 and 12 → 34. The integral is then

$$\frac{1}{8}\frac{N(N-1)(N-2)(N-3)}{V^4}\int d^3\vec{r}_1 d^3\vec{r}_2 d^3\vec{r}_3 d^3\vec{r}_4 f_{12}f_{34} \approx \frac{1}{2}\left(\begin{smallmatrix}\bullet\\ |\\ \bullet\end{smallmatrix}\right)^2.$$

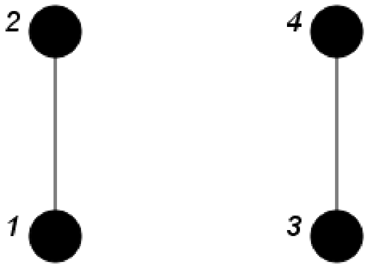


Figure 5.3: The diagram for two disconnected links

If we continued further we would get

$$\frac{Z}{Z_{id}} = 1+ \overset{\bullet}{\underset{\bullet}{|}} + \bullet\!-\!\overset{\bullet}{\underset{\bullet}{|}} + \overset{\bullet}{\underset{\bullet}{|}} \cdot \overset{\bullet}{\underset{\bullet}{|}} + \bullet\!-\!\overset{\bullet}{\underset{\bullet}{|}}\!-\!\bullet +...+ \overset{\bullet}{\underset{\bullet}{|}} \cdot \bullet\!-\!\overset{\bullet}{\underset{\bullet}{|}} + \overset{\bullet}{\underset{\bullet}{|}} \cdot \overset{\bullet}{\underset{\bullet}{|}} \cdot \overset{\bullet}{\underset{\bullet}{|}} +...$$

The is called cluster expansion. We make an approximation ($f \ll 1$) and take a subject of connected diagrams (ireducible diagrams). Then connect them and form higher-order terms, so that they can be cut. We take the simplest, S_1. So we get

$$\frac{Z}{Z_{id}} \approx 1+ \overset{\bullet}{\underset{\bullet}{|}} + \frac{1}{2}\left(\overset{\bullet}{\underset{\bullet}{|}}\right)^2 + \frac{1}{3!}\left(\overset{\bullet}{\underset{\bullet}{|}}\right)^3 + ... = \exp\left(\overset{\bullet}{\underset{\bullet}{|}}\right). \tag{5.1}$$

This is called Dyson equation.

2. <u>The free energy and pressure</u>

We know that $S_1 = -NnB_2$. First we calculate the free energy

$$\begin{aligned} F &= -k_BT\ln\frac{Z}{Z_{id}} + F_{id} \approx F_{id} - k_BT\ln(\exp(S_1)) - F_{id} - k_BT\,\overset{\bullet}{\underset{\bullet}{|}} = \\ &= F_{id} + k_BTNnB_2, \qquad B_2 = -2\pi\int drr^2 f(r). \end{aligned}$$

Now we calculate the pressure,

$$P = -\left(\frac{\partial F_{id}}{\partial V}\right)_{T,N} - k_BTN\left(-\frac{N}{V^2}\right)B_2 = \frac{Nk_BT}{V} + Nk_BTn\frac{B_2}{V}.$$

Therefore we get a correction to the equation of state for gases,

$$\frac{PV}{Nk_BT} = 1 + nB_2. \tag{5.2}$$

5.2 Van-der-Waals equation

Let the potential be

$$u(r) = \begin{cases} \infty, & r < r_0 \\ -\frac{c}{r^m}, & r > r_0 \end{cases}.$$

We calculate the second virial coefficiant,

$$\begin{aligned}
B_2 &= -2\pi \int_0^\infty dr r^2 f(r) = -2\pi \int_0^\infty dr r^2 (\exp(-\beta u) - 1) = \\
&= -2\pi \int_0^{r_0} dr r^2 (\exp(-\infty) - 1) - 2\pi \int_{r_0}^\infty dr r^2 (1 - \beta u - 1) = \\
&= \underbrace{2\pi \frac{1}{3} r_0^3}_{\equiv b} + \frac{1}{k_B T} \underbrace{2\pi \int_{r_0}^\infty dr r^2 \left(-\frac{c}{r^m}\right)}_{\equiv -a} = \\
&= b - \frac{a}{k_B T}.
\end{aligned}$$

Then

$$\begin{aligned}
\frac{PV}{N k_B T} &= 1 + nb - \frac{na}{k_B T} \approx \frac{1}{1 - nb} - n \frac{a}{k_B T}, \\
P &\approx N k_B T \frac{1}{V} \left(\frac{1}{1 - nb} \right) - N k_B T \frac{1}{V} \frac{N}{V} \frac{a}{k_B T}.
\end{aligned}$$

So we obtain the Van-der-Waals equation,

$$(P + an^2)(V - Nb) = N k_B T. \tag{5.3}$$

We call Nb the exclusion volume and say that an^2 is the pressure from the attrative long distance force.

6 Thermodynamics

6.1 Work and pressure

We consider a box with a volume V which can be compressed by a pisten moving dx with the area A. So we get $V \to V + dV$,

$$dV = -Adx.$$

The work done by the pisten on the gas is

$$dW = Fdx = PAdx = -PdV.$$

Remark The work by the gas is $+PdV$.

- In going from thermodynamic state 1 to 2 the work done on the system is

  $$W = -\int_1^2 PdV.$$

  Assumption: Such (and similar) formula hold for *quasistatic* processes only. Quasistatic means *very very slow*. That is slower than the relaxation in the system. The system is (close to) in equilibrium.

- Important: dW is the infinitesimal work - this is not an exact differential. Sometimes dW is written as $\text{đ}W$.

- Exact differential df performs like

  $$\int_1^2 df = f(2) - f(1) \quad \Rightarrow \quad \int_1^1 df = 0.$$

- Imperfect differential dg performs like

$$\int_1^1 dg \neq 0.$$

  The integration of $\int_1^2 dg$ depends on the *path* from 1 to 2.

- Example: Let $f(x,y) = xy$. So we see that $df = ydx + xdy$ is an exact differential. If we now just take $dg = ydx$ we get this imperfect differential.

$$\int_{(0,0)}^{(1,1)} dg = \begin{cases} 1/2, \\ 0, \end{cases}$$

  if the first way is $x = y$ (straight line) and the second way is from the x-axis to the y-axis (y is zero for the first part).

- Functions f whose infinitesimal df is an exact differential are called <u>state functions</u>. Popular examples are E, S, F. State functions depend on the *state*, not on the *path*. Example: Ideal gas at constant T. If we change the volume from $V_1 \to V_2$,

$$W = -\int_1^2 PdV = -\int_{V_1}^{V_2} PdV = \left| \begin{array}{c} PV = Nk_BT, \\ P = \frac{Nk_BT}{V} \end{array} \right| = -Nk_BT \ln\left[\frac{V_2}{V_1}\right].$$

6.2 The first law of thermodynamics

Energy conservation in form of

$$dE = dQ + dW.$$

In this case dE is the increase of internal energy ($E, \overline{E}, U$) of the system, dQ is the amount of heat added <u>to</u> the system and dW is the amount of work done <u>on</u> the system.

- $dE = dQ - PdV$ is an exact differential. Therefore dQ must be an imperfect differential (since PdV is an imperfect differential). The dimension of energy is Joule [J]. The dimension of *thermal energy on the move* (heat) is also Joule, but more often it is given in calories,

$$1 \text{ cal} = 4.186 \text{ J}.$$

One calory is the amount of energy needed to raise the temperature of 1 g of water from 14.5 °C to 15.5 °C. The food industry also introduced

$$1 \text{ Cal} = 4186 \text{ J} = 1000 \text{ cal} = 1 \text{ kcal}.$$

- Some terminology is needed for many processes.
    - **adiabatic** process: $dQ = 0$.
    - **isentropic** system - adiabatic and quasistatic - $dS = 0$.
    - **isothermal** system has $dT = 0$.
    - **isobaric** system has $dP = 0$.
    - **isochoric** system has $dV = 0$.
    - Extensive quantities depend on the size of the system ($\propto N$) - like $E, S, F, V, N, ...$, while intensive quantities donot depend on the size like $T, P, \mu, n = N/V, ...$

6.3 Enthalpy and heat capacities

We know that

$$dQ = dE + PdV.$$

For the heat capacity we calculated

$$c = \left(\frac{dQ}{dT}\right)_{\text{process}}.$$

We also saw that

$$c_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dE}{dT}\right)_V.$$

Experimentally it is easier to measure

$$c_P = \left(\frac{dQ}{dT}\right)_P .$$

We get to this point by doing a simple Legendre-Transformation,

$$dQ = dE + PdV = dE + d(PV) - VdP = d(E + PV) - VdP = dH - VdP.$$

We call H the enthalpy,

$$H = E + PV, \qquad c_P = \left(\frac{dH}{dT}\right)_P . \tag{6.1}$$

Example: Ideal gas with $E = \frac{3}{2}Nk_BT$, $PV = Nk_BT$ gives us

$$H = \frac{5}{2}Nk_BT, \qquad c_V = \frac{3}{2}Nk_B, \qquad c_P = \frac{5}{2}Nk_B.$$

So we do see that $c_V > c_P$. This relation is always given.

6.4 Second law of thermodynamics

Ireversibility: There exists a state function, called entropy S, such that in an isolated system $\Delta S \geq 0$.

- In a quasistatic process, $dS = dQ/T$, or $S(2) - S(1) = \int_1^2 dQ/T$, with dS being an *exact* differential. Therefore dQ/T is an exact differential, which is quite remarkable. Since S is a state function we see that $S \equiv S(E, V, N)$ like in the microcanonical ensemble (in the thermodynamic limit all ensembles are the same). So we get

  $$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV,$$

  with N being constant and not considering variations with N for simplicity. The first law then states that

  $$dE = dQ - PdV \quad \Rightarrow \quad \frac{dS}{(\partial S/\partial E)_V} = dQ \quad \Rightarrow \quad dQ\left(\frac{\partial S}{\partial E}\right)_V = \frac{dQ}{T}.$$

- The entropy is extensive:

$$S_{A+B} = S_A + S_B.$$

- The heat flows from a hotter to a cooler object. Consider two systems A, B connected. $T_A > T_B$ and $\Delta Q_A = -\Delta Q_B$. So we calculate

$$\Delta S_{A+B} = \Delta S_A + \Delta S_B = \frac{\Delta Q_A}{T_A} + \frac{\Delta Q_B}{T_B} = \Delta Q_B \underbrace{\left(\frac{1}{T_B} - \frac{1}{T_A}\right)}_{\geq 0} \geq 0.$$

  Therefore we see that ΔQ_B must be greater than zero - which means that the heat does indeed only flow from a hotter to a cooler object.

- Removing internal constraints lead in general to entropy increase. This also causes some irritations because we can show that from the SEQ we can see that in the microscopic context $dS/dt = 0$. But according to the second law $dS/dt \geq 0$. Therefore from microscopic to macroscopic something happens (the reason for this is still unknown - this is why it is called a law). Things are ireversible.

6.5 Third law of thermodynamics

At the limit $T \to 0$ we must have $c_V(T) \to 0$.

Remark As $T \to 0$, S goes to zero or a finite number so that $S/N \to 0$. Classical ideal gas does not follow the third law of thermodynamics, because c_V is a constant. This is fixed for Fermi and Bose gases.

6.6 Free energies

- 1st law: $dE = TdS - PdV + \mu dN$, with the new term μdN. There μ is the energy the system gains when a particle is added to it, keeping V and S constant.

  Remark Since for bosons $\mu < 0$ (if $\varepsilon_k > 0$), if bosons can be created, $\mu \to 0$ otherwise the energy would be decreased to $-\infty$ (by producing ∞ bosons).

- 2nd law: $\Delta S \geq 0$. Therefore in equilibrium S has its maximum (maximum uncertainty).

1. Helmholtz free energy F

   Consider a system in contact with a reservoir. We have V, N fixed, but the energy can be exchanged,

   $$\Delta E + \Delta E_R = 0,$$

   because the whole system is isolated. In this notation ΔE is for the system and ΔE_R for the reservoir. But the 2nd law states that

   $$\Delta S + \Delta S_R \geq 0.$$

   Since the reservoir is not affected we have $\Delta E_R = T \cdot \Delta S_R$ (from the 1st law). This brings us to

   $$\Delta S_R = \frac{1}{T}\Delta E_R = -\frac{1}{T}\Delta E.$$

   Then we have

   $$\Delta S + \Delta S_R = \frac{1}{T}\left(T\Delta S - \Delta E\right) \geq 0.$$

   As $T > 0$ we find that

   $$\Delta E - T\Delta S = \Delta F \leq 0.$$

   We found the Helmholtz free energy F,

   $$F(T, V, N) = E - TS. \tag{6.2}$$

   From the 2nd law we see that for a system in contact with reservoir, fixed T, V, N $\Delta F \leq 0$. Therefore in equilibrium F has a minimum.

2. G, H, Φ

   In the same way we can show that if the system is in contact with a reservoir for fixed T, P, N we get the Gibbs free energy G,

$$G(T, P, N) = E - TS + PV. \tag{6.3}$$

We see directly that G reaches minimum, $\Delta G \leq 0$. For S, P, N we get the Enthalpy H,

$$H(S, P, N) = E + PV. \tag{6.4}$$

Again H reaches the minimum with $\Delta H \leq 0$. Finally we get the Grand Potential Φ which reaches the minimum as well ($\Delta\Phi \leq 0$) for T, V, μ,

$$\Phi(T, V, \mu) = F - \mu N. \tag{6.5}$$

Legendre transformation

Take $f(x_1, ..., x_n)$ with $df = \sum_i u_i dx_i$, $u_i = \left(\frac{\partial f}{\partial x_i}\right)_{x_j}$. Now consider

$$g = f - \sum_{i=r+1}^{n} u_i x_i, \qquad dg = \sum_{i=1}^{n} u_i dx_i - \sum_{i=r+1}^{n} du_i x_i - \sum_{i=r+1}^{n} u_i dx_i.$$

This gives us

$$dg = \sum_{i=1}^{r} u_i dx_i - \sum_{i=r+1}^{n} x_i du_i \quad \Rightarrow \quad g \equiv g(x_1, ..., x_r, u_{r+1}, ..., u_n).$$

We say that (u, x) are conjugate variables.

Different free energies are connected by Legendre transformation. An example would be:

$$S = S(E, V, N), \qquad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}.$$

Thus (T^{-1}, E) are conjugate variables. We perform the Legendre transformation and obtain

$$S - \frac{1}{T}E = -\frac{1}{T}(E - TS) = -\frac{F}{T}.$$

6.7 Maxwell's relations

Take $\left(\frac{\partial S}{\partial V}\right)_{T,N}$ for instance. First find out which free energy (potential) has T, V, N as natural variables? We see that this is the Helmholtz free energy F with the differential $dF = -SdT - PdV + \mu dN$. Now we use the permutation of the second derivative and obtain

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial^2 F}{\partial T \partial V}\right) = \left(\frac{\partial^2 F}{\partial V \partial T}\right) = \left(\frac{\partial P}{\partial T}\right)_{V,N}.$$

This is a Maxwell's relation. Another example would be $\left(\frac{\partial S}{\partial P}\right)_{T,N}$. Here the potential would be $dG = -SdT + VdP + \mu dN$. We obtain

$$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}.$$

We can use this to investigate the **relation between** c_V **and** c_P. For this we fix N. We get

$$c_P = T\left(\frac{\partial S}{\partial T}\right)_P, \qquad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV.$$

By taking the derivate we obtain

$$\underbrace{\left(\frac{\partial S}{\partial T}\right)_P}_{\frac{1}{T}c_P} = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}_{\frac{1}{T}c_V} + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P}_{\text{Maxwell}}.$$

By using Maxwell's relations we get

$$\frac{1}{T}c_P = \frac{1}{T}c_V - \left(\frac{\partial P}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2.$$

We now define two important variables,

$$\begin{aligned} \kappa_T &\equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{(compressibility)}, \\ \alpha &\equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{(expansibility)}. \end{aligned}$$

We can now write

$$c_P - c_V = V\frac{T}{\kappa_T}\alpha^2 > 0.$$

6.8 Gibbs-Duhem relation

First we need to know something about *homogeneous functions*. Let $f = f(x)$ be such that $f(\lambda x) = \lambda^k f(x)$. Then f is called homogeneous of k-order. We now consider $k = 1$, thus $f(\lambda x) = \lambda f(x)$. By taking the derivative $d/d\lambda$ we see that

$$\frac{f(\lambda x)}{d(\lambda x)}\frac{d(\lambda x)}{d\lambda} \overset{!}{=} f(x) \quad \Rightarrow \quad f(x) = x \cdot \frac{df(x)}{dx}.$$

For n variables we have the famous *Euler relation*,

$$f(x_1, ..., x_n) = \sum_i x_i \left(\frac{\partial f}{\partial x_i}\right)_{x_j}. \tag{6.6}$$

Back to thermodynamics. This is useful for extensive functions, like $E = E(S, V, N)$, e.g. $E(2S, 2V, 2N) = 2E(S, V, N)$. We see that

$$E = \left(\frac{\partial E}{\partial S}\right)_{V,N} S + \left(\frac{\partial E}{\partial V}\right)_{S,N} V + \left(\frac{\partial E}{\partial N}\right)_{S,V} N.$$

From the 1st law we already know that $E = TS - PV + \mu N$. But since the differential of the from the Euler's equation obtained function is

$$dE = dTS + TdS - dPV - PdV + d\mu N + \mu dN \overset{!}{=} TdS - PdV + \mu dN,$$

we see directly that

$$SdT - VdP + Nd\mu = 0. \tag{6.7}$$

This is the Gibbs-Duhem relation. Applications of this equation would be

$$G = E_T S + PV = TS - PV + \mu N - TS + PV = \mu N, \qquad \Phi = E - TS - \mu N = -PV.$$

So overall we can see that

$$G = \mu N, \qquad \Phi = -PV. \tag{6.8}$$

6.9 Conditions for thermodynamic equilibrium and stability

From the 2nd law we know that when E, V, N are constant we have $\Delta S \geq 0$. Therefore S has a maximum in equilibrium.

1. Principal of minimal E at S, V, N, constant Removing the constraint at fixed E leads to $\Delta S(E) \geq 0$. Put the system in contact with reservoir, such that E can change, but S is kept constant. So $\Delta S(E + \Delta E)$. A Taylor expansion gives us

   $$\Delta S(E) + \left(\frac{\partial S}{\partial E}\right)_{V,N} \Delta E = 0, \qquad \Delta E = -T\Delta S(E) \leq 0.$$

   So we found that ΔE must be smaller than 0 when we have fixed S, V, N.

   Remark We already know that $E = \sum_i \varepsilon_i p_i$. This gave us

   $$\delta E = \sum_i \delta\varepsilon_i p_i + \sum_i \varepsilon_i \delta p_i,$$

   meaning that we have a work and an entropy part. Therefore the average E at fixed S, V, N has a minimum in equilibrium. This gives us a contrast:

   - Fixed E, V, N: S has maximum.
   - Fixed S, V, N: E has minimum.

   One analogy to this would be a circle with a perimeter. The circle is an object which has for a fixed area a minimum perimeter and for a fixed perimeter a maximum area (Area ↔ entropy, perimeter ↔ energy).

2. Conditions for equilibrium

   We consider S, V, N constant and

$$\begin{aligned} S &= S_A + S_B \quad \Rightarrow \quad \delta S_A = -\delta S_B, \\ V &= V_A + V_B \quad \Rightarrow \quad \delta V_A = -\delta V_B, \\ N &= N_A + N_B \quad \Rightarrow \quad \delta N_A = -\delta N_B. \end{aligned}$$

Removal of an internal constaint in *equilibrium* gives δE, change in energy:

$$\delta E \approx \delta E^{(1)} = (T_A - T_B)\delta S_A - (P_A - P_B)\delta V_A + (\mu_A - \mu_B)\delta N_A = 0,$$

because $E = E(S, V, N)$ has a minimum. In equilibrium we have

- $T_A = T_B$ the thermal equilibrium,
- $P_A = P_B$ the mechanical equilibrium and
- $\mu_A = \mu_B$ the chemical equilibrium.

We call $T = \text{const.}$, $P = \text{const.}$ and $\mu = \text{const.}$ the thermodynamic equilibrium.

Example We consider two connected boxes with $\mu_A > \mu_B$ with particles can be exchanged. We do want to know about the particle flow. We know that V and E are fixed and $\Delta N_A = -\Delta N_B$. Since ΔE is fixed (energy conservation) we see that

$$\Delta E = 0 = T\Delta S + \mu\Delta N \quad \Rightarrow \quad \Delta S = -\frac{\mu}{T}\Delta N.$$

So overall we have

$$\Delta S = \Delta S_A + \Delta S_B = -\frac{\mu_A}{T}\Delta N_A - \frac{\mu_B}{T}\Delta N_B = -\frac{1}{T}(\mu_A - \mu_B)\Delta N_A \geq 0.$$

So we know that ΔN_A must be lower than 0 which gives us the particle flow from A to B. The particles flow from higher to lower μ.

3. Conditions for stability

$E = E(S, V, N)$ should have a minimum in equilibrium. In equilibrium we have

$$(\delta E)_{S,V,N} = 0, \qquad (\delta^2 E)_{S,V,N} \geq 0.$$

Remark This could be a confusion, since the 2nd law of thermodynamics states $\Delta E \leq 0$. But this is only in equilibrium (going into the equilibrium by removing internal constraints). In this case we are looking at spontaneous changes $\delta E \geq 0$, thus going away from equilibrium.

Suppose a gas in equilibrium and a pushable wall between two boxes (spontaneous fluctuation). We say that

- $\delta^2 E > 0$ is stable equilibrium.
- $\delta^2 E = 0$ is a state which cannot decide. We do have to look at higher variations.
- $\delta^2 E < 0$ is unstable equilibrium.

Now consider $\delta N_A = \delta N_B = 0$ and $\delta V_A = \delta V_B = 0$. We also have $\delta S_A = -\delta S_B$. We calculate

$$\begin{aligned}
\delta^2 E &= \delta^2 E_A + \delta^2 E_B = \frac{1}{2}\left(\frac{\partial^2 E_A}{\partial S_A^2}\right)_{V_A,N_A} \delta S_A^2 + \frac{1}{2}\left(\frac{\partial^2 E_B}{\partial S_B^2}\right)_{V_B,N_B} \delta S_B^2 = \\
&= \frac{1}{2}\left[\left(\frac{\partial^2}{E_A}\partial S_A^2\right)_{V_A,N_A} + \left(\frac{\partial^2}{E_B}\partial S_B^2\right)_{V_B,N_B}\right]\delta S_A^2 = \frac{1}{2}\left[\frac{T_A}{c_{V,A}} + \frac{T_B}{c_{V,B}}\right]\delta S_A^2 = \\
&= |T_A = T_B| = \frac{1}{2}T_A\left(\frac{1}{c_{V,A}} + \frac{1}{c_{V,B}}\right)\delta S_A^2 > 0.
\end{aligned}$$

This follow because the partition ration A to B is arbitrary. Therefore we found that $c_V > 0$! We did already know this from chapter **??**.

Consider the Helmholtz free energy $F = F(T, V, N)$. We see that $\delta F = 0$ and $\delta^2 F > 0$ with fixed T, V, N. By looking at $T_A = T_B$ with N_A, N_B fixed and $\delta V_A = -\delta V_B$ we see that

$$\delta^2 F = -\frac{1}{2}\left[\left(\frac{\partial P_A}{\partial V_A}\right)_{T_A,N_A} + \left(\frac{\partial P_B}{\partial V_B}\right)_{T_B,N_B}\right]\delta V_A^2 > 0.$$

So we conclude that $\partial P/\partial V < 0$ for fixed T, N. We see also that $\kappa > 0$ and $c_P > c_V > 0$.

Remark We can partition extensive variables only! For example we cannot say that $T_A + T_B$ is fixed.

7 Phase transitions and critical phenomena

7.1 Phase equilibria

From the Gibbs-Duhem relation $SdT - VdP + Nd\mu = 0$ we get that

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP = -sdT + vdP, \qquad s = S/N, \quad v = V/N.$$

Therefore we conclude that μ is a function of the two variables T, P only, $\mu \equiv \mu(T, P)$. Suppose now that we have ν different phases. A phase can be a gas, liquid or solid etc.

- Question Can different phases coexist (be together) in equilibrium?

  Answer T, P are equal for all phases (μ must be equal) so that

  $$\mu_1(T, P) = \mu_2(T, P) = ... = \mu_\nu(T, P).$$

  So we have $\nu - 1$ equations.

- Define f, the number of degrees of freedom, which is the number of unknown variables minus the number of equations, so

  $$f = 2 - (\nu - 1) = 3 - \nu. \tag{7.1}$$

  This is the so called Gibbs phase rule.

- Discussion
  - For $\nu = 3$ we get $f = 0$ which is a unique solution (T_0, P_0) (triple point or TP). *Three phases can coexist in a point in the (P, T) plane.*

- For $\nu = 2$ we get $f = 1$ which gives us $P \equiv P(T)$ - that specifies a line. *Two phases can coexist along a coexistence line (curve).*

  Remark The strategy to solve $\mu_1(T, P) = \mu_2(T, P)$ is to fix T first and then to get $P(T)$.

- For $\nu = 1$ we get $f = 2$ and thus the whole (P, T) plane. *One phase exists in a plane.*
- For $\nu \geq 4$ we find that *four or more different phases cannot coexist together in a one component system.*
- If the system has r components (types of atoms / molecules) then we have

$$f = 2 + r - \nu. \tag{7.2}$$

  Therefore in a two component system for example we can have 4 phases in a point.

- A generic phase diagram is shown in figure 7.1.

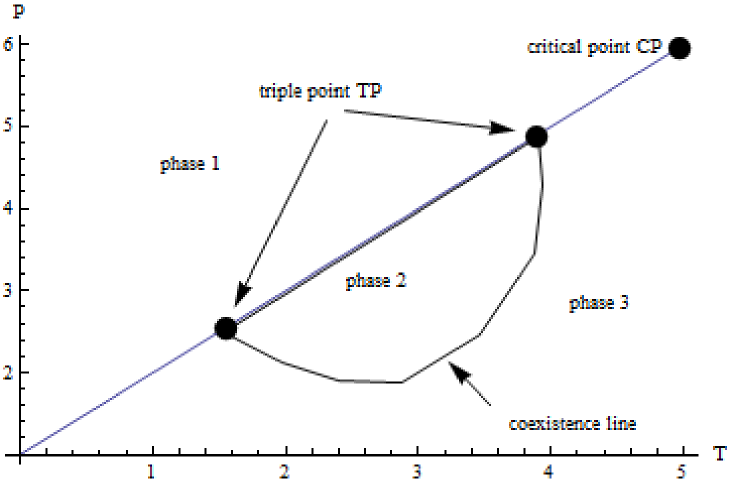


Figure 7.1: A valid phase diagram with three phases, two triple points and a critical point

We can build an invalid phase diagram by having another phase in it, with a point where all phases are combined but having only a one component system. Therefore we do have to look for the intersection of such coexistence lines.

- At the critical point is a phase transition of the 2nd type (continuous). Above the critical point (CP) we cannot distinguish between phases. So by going through a line of coexistence we are able to see the change (e.g. in entropy) but if we go from one phase to the other above the critical point we see not difference between the phases. So for example we would say that water and vapor are the same!

7.2 Abrupt phase transitions - Clausius-Clapeyron equation

We set $G = \mu N$ and consider two phases with G_1 and G_2. We say that

- if $G_1 < G_2$ then phase 1 wins,
- if $G_1 > G_2$ then phase 2 wins and
- if $G_1 = G_2$ then we have $\mu_1 = \mu_2$ and therefore coexistence.

We can draw phase diagram like the graphs in figure 7.2.

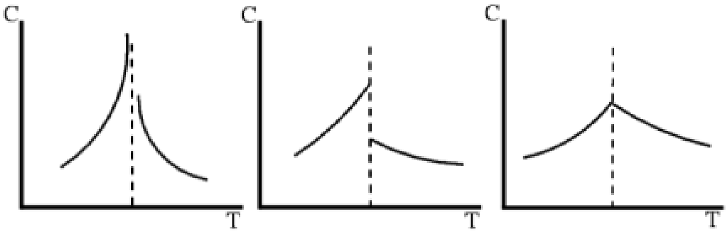


Figure 7.2: Possible graphs of heat capacity (C) against temperature (T) at a phase transition

- We derive that

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} = N\left(\frac{\partial \mu}{\partial P}\right)_T, \qquad v = \left(\frac{\partial \mu}{\partial P}\right)_T.$$

- In the same way we obtain that

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} = -N\left(\frac{\partial \mu}{\partial T}\right)_P, \qquad s = -\left(\frac{\partial \mu}{\partial T}\right)_P.$$

- At the coexistence curve we have a densities change $v_1 \neq v_2$ and latent heat $s_1 \neq s_2$. This is called *abrupt transition*.
- At the critical point we have $v_1 = v_2$ and $s_1 = s_2$. This is why this is called continuous transition (higher derivatives of G are not continuous).
- At the coexistence line we have $\mu_1(T, P) = \mu_2(T, P)$. Along the coexistence line we find $d\mu_1 = d\mu_2$. By using the Gibbs-Duhem relation $d\mu = -sdT + vdP$ we obtain that

  $$d\mu_1 = -s_1 dT + v_1 dP \overset{!}{=} -s_2 dT + v_2 dP = d\mu_2.$$

  This gives us $dP(v_1 - v_2) = dT(s_1 - s_2)$ which leads to the Clausius-Clapeyron equation,

  $$\frac{dP}{dT} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{l}{T}\frac{1}{\Delta v}. \tag{7.3}$$

  We introduced the latent heat of the transition l, with $s_1 - s_2 = \Delta s = l/T$, by using the temperature of the transition T. The solution of this equation is $P \equiv P(T)$, the coexistence curve.
- Typical phase diagrams are shown in figure 7.3.

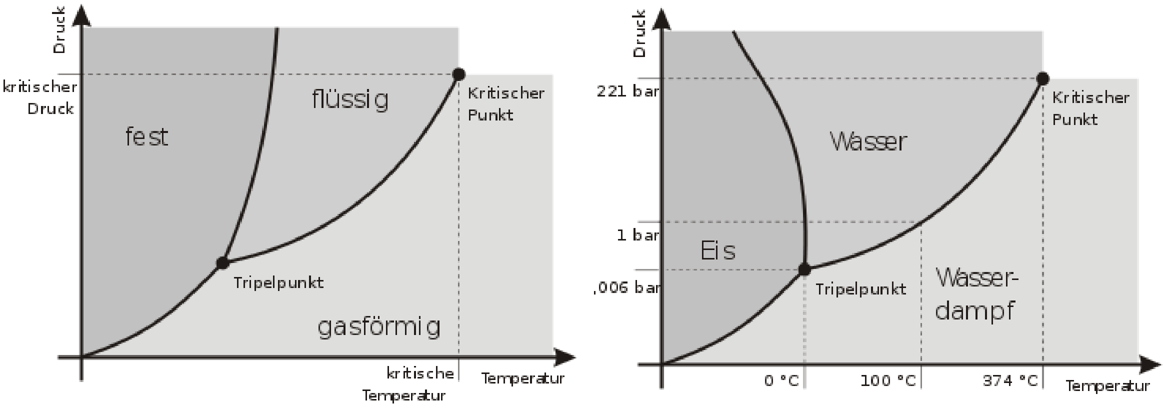


Figure 7.3: The phase diagrams for a generic (1st picture) and water (2nd picture) substance

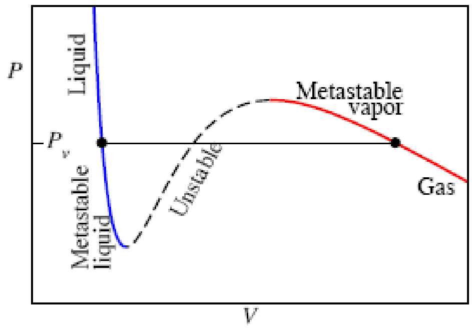


Figure 7.4: A $P - V$ diagram for the phase transition of a generic (not an anomaly) substance

7.3 Nucleation

Vapor to liquid transition at temperature T_{tr}. Condensation into water droplets. Droplets growth is irupeded by surface tension σ. *It costs energy $4\pi R^2\sigma$ to grow a droplet of radius R.*

- At $T = T_{tr}$ we have $G_{gas} = G_{liquid}$.
- At $T = T_{tr} + \Delta T$ we can make a Taylor expansion and get

$$G_{gas} - G_{liquid} \approx \frac{\partial}{\partial T}(G_{gas} - G_{liquid})\bigg|_{T=T_{tr}} \Delta T = -(S_{gas} - S_{liquid})\big|_{T_{tr}} \Delta T = -N\Delta s \Delta T.$$

We can rewrite this and obtain

$$G_{liquid} = G_{gas} + Vn\frac{l}{T_{tr}}\Delta T.$$

- If $\Delta T > 0$ we get that $G_{liquid} > G_{gas}$ and therefore we are in the gas phase.
- If $\Delta T < 0$ we get that $G_{liquid} < G_{gas}$ and therefore we are in the liquid phase.

Consider the energy required to make one droplet of radius R. Cost of energy compared to having just gas is

$$\Delta E|_{Droplet} = G_{liquid} + 4\pi R^2\sigma - G_{gas}.$$

Therefore we obtain that

$$\Delta E|_{Droplet} = \underbrace{\frac{4}{3}\pi R^3}_{=V_{Droplet}} n_{liquid}\frac{l}{T_{tr}} \underbrace{\Delta T}_{<0} + 4\pi R^2\sigma = -\alpha R^3 + \beta R^2.$$

We get a plot like the one shown in figure 7.5.

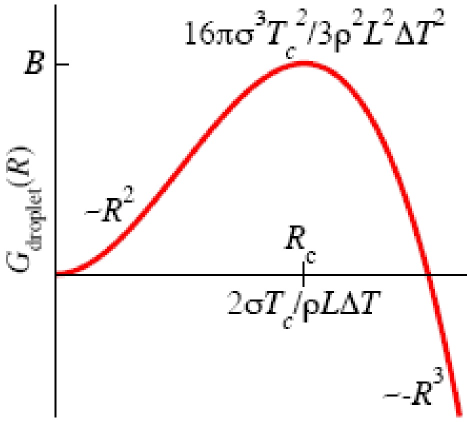


Figure 7.5: The cost of energy ΔE to make one droplet of radius R

The cost of energy to go from gas to water is given by a barrier called B. We see a maximum at R_C which gives us this barrier B. We can calculate that

$$\Delta E'(R = R_C) = 0 \quad \Rightarrow \quad R_C = -\frac{2\sigma T_{tr}}{n_{liquid} l \Delta T} \propto \sigma/\Delta T.$$

For the barrier B we obtain that

$$B = \Delta E(R = R_C) = \frac{16\pi\sigma^3 T_{tr}^2}{3n_{liquid}^2}\frac{1}{l^2}\frac{1}{\Delta T^2} \propto \sigma^3/\Delta T^2.$$

The droplet creation (nucleation) rate is given by

$$\propto \exp(-B/k_B T_{tr}).$$

An application of this would be how to boil water in a microwave. By using a clean glass (washed by a dishwasher) we have a large σ and thus a large R_C. Therefore we obtain large bubbles which could damage the glass. If we use a cloth to wipe out the glass we have a reduced σ and thus the boiling is less violent.

7.4 Continuous phase transitions - Landau's theory

1st order phase transitions (abrupt) are claled nucleation (last section). 2nd order phase transitions (continuous) perform spontaneous symmetry breaking.

1. mechanical analog (rod-spring model)

   The question is in which direction does the rod fall? The Hamiltonian ist symmetric with respect to the possible directions. But the physical realization (ground state) is not! Thus we say that the symmetry is broken.

   We now support the rod with springs. We have to find two potential energies:

   - The potential energy of the two springs.
   - The potential energy of the rod.

   We find that

$$\begin{aligned} u_{\text{spring}} &= 2\frac{1}{2}k(\text{displacement/streching})^2 = kR^2\varphi^2, \\ u_{\text{rod}} &= mg\frac{l}{2}\cos\varphi \approx G\frac{l}{2}\left(1 - \frac{1}{2}\varphi^2 + \frac{1}{24}\varphi^4\right). \end{aligned}$$

   The total energy is then given by

$$u = u_{\text{spring}} + u_{\text{rod}} = \frac{1}{2}Gl + \frac{1}{2}\left(2kR^2 - \frac{1}{2}Gl\right)\varphi^2 + \frac{Gl}{48}\varphi^4.$$

   We have to dinstinguish now two cases:

   - $2kR^2 > \frac{1}{2}Gl$. We see in figure 7.6 (Graph 1) that we have a minimum at $\varphi = 0$. Therefore we are in equilibrium and are always stable!
   - $2kR^2 < \frac{1}{2}Gl$. We see in figure 7.6 (Graph 2) that we have two minima - therefore we have two equal choices. This is called spontaneous symmetry breaking. The minima occur at $\pm\varphi_0$ with

$$\varphi_0 = \sqrt{12\left(\frac{1}{2} - \frac{2kR}{Gl}\right)} = \sqrt{6\frac{G - G_c}{G}} \propto (G - G_c)^{1/2}, \qquad G_c \equiv 4kR^2/l.$$

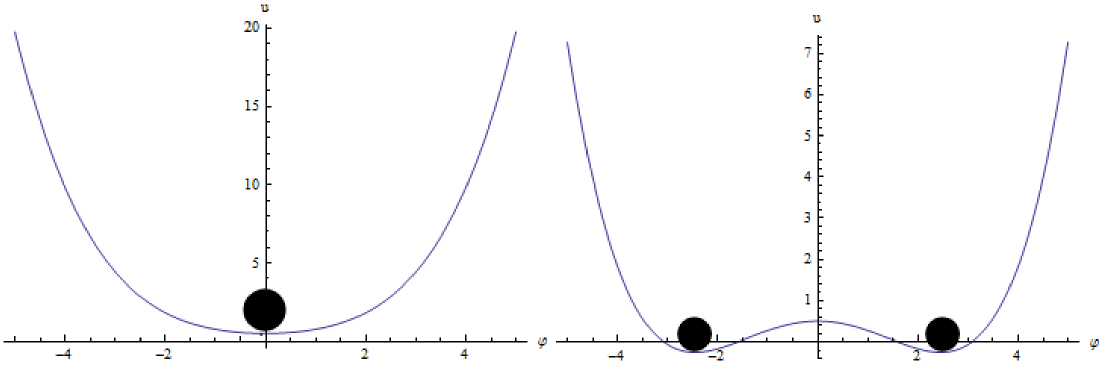


Figure 7.6: The first graph is always stable in $\varphi = 0$ while in the second graph the symmetry is broken for the second case with two minima - symmetric in φ

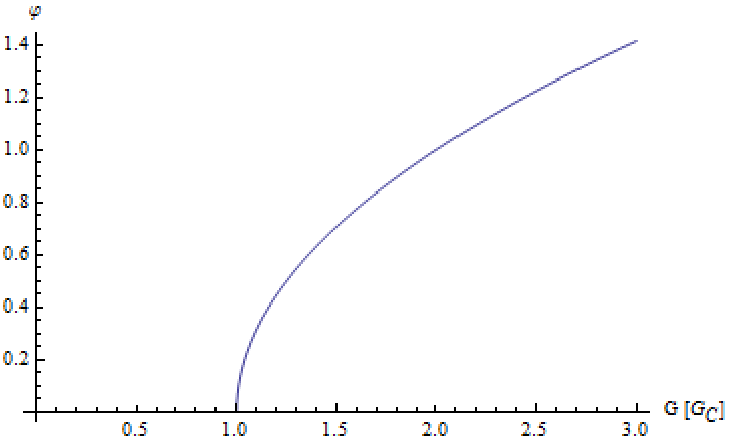


Figure 7.7: We see no jump in $\varphi \propto \sqrt{G - G_c}$ - therefore continuous

We say that 1/2 is the critical exponent. We see in figure 7.7 that $\varphi \propto \sqrt{G - G_c}$ for $G > G_c$.

we call φ the order-parameter with two special variants:

- $\varphi = 0$: *disordered phase*
- $\varphi \neq 0$: *ordered phase*

Going through G_c is a phase transition. The order parameter φ changes continuously at $G = G_c$. Thus we have a *continuous* phase transition. The three most important graphs are shown in figure 7.8.

The system is symmetric when we have $u(\varphi) = u(-\varphi)$.

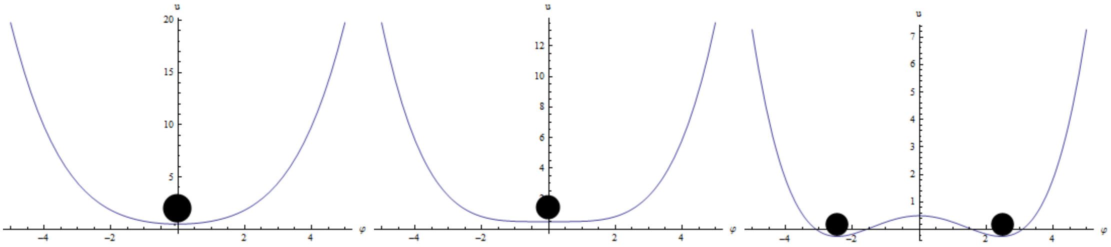


Figure 7.8: The graphs for $G < G_c$, $G = G_c$ and $G > G_c$ (phase transition)

2. Landau theory of paramagnet-ferromagnet transitions

   Experimental we get a graph like the one shown in figure 7.9. From Landau comes the concept of order parameter - here: magnetization M.

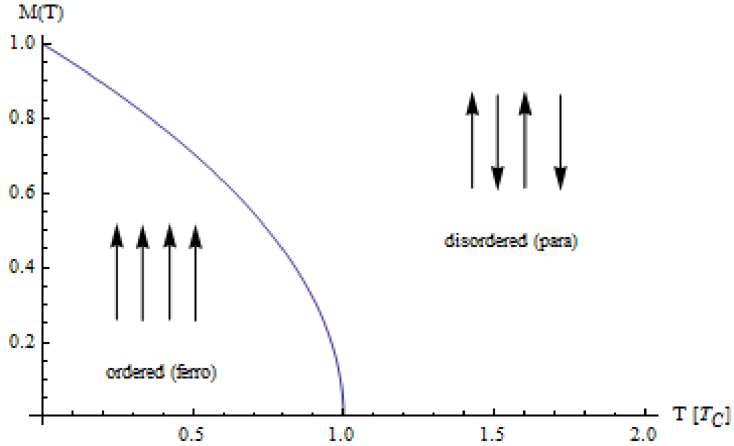


Figure 7.9: Experimental picture with the temperature T in units of the critical temperature T_C

The Landau free energy is defined as

$$F \equiv F(T, V, M) = F_0(T, V) + \frac{1}{2}aM^2 + \frac{1}{4}bM^4, \quad a \equiv a(T), b \equiv b(T) > 0.$$

This is valid close to T_C, where M is small. We set $b(T) > 0$ due to stability. If it would be negative we would have to look at higher orders.

Question Why there are no odd powers of M?

Answer $F(M) = F(-M)$ - so symmetry is the reason!

- In equilibrium we see that F will have a minimum, so

$$\frac{\partial F}{\partial M} = 0 \quad \Rightarrow \quad aM + bM^3 = 0.$$

- For $a > 0$ we only have $M = 0$.
- For $a < 0$ we have

$$M = \pm\sqrt{-\frac{a}{b}}.$$

- The big idea from Landau was that $a \equiv a(T)$ and that the 'most reasonable' (sometimes called *biblical*) ansatz would be

$$a \propto (T - T_C).$$

- At $T < T_C$ we have

$$M = \pm\sqrt{-\frac{\alpha}{b}(T - T_C)} \propto (T_C - T)^{1/2},$$

  with the critical exponent β being 1/2. So we say that 'Magnetization at $T < T_C$, but close to T_C, goes as $(T_C - T)^{1/2}$.'

3. Critical exponents

Close to T_C we have:

$$\begin{aligned}
M &\propto (T_C - T)^{\beta}, \quad T < T_C, \\
M &\propto B^{1/\delta}, \quad T = T_C, \\
\chi &\propto (T - T_C)^{-\gamma}, \quad T > T_C, \\
\chi &\propto (T_C - T)^{-\gamma'}, \quad T < T_C, \\
c_B &= T\left(\frac{\partial S}{\partial T}\right)_B \propto (T - T_C)^{-\alpha}, \quad T > T_C, \\
c_B &\propto (T_C - T)^{-\alpha'}, \quad T < T_C.
\end{aligned}$$

So we have critical exponents $\alpha, \beta, \gamma, \delta, ...$!

4. Critical exponents in Landau-theory

In a magnetic field B we have

$$F = F_0 + \frac{1}{2}aM^2 + \frac{1}{4}bM^4 - BM.$$

From our *minimum condition* we get

$$\frac{\partial F}{\partial M} = aM + bM^3 - B = 0 \quad \Rightarrow \quad M(a + bM^2) = B.$$

Therefore at $T = T_C$ with $a = 0$ we get

$$bM^3 = B \quad \Rightarrow \quad M \propto B^{1/3}.$$

So we found out that $\delta = 3$.

We can do the same for χ. We know that

$$\chi = \mu_0 \left(\frac{\partial M}{\partial B}\right), \qquad aM + bM^3 = B \quad \Rightarrow \quad a\frac{\partial M}{\partial B} + 3bM^2\frac{\partial M}{\partial B} = 1.$$

So we see that at $T > T_C$ with $M = 0$ we have

$$\chi = \frac{\mu_0}{a} \propto \frac{1}{T - T_C} = (T - T_C)^{-1},$$

which is $\gamma = 1$. At $T < T_C$ we haev $M^2 = -a/b$ and thus

$$\chi = \frac{\mu_0}{a - 3a} = -\mu_0/2a \propto (T_C - T)^{-1}.$$

Therefore $\gamma' = 1$ as well. This gives us a graph like the one in figure 7.10.

We set $B = 0$ and get F. At $T > T_C$ we see that $S = S_0$. At $T < T_0$ we obtain that

$$S = S_0 + \frac{1}{2}\frac{\alpha^2}{b}(T - T_C).$$

So 'F and S are continuous at $T = T_C$'.

We now calculate c_B which is (close to T_C)

$$c_B = T_C \left(\frac{\partial S}{\partial T}\right)_B.$$

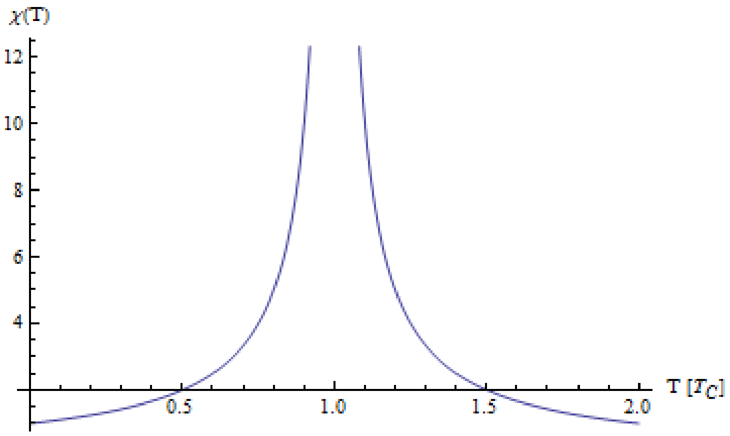


Figure 7.10: χ diverges at T_C as we calculated with the temperature in units of T_C

We obtain that at $T > T_C$ we have c_{B0} and at $T < T_C$ we have $c_{B0} + \frac{1}{2}\frac{\alpha^2}{b}T_C$. So we say that the critical exponent is 0 in Landau's theory. We also see from picture 7.11 that c_B has a jump at T_C. So this is discontinuous / abrupt!

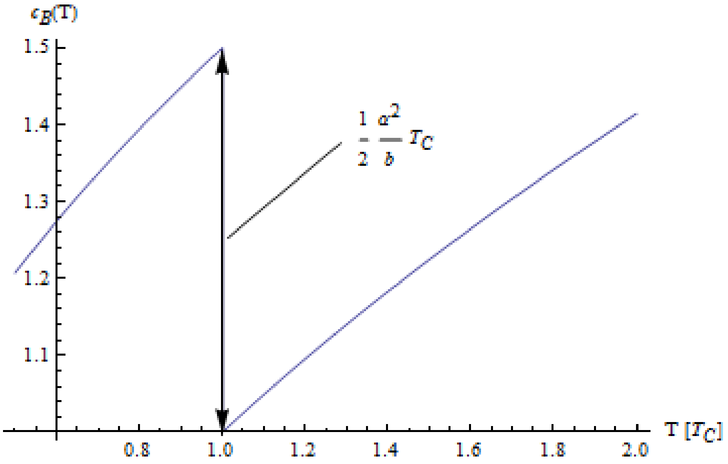


Figure 7.11: c_B has a jump at $T = T_C$ with c_{B0} being a function of T in units of the critical temperature

The gap is $\frac{1}{2}T_C\alpha^2/b$.

7.5 The Ising model: One dimensional

Let the Hamilton operator be

$$H = -J \sum_{\langle i,j \rangle} s_i s_j,$$

with the nearest neighbors $\langle i, j \rangle$, $s_i = \pm 1$ and J the exchange intergral (exchange coupling). We know that

- $J > 0$ for ferromagnetic ground state (↑↑↑↑) and
- $J < 0$ for antiferromagnetic ground state (↑↓↑↓).

Note In quantum mechanics we learned that Coulomb interaction and Pauli principle lead to the Heisenberg Hamiltonian

$$H = -J\vec{s}_1 \cdot \vec{s}_2$$

for two electrons. The Ising model is a simplified classical version.

Let us solve the one dimensional Ising model. We need to calculate the partition sum,

$$Z \equiv Z(\beta) = \sum_{\{s\}} \exp(-\beta H(s)) = \sum_{s_1=\pm 1} \sum_{s2=\pm 1} \cdots \sum_{s_N=\pm 1} \exp(\beta J s_1 s_2 + \beta J s_2 s_3 + ... + \beta J s_{N-1} s_N).$$

- Take first the last sum

$$\sum_{s_N} \exp(\beta J s_{N-1} s_N) = \exp(\beta s_{N-1}) + \exp(-\beta s_{N-1}).$$

- The good thing is that for $s_{N-1} = \pm 1$ we have

$$\sum_{s_N} \exp(\beta J s_{N-1} s_N) = 2\cosh(\beta J),$$

  which is independent of s_{N-1}!

- We get

$$\begin{aligned} s_{N-1} = 1 \quad &: \quad \exp(\beta J) + \exp(-\beta J) = 2\cosh(\beta J), \\ s_{N-1} = -1 \quad &: \quad \exp(-\beta J) + \exp(\beta J) = 2\cosh(\beta J). \end{aligned}$$

- This leads to

$$\begin{aligned} Z &= \sum_{s_1}\sum_{s_2}\cdots\sum_{s_{N-1}}\exp(\beta J(s_1 s_2 + ... + s_{N-2}s_{N-1}))2\cosh(\beta J) = \\ &= \sum_{s_1}\cdots\sum_{s_{N-2}}\exp(\beta J(s_1 s_2 + ... + s_{N-3}s_{N-2}))(2\cosh(\beta J))^2 = \\ &= (2\cosh(\beta J))^{N-1}\underbrace{\sum_{s_1=\pm 1} 1}_{=2} = 2^N\cosh^{N-1}(\beta J) \overset{N\gg 1}{=} (2\cosh(\beta J))^N, \end{aligned}$$

  which is exact in the thermodynamic limit! We will now calculate the thermodynamic quantities.

- The free energy is

$$F = -k_B T \ln Z = -k_B T N \ln(2\cosh(\beta J)).$$

- The internal energy is

$$\overline{E} = -\frac{d}{d\beta}\ln Z = -NJ\tanh(\beta J).$$

  For the limit $T \to 0$ with $\beta \to \infty$ we obtain that $\overline{E} \to -NJ$. Otherwise for $T \to \infty$ with $\beta \to 0$ we see that $-NJ^2\beta \to 0$. Since F is analytic (no divergences in its derivation) at all $T > 0$, there are no phase transitions in the one dimensional Ising model! In one dimensional Ising model the phase is a paramagnet at all $T > 0$! In $T = 0$ it is a ferromagnet - but since $T = 0$ cannot be reached it is obsolete.

7.6 One dimensional Ising model: renormalization group (RG)

K. Wilson calculated this in the 1970′s starting with

$$Z = \sum_{\{s\}}\exp\left(\beta J\sum_{\langle i,j\rangle} s_i s_j\right) = \sum_{\{s\}}\exp\left(K\sum_{\langle i,j\rangle} s_i s_j\right),$$

with $K = \beta J = J/k_B T$. We consider a one dimensional Ising model with periodic boundary conditions, meaning $s_{N+1} \equiv s_1$. We calculate

$$\begin{aligned} Z &= \sum_{\{s\}} \exp\left(K \sum_{i=1}^{N} s_i s_{i+1}\right) = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} \exp(K(s_1 s_2 + s_2 s_3 + ...)) = \\ &= \sum_{s_1} \cdots \sum_{s_N} \exp(K s_2 (s_1 + s_3) + K s_4 (s_3 + s_5) + ...). \end{aligned}$$

- Let us sum over all the *even* spins only:

  $$Z = \sum_{s_1} \sum_{s_3} \cdots \left[e^{K(s_1+s_3)} + e^{-K(s_1+s_3)}\right] \left[e^{K(s_3+s_5)} + e^{-K(s_3+s_5)}\right] [...] \,.$$

  We now want to rewrite this new (called decimated) system to look like the old one. We see that the effective distance has increased from $a \to 2a$ and the coupling constant has changed from $K \to K'$. This is called resclaing or coarse graining. Mathematically this is

  $$\exp(K(s_1 + s_3)) + \exp(-K(s_1 + s_3)) \overset{?}{=} A(K) \exp(K' s_1 s_3).$$

- We know that when $s_1 = s_3 = \pm 1$ we have

  $$\exp(2K) + \exp(-2K) \overset{!}{=} A(K) \exp(K').$$

  We also know that for $s_1 \neq s_3 = \pm 1$ we obtain that

  $$1 + 1 \overset{!}{=} A(K) \exp(K').$$

  So we have two equations with two unknown variables. This can be solved. We get

  $$A(K) = 2 \exp(K'), \qquad 2 \cosh(2K) = A(K) \exp(K') = 2 \exp(2K').$$

  Therefore afterall we have

  $$K' = \frac{1}{2} \ln \cosh(2K), \qquad A(K) = 2 \sqrt{\cosh(2K)}. \tag{7.4}$$

- Then we take

$$Z = \sum_{\text{odd spins}} [A(K)]^{N/2} \exp(K'(s_1 s_3 + s_3 s_5 + ...)).$$

  Let us write

$$Z \equiv Z(K, N) = [A(K)]^{N/2} Z(K', N/2).$$

- We introduce now $f = (\ln Z)/N = -F/k_B TN$ with our free potential $F = -k_B T \ln Z$. We calculate

$$\begin{aligned} f &= f(K) = \frac{1}{N} \ln Z(K, N) = \frac{1}{N} \ln\left([A(K)]^{N/2} Z(K', N/2)\right) = \\ &= \frac{1}{N}\frac{N}{2} \ln A(K) + \frac{1}{N} \ln Z(K', N/2) = \frac{1}{2} \ln A(K) + \underbrace{\frac{2}{N}\frac{1}{2} \ln Z(K', N/2)}_{=\frac{1}{2} f(K')} = \\ &= \frac{1}{2} \left[\ln A(K) + f(K')\right]. \end{aligned}$$

  So we see that

$$f(K') = 2f(K) - \ln A(K) = 2f(K) - \ln\left[2\sqrt{\cosh(2K)}\right].$$

  We found the renormalization group equations, which give us the renormalization group flow,

$$K' = \frac{1}{2} \ln\left[\cosh(2K)\right], \qquad f(K') = 2f(K) - \ln\left[2\sqrt{\cosh(2K)}\right]. \tag{7.5}$$

- Let's take for example $K = 1$. Then K' is 1. By calculating K'' we receive 0.66 then 0.35 then 0.11 and so on... Therefore we see that
  - At $K = 0$ which is $T = \infty$ we have a stable renormalization group fixed point, because $K = 0$ gives us $K' = 0$.
  - At $K = \infty$ which is $T = 0$ we have an unstable renormalization group fixed point.

So the flow is from $K = \infty$ to $K = 0$. We say that $K = \infty$ is ordered while everything else is disordered. We also see a phase transition at $T = 0$.

- A fixed point is where all length scales are equivalent. So fractal, universality, power laws. Therefore we see that a critical exponent is the same for all ferromagnets.
- Universality means that $\alpha, \beta, \gamma, \delta, ...$ depend on the dimensionality and geometry. If $d \geq 4$ all systems behave as in Landau's theory. The reason for this is that Landau neglected fluctuations, which are very important for systems with $d < 4$.

7.7 Ising model in two dimensions: Renormalization Group

By rotating a square lattice by $\pi/4$ (decimation), and therefore summing over every other spin. We are doing the in figure 7.12 shown process on the lattice.

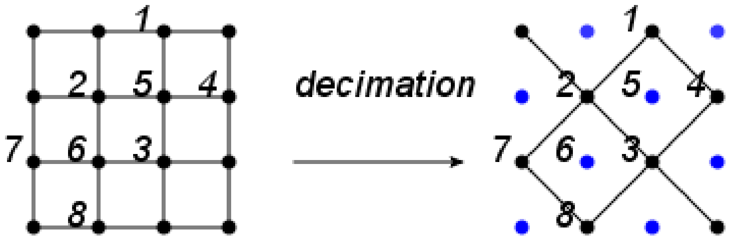


Figure 7.12: The rough sketch of the setup used for our calculation

Let us look at the structure of the partition function,

$$\begin{aligned} Z &= \sum_{\{s\}} \exp(K(s_1 s_5 + s_2 s_5 + ...)) = \sum_{\{s\}} \exp(K s_5 (s_1 + s_2 + ...)) \exp(K s_6 (s_2 + s_3 + ...)) = \\ &= \sum{}' \cdots [\exp(K(s_1 + s_2 + s_3 + s_4)) + \exp(-K(s_1 + s_2 + s_3 + s_4))] \cdots \\ &\quad \cdots [\exp(K(s_2 + s_3 + s_7 + s_8)) + \exp(-K(s_2 + s_3 + s_7 + s_8))] . \end{aligned}$$

We would like to find K' and $A(K)$ such that

$$\exp(K(s_1+s_2+s_3+s_4))+\exp(-K(s_1+s_2+s_3+s_4)) \overset{!}{=} A(K)\exp(K'(s_1s_2+s_1s_4+s_2s_3+s_4s_4)).$$

We have 4 inequivalent choices of s_1, s_2, s_3, s_4:

- For $s_1 = s_2 = s_3 = s_4 = \pm 1$.
- For $s_1 = s_2 = s_3 = -s_4 = \pm 1$.
- For $s_1 = s_2 = -s_3 = -s_4 = \pm 1$.
- For $s_1 = -s_2 = s_3 = -s_4 \pm 1$.

But only 2 unknown K', A. We need to make the Hamiltonian *bigger*. So we proceed

$$\begin{aligned} &\exp(K(s_1+s_2+s_3+s_4))+\exp(-K(s_1+s_2+s_3+s_4)) \overset{!}{=} \\ &\overset{!}{=} A(K)\exp(\frac{1}{2}K_1(s_1s_2+s_1s_4+s_2s_3+s_4s_4)+K_2(s_1s_3+s_2s_3)+K_3(s_1s_2s_3s_4)). \end{aligned}$$

Remark A system with three spins s_1, s_2, s_3 is not possible because it violates up and down symmetry. Let us insert the four possibilities for s. We obtain

$$\begin{aligned} \exp(4K)+\exp(-4K) &= A(K)\exp(2K_1+2K_2+K_3), \\ \exp(2K)+\exp(-2K) &= A(K)\exp(-K_3), \\ 2 &= A(K)\exp(-2K_2+K_3), \\ 2 &= A(K)\exp(-2K_1-2K_2-K_3). \end{aligned}$$

The solution is

$$K_1 = \frac{1}{4}\ln\cosh(4K), \qquad K_2 = \frac{1}{8}\ln\cosh(4K), \qquad K_3 = \frac{1}{8}\ln\cosh(4K) - \frac{1}{2}\ln\cosh(2K).$$

Let us go back to the partition function, we have

$$\begin{aligned} Z(K,N) &= (A(K))^{N/2}\sum_{\{s\}}{}' \cdots\left[\exp(\frac{K_1}{2}(s_1s_2+s_1s_4+s_2s_3+s_4s_4)+K_2(s_1s_3+s_2s_4)+K_3(s_1s_2s_3s_4))\right]\cdots \\ &\cdots\left[\exp(\frac{K_1}{2}(s_3s_8+s_8s_7+s_2s_3+s_7s_2)+K_2(s_2s_8+s_7s_3)+K_3(s_2s_3s_7s_8))\right]. \end{aligned}$$

Each nearest neighbour bond appears twice ($s_2 s_3$). We conclude

$$Z(K,N) = (A(K))^{N/2} \sideset{}{'}\sum_{\{s\}} \exp\left(K_1 \sum_{\langle i,j \rangle} s_i s_j + K_2 \sum_{\langle\langle i,j \rangle\rangle} s_i s_j + K_3 \sum_{\square} s_i s_i s_k s_l \right),$$

with $\langle i,j \rangle$ nearest neighbors, $\langle\langle i,j \rangle\rangle$ next nearest neighbors and the plaquette $\square$. Up to now we have made no approximation. Since things are quite complicated we will now make an approximation.

1. Take $K_2 = K_3 = 0$. Then we see that

   $$Z(K,N) \approx (A(K))^{N/2} Z(K_1, N/2), \qquad K_1 = \frac{1}{4} \ln\cosh(4K).$$

   This is the same renormalization group flow as in the one dimensional Ising model, where we had $K' = \frac{1}{2} \ln\cosh(2K)$.

2. A better choice would be $K_3 = 0$. We motivate the selection of K_2 physically by including the next nearest neighbor in the coupling as if it would be a first nearest neighbor coupling. We obtained

   $$K_1 \sum_{\langle i,j \rangle} + K_2 \sum_{\langle\langle i,j \rangle\rangle} s_1 s_2 \approx K'(K_1, K_2) \sum_{\langle i,j \rangle} s_1 s_2.$$

   Take all spins $s_i = 1$. We see

   $$K_1 2\frac{N}{2} + K_2 2\frac{N}{2} = K' 2\frac{N}{2}.$$

   Remark For N lattice points there are $2N$ bounds. So we have

   $$K' = K_1 + K - 2 = \frac{3}{8} \ln\cosh(4K).$$

   The approximate renormalization group flow is then given by

   $$K' = \frac{3}{8} \ln\cosh(4K). \tag{7.6}$$

So now we have a non-trivial behaviour for our system (just by changing $1/4 = 2/8$ to $3/8$). We can calculate that for $K_C = 0.50698$ we have a fixed point. Below the fix point we have a paramagnet with a fow to $K = 0$ ($T = \infty$) and above we have a flow to $K = \infty$

($T = 0$) - which is a ferromagnet. So we have a phase transition at K_C! This corresponds to

$$k_B T_C = 1.972\,\mathrm{J} \qquad \approx \qquad (k_B T_C)_{\text{exact}} = 2.269\,\mathrm{J}.$$

We are able to obtain this K_C by solving the equation

$$K_C = \frac{3}{8} \ln \cosh(4K_C).$$

Therefore we can find the very important critical exponent (universality). These critical exponents are very important, because they do only depend on the geometry and the dimensionality of the system, while T_C depends on microsocopics (J). Illustration of universality is

$$\alpha = 2 - \frac{\ln 2}{\ln \left| \frac{dK'}{dK} \right|_{K=K_C}}.$$

The exact α would be 0 - or log. Therefore we have $C \propto \ln(T - T_C)$. For our renormalization group model we have

$$\alpha = 2 - \frac{\ln 2}{\ln \frac{3}{2} \tanh(4K_C)} = 0.131.$$

8 Appendix

8.1 Volume of a sphere in n dimensions

Let us denote

$$\begin{aligned} r^2 &= x_1^2 + ...x_N^2, \\ V_n &= \int_{r^2 \leq R^2} dx_1 dx_2 \cdots dx_N = \int_0^R dr R^{n-1} \int d\Omega_n = \\ &= \frac{1}{n} R^n \Omega_n, \end{aligned}$$

where Ω_n is the solid angle. We use the following trick to get Ω_n:

$$I = \int_{-\infty}^{\infty} dx_1 dx_2 \cdots dx_N \exp(-x_1^2 - x_2^2 - ... - x_N^2).$$

We solve it by two methods:

1. First by a gaussian integral

$$\begin{aligned} I &= \int_{-\infty}^{\infty} \exp(-x_1^2) dx_1 \int_{-\infty}^{\infty} \exp(-x_2^2) dx_2 \cdots \int_{-\infty}^{\infty} \exp(-x_N^2) dx_N = \\ &= \left[\int_{-\infty}^{\infty} dx \exp(-x^2) \right]^n = \sqrt{\pi}^n = \pi^{\frac{n}{2}}. \end{aligned}$$

2. Second by substituting $t = r^2$ and $dr = \frac{1}{2} \frac{1}{\sqrt{t}} dt$,

$$\begin{aligned} I &= \int_0^R drr^{n-1}\exp(-r^2)\int d\Omega_n = \Omega_n\int_0^R drr^{n-1}\exp(-r^2) = \\ &= \Omega_n\int_0^\infty \frac{1}{2}\frac{dt}{\sqrt{t}}t^{\frac{n}{2}-\frac{1}{2}}\exp(-t) = \\ &= \frac{1}{2}\Omega_n\int_0^\infty dtt^{\frac{n}{2}-1}\exp(-t) = \frac{1}{2}\Omega_n\Gamma\left(\frac{n}{2}\right). \end{aligned}$$

We note that $\Gamma(x)$ is Eulers Gamma Function.

By comparing these two methods we get that

$$\Omega_n = \frac{2\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2})}. \tag{8.1}$$

Basic properties of the Γ-Function:

$$\begin{aligned} \Gamma(\frac{1}{2}) &= \sqrt{\pi}, \\ \Gamma(1) &= 1, \\ \Gamma(x+1) &= x\Gamma(x), \\ \Gamma(x) &= (x-1)!, \\ \Gamma(\frac{n}{2}) &= \frac{(n-2)!!\sqrt{\pi}}{2^{\frac{(n-1)}{2}}}. \end{aligned}$$

The volume of the n-sphere is

$$V_n = \frac{2\pi^{\frac{n}{2}}R^n}{n\Gamma(\frac{n}{2})} = \frac{\pi^{\frac{n}{2}}R^n}{\frac{n}{2}\Gamma(\frac{n}{2})} = \frac{\pi^{\frac{n}{2}}R^n}{\Gamma(\frac{n}{2}+1)}. \tag{8.2}$$

8.2 Stirling's formula

The Stirling formula gives an approximation to the factorial of a large number, $N \gg 1$. In its **simple form** it is,

$$N! \approx \left(\frac{N}{e}\right)^N \quad \Longrightarrow \quad \ln N! \approx N\ln N - N \quad \Longrightarrow \quad \frac{d\ln N!}{dN} \approx \ln N. \tag{8.3}$$

The easy-to-remember proof is in the following intuitive steps:

$$\ln N! = \ln 1 + \ln 2 + \ ... \ + \ln N \approx \int_1^N dx \ \ln x = N \ln N - N + 1 \approx N \ln N - N. \tag{8.4}$$

The **stronger form** of the Stirling formula reads,

$$N! \approx \left(\frac{N}{e}\right)^N \sqrt{2\pi N} \quad \Longrightarrow \quad \ln N! \approx N \ln N - N + \frac{1}{2} \ln 2\pi N. \tag{8.5}$$

The proof is more subtle and uses the Euler Γ function. Recall that

$$N! = \Gamma(N+1) = \int_0^\infty dx \, x^{N+1-1} e^{-x} = \int_0^\infty dx \, x^N e^{-x}. \tag{8.6}$$

Denote

$$\phi(x) = N \ln x - x, \tag{8.7}$$

so that

$$x^N e^{-x} = e^{\phi(x)}. \tag{8.8}$$

The function $\phi(x)$ has maximum at x_0 such that $\phi'(x_0) = 0$. We can find it,

$$\phi'(x) = \frac{N}{x} - 1 \quad \Longrightarrow x_0 = N. \tag{8.9}$$

Let us expand $\phi(x)$ around x_0:

$$\phi(x) = \phi(x_0) + \phi'(x_0)(x - x_0) + \frac{1}{2}\phi''(x_0)(x - x_0)^2 + \ ... \tag{8.10}$$

The linear term vanishes, since $\phi'(x_0) = 0$, while the second derivative is

$$\phi''(x) = -\frac{N}{x^2} \quad \Longrightarrow \quad \phi''(x_0) = -\frac{N}{x_0^2} = -\frac{1}{N}. \tag{8.11}$$

We then have up to the second order,

$$\phi(x) \approx N \ln N - N - \frac{1}{2N}(x - N)^2. \tag{8.12}$$

Or,

$$e^{\phi(x)} \approx e^{N \ln N - N} e^{-(x-N)^2/2N} = \left(\frac{N}{e}\right)^N e^{-(x-N)^2/2N}. \tag{8.13}$$

We thus get the Gaussian integral,

$$N! = \int_0^\infty dx\, e^{\phi(x)} \approx \left(\frac{N}{e}\right)^N \int_0^\infty e^{-(x-N)^2/2N} \approx \left(\frac{N}{e}\right)^N \int_{-\infty}^\infty e^{-(x-N)^2/2N} = \left(\frac{N}{e}\right)^N \sqrt{2\pi N}. \quad (8.14)$$

Note the change of the lower integration limit from 0 to $-\infty$ in the last integral. This change is possible since the integrand has maximum at N, so at $x < 0$ the integrand is negligible.

This completes the proof. The above method of approximating integrals by expanding the exponent is called the *saddle-point approximation*. This trick is used to calculate things in statistical physics and quantum field theory.

8.3 Bose-Einstein and Fermi-Dirac Integrals

Consider an integral of the form

$$I(p) = \int_0^\infty dx \frac{x^{p-1}}{\exp(x) - 1}, \quad p > 1.$$

We can solve such an integral by using the geometric series expansion. In the end we have

$$I(p) = \zeta(p)\Gamma(p).$$

We can do the same for

$$J(p) = \int_0^\infty dx \frac{x^{p-1}}{\exp(x) + 1}, \quad p > 1.$$

With some little tricks we arrive at

$$J(p) = \left(1 - \frac{1}{2^{p-1}}\right)\zeta(p)\Gamma(p).$$

Some important values of $\zeta(p)$ and $\Gamma(p)$ are listed below:

$$
\begin{array}{lll}
p = 3/2, & \zeta(p) = 2.612, & \Gamma(p) = \sqrt{\pi}/2, \\
p = 5/2, & \zeta(p) = 1.341, & \Gamma(p) = 3\sqrt{\pi}/4, \\
p = 3, & \zeta(p) = 1.202, & \Gamma(p) = 2, \\
p = 4, & \zeta(p) = \pi^4/90, & \Gamma(p) = 6, \\
p = 6, & \zeta(p) = \pi^6/945, & \Gamma(p) = 120.
\end{array}
$$

8.4 Equipartition theorem

We essentially follow the proof given by K. Huang, Statistical Physics, and adopt it to the notation used in the class.

We have learned in chapter 3.1 (i), that for N indistinguishable classical particles of total energy E, the microcanonical averages of a physical observable $A(Q,P)$, are,

$$\overline{A} = \frac{1}{g(E)} \int \frac{dQdP}{h^{3N}N!} A(Q,P)\delta\left[E - H(Q,P)\right], \tag{8.15}$$

where the density of states is related to the number of states below energy E,

$$g(E) = \frac{d\Gamma(E)}{dE}; \quad \Gamma(E) = \int \frac{dQdP}{h^{3N}N!}\Theta\left[E - H(Q,P)\right] = \int_{H(Q,P)<E} \frac{dQdP}{h^{3N}N!}. \tag{8.16}$$

Make a specific choice for the observable A, as

$$A = x_i \frac{\partial H}{\partial x_j}, \tag{8.17}$$

where x_i denote either the generalized coordinate q_i or generalized momentum p_i. Here index i goes from 1 to $3N$. Then

$$\overline{x_i \frac{H}{\partial x_j}} = \frac{1}{g} \int \frac{dQdP}{h^{3N}N!} x_i \frac{\partial H}{\partial x_j} \delta(E - H) \tag{8.18}$$

$$= \frac{1}{g}\frac{\partial}{\partial E} \int_{H(Q,P)<E} \frac{dQdP}{h^{3N}N!} x_i \frac{\partial H}{\partial x_j} \tag{8.19}$$

$$= \frac{1}{g}\frac{\partial}{\partial E} \int_{H(Q,P)<E} \frac{dQdP}{h^{3N}N!} x_i \frac{\partial (H - E)}{\partial x_j} \tag{8.20}$$

$$= \frac{1}{g}\frac{\partial}{\partial E} \int_{H(Q,P)<E} \frac{dQdP}{h^{3N}N!} \frac{\partial [x_i(H - E)]}{\partial x_j} - \delta_{ij}\frac{1}{g}\frac{\partial}{\partial E} \int_{H(Q,P)<E} \frac{dQdP}{h^{3N}N!}(H - E). \tag{8.21}$$

The first integral on the right-hand side of the last line vanishes, since

$$\int_{H(Q,P)<E} dQdP \frac{\partial[x_i(H-E)]}{\partial x_j} = 0, \tag{8.22}$$

as it can be transformed to a surface integral, with the surface defined by $H(Q,P) = E$, of $x_i(H-E)$ which vanishes identically on that surface; we always have $H = H(Q,P)$, just shortening the notation and omitting (Q,P).

Finally, we then write that

$$\overline{x_i \frac{H}{\partial x_j}} = -\delta_{ij} \frac{1}{g} \frac{\partial}{\partial E} \int_{H(Q,P)<E} \frac{dQdP}{h^{3N}N!}(H-E) \tag{8.23}$$

$$= -\delta_{ij} \frac{1}{g} \int \frac{dQdP}{h^{3N}N!} \frac{\partial}{\partial E} \left[\Theta(E-H)(H-E)\right] \tag{8.24}$$

$$= \delta_{ij} \frac{1}{g} \int \frac{dQdP}{h^{3N}N!} \Theta(E-H) \tag{8.25}$$

$$= \delta_{ij} \frac{1}{g} \Gamma = \delta_{ij} \frac{\Gamma}{d\Gamma/dE} = \delta_{ij} \frac{1}{d \ln \Gamma / dE} \tag{8.26}$$

$$= \delta_{ij} k_B \left(\frac{dk_B \ln \Gamma}{dE} \right)^{-1} \tag{8.27}$$

$$= \delta_{ij} k_B \left(\frac{dS}{dE} \right)^{-1} \tag{8.28}$$

$$= \delta_{ij} k_B T. \tag{8.29}$$

In the above derivation we have used the following formulas derived for the microcanonical ensemble in the class:

$$S = k_B \ln \Gamma, \tag{8.30}$$

$$\frac{1}{T} = \frac{\partial S}{\partial E}. \tag{8.31}$$

To summarize, the generalized equipartition theorem reads,

$$\overline{x_i \frac{H}{\partial x_j}} = \delta_{ij} k_B T. \tag{8.32}$$

If we choose for x_i either q_i or p_i, we get individually the equipartition theorem for generalized coordinates and momenta:

$$\overline{q_i \frac{H}{\partial q_i}} = \overline{p_i \frac{H}{\partial p_i}} = k_B T. \tag{8.33}$$

The above was the starting point to derive the virial theorem in the class.

8.5 Sommerfeld's expansion

Consider integral,

$$I(\mu) = \int_0^\infty d\varepsilon \, \frac{\varphi(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1}, \tag{8.34}$$

where $\varphi(\varepsilon)$ is some well behaved function. Let us introduce a new variable x,

$$x = \beta(\varepsilon - \mu), \quad \varepsilon = \mu + k_B T x. \tag{8.35}$$

The integral transforms to

$$I(\mu) = k_B T \int_{-\mu/k_B T}^{\infty} dx \, \frac{\varphi(\mu + k_B T x)}{e^x + 1} = k_B T \int_{-\mu/k_B T}^{0} dx \, \frac{\varphi(\mu + k_B T x)}{e^x + 1} + k_B T \int_0^\infty dx \, \frac{\varphi(\mu + k_B T x)}{e^x + 1}. \tag{8.36}$$

Let us work little bit on the first integral on the right,

$$\begin{aligned}\int_{-\mu/k_B T}^{0} dx \, \frac{\varphi(\mu + k_B T x)}{e^x + 1} &= |x \to -x| = \int_0^{\mu/k_B T} dx \, \frac{\varphi(\mu - k_B T x)}{e^{-x} + 1} = \\ &= \left| \frac{1}{e^{-x} + 1} = 1 - \frac{1}{e^x + 1} \right| = \frac{1}{k_B T} \int_0^\mu dz \, \varphi(z) - \int_0^{\mu/k_B T} dx \, \frac{\varphi(\mu - k_B T x)}{e^x + 1}.\end{aligned}$$

We have introduced new variable z, by

$$z = \mu - k_B T x, \tag{8.37}$$

in the first integral on the right. Our original integral now reads,

$$I(\mu) = \int_0^\mu dz \, \varphi(z) + k_B T \int_0^\infty dx \, \frac{\varphi(\mu + k_B T x)}{e^x + 1} - k_B T \int_0^{\mu/k_B T} dx \, \frac{\varphi(\mu - k_B T x)}{e^x + 1} \tag{8.38}$$

Thus far we have made no approximation. In the following, we make two: (i) In the degenerate limit, we have

$$\frac{\mu}{k_B T} \approx \frac{\varepsilon_F}{k_B T} \gg 1, \tag{8.39}$$

so that we can extend the integration in the last term of Eq. 8.38 to infinity; note that the integrand of this term decreases rapidly with increasing x—this is why the upper limit of that integral is irrelevant. We cannot do the same with the first term, for example. We obtain:

$$I(\mu) = \int_0^\mu dz \, \varphi(z) + k_B T \int_0^\infty dx \, \frac{1}{e^x + 1} \left[\varphi(\mu + k_B T x) - \varphi(\mu - k_B T x) \right]. \tag{8.40}$$

(ii) As a second approximation, we expand $\varphi(\mu \pm k_B T x)$ in Taylor series about $k_B T x = 0$, again for the reason that the integrand decreases exponentially with increasing x as well as that $k_B T \ll \mu$:

$$\varphi(\mu+k_BTx)-\varphi(\mu-k_BTx) \approx \varphi(\mu)+k_BTx\frac{d\varphi(\mu)}{d\mu}+\ ...\ -\varphi(\mu)+k_BTx\frac{d\varphi(\mu)}{d\mu}-\ ...\ = 2k_BTx\frac{d\varphi(\mu)}{d\mu}+\ ... \tag{8.41}$$

Substituting to our integral, Eq. 8.42, we get

$$I(\mu) = \int_0^{\mu} dz\,\varphi(z) + 2(k_BT)^2\frac{d\varphi(\mu)}{d\mu}\int_0^{\infty} dx\,\frac{x}{e^x+1}. \tag{8.42}$$

The second integral on the right can be evaluated by expanding $(e^x+1)^{-1}$ into a geometric series (see Appendix 2 to IV.10.):

$$\int_0^{\infty} dx\,\frac{x^{p-1}}{e^x+1} = \left(1-\frac{1}{2^{p-1}}\right)\zeta(p)\Gamma(p). \tag{8.43}$$

Then, for $p = 2$,

$$\int_0^{\infty} dx\,\frac{x}{e^x+1} = \frac{1}{2}\zeta(2)\Gamma(2) = \frac{1}{2}\times\frac{\pi^2}{6}\times 1 = \frac{\pi^2}{12}. \tag{8.44}$$

Using this result, we finally obtain for the low temperature ($T \ll T_F$) expansion,

$$I(\mu) \approx \int_0^{\mu} dz\,\varphi(z) + \frac{\pi^2}{6}(k_BT)^2\frac{d\varphi(\mu)}{d\mu} +\ ... \tag{8.45}$$

The above result is called Sommerfeld's expansion. It is useful to calculate physical observables of degenerate Fermi gases. For example, if $\varphi(\varepsilon) = \varepsilon^{1/2}$, one needs to substitute $\varphi(z) = z^{1/2}$ and $\varphi(\mu) = \mu^{1/2}$ in the above to obtain

$$I(\mu) = \left|\text{for } \ \varphi(\varepsilon) = \varepsilon^{1/2}\right| = \frac{2}{3}\mu^{3/2} + \frac{\pi^2}{12}\frac{(k_BT)^2}{\mu^{1/2}}. \tag{8.46}$$

This result is used in the class to derive the expression for the chemical potential.

8.6 Pressure and entropy in statistics

The internal energy is given by

$$E = \sum_n E_n p_n, \qquad p_n = \frac{1}{Z}\exp(-\beta E_n).$$

We know that $E_n \equiv E_n(V)$. Therefore we change the volume quasistatically. We get

$$\delta E_n = \frac{\partial E_n}{\partial V}\delta V.$$

An example would be a line of length L with $E_n \propto 1/L^2$. In general we have

$$\delta E = \sum_n \delta E_n p_n + \sum_n E_n \delta p_n = \sum_n \underbrace{\left(\frac{\partial E_n}{\partial V}\right)}_{-P_n} p_n \delta V + \sum_n p_n \delta p_n.$$

We see directly that the outcome of this variation is

$$\delta E = -\sum_n p_n P_n \delta V + \sum_n E_n \delta p_n = -P\delta V + \sum_n E_n \delta p_n.$$

The first term is the same if V or $V + \delta V$. Therefore the second term must be responsible for the relaxation and therefore for the ireversibility. Thus

$$\sum_n E_n \delta p_n = T\delta S, \qquad \delta E = -P\delta V + T\delta S.$$