Statistical Mechanics

Summary/Overview

created by Tizian Römer

based on the lecture
Statistical Mechanics
of Prof. Hui Pak Ming
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Contact via E-Mail: tiroemer@yahoo.de

Content

1 Revision and Introduction

1.1 Summary of Thermodynamics

0. Law: The relation of the equilibrium is transitive; two systems in equilibrium have the same temperature.

1. Law: $dU = \delta Q + \delta W$, change in internal energy U is due to heat Q supplied to or work W done on the system.

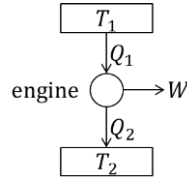2. Law: The Carnot-process is the most efficient. Effieciency for any engine:
$\eta = W/Q_1 = 1 - Q_2/Q_1$
(using $Q_1 = Q_2 + W$)
Efficiency of a Carnot-process:
$\eta_C = 1 - T_2/T_1$
All reservible processes have the efficiency η_C!

Reversible processes:
$$1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \quad \Leftrightarrow \quad \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \quad \Rightarrow \quad \oint \frac{dQ}{dT} = 0$$
define entropy of reversible processes $dS := dQ_{\text{rev}}/T$
Since $\oint dS = 0$, S is a state function and path-independent, so that $\int_A^B dS = S_B - S_A$.
$dQ = TdS$ and $dW = pdV$ yield $dU = TdS + pdV$

Irreversible processes:
$$1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1} \quad \Leftrightarrow \quad \frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0 \quad \Rightarrow \quad \oint \frac{dQ}{dT} < 0$$
Also: $\int_A^B dS < S_B - S_A$, so that $dQ/T < dS$

Summary for any process:
$$\oint \frac{dQ}{T} \leq 0, \qquad \frac{dQ}{T} \leq dS$$
$$\Rightarrow \quad dS \geq 0 \text{ for } dQ = 0 \text{ (isolated system)}$$
In general, $dU = \delta Q + \delta W = TdS - pdV$ is correct, but $\delta Q = TdS$ and $\delta W = -pdV$ is only true for rev. proc.

Including the exchange of particles and writing E instead of U:
$$dE = TdS - pdV + \mu dN \quad \Leftrightarrow \quad dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$
Obviously it is $E \equiv E(S,V,N)$ and $S \equiv S(E,V,N)$ and Boltzmanns idea was $S(E,V,N) = k\ln(W(E,V,N))$.
Helmholtz free energy: $F := E - TS$ and it follows
$$dF = -pdV - SdT \quad \Rightarrow \quad F \equiv F(T,V)$$
Similarly is $H \equiv H(S,p) = U + pV$ the enthalpy and $G \equiv G(T,p) = F + pV$ the Gibb's free energy.

1.2 Example: Distribution of Gas Molecules

Consider a Volume V with N gas molecules with a smaller Volume v inside V. How many molecules n are inside v in average?

Define $p := v/V$ (probability, that a given molecule is in v) and $q := 1 - p$. Then the probability that n of N molecules are inside v is given by $P_N(n) := \binom{N}{n} p^n q^{N-n}$, which is normalized, since $\sum_{n=0}^N P_N(n) = (p+q)^N = 1^N = 1$. Now, the average number of molecules inside v is:

$$\langle n \rangle = \sum_{n=0}^N n\, P_N(n) = \sum_{n=1}^N n\, P_N(n) = \sum_{n=1}^N \frac{N!}{(n-1)!\,(N-n)!} p^n q^{N-n}$$

$$= Np \sum_{n=1}^N \frac{(N-1)!}{(n-1)!\,(N-n)!} p^{n-1} q^{N-n}$$

$$= Np \sum_{n=0}^{N-1} \frac{(N-1)!}{n!\,(N-n-1)!} p^n q^{N-n-1} = Np(p+q)^{N-1} = Np$$

$$= N\frac{v}{V}$$

(which is what you would expect)

What about the fluctuation?
$$\sigma^2 = \langle (n - \langle n \rangle)^2 \rangle = \langle n^2 - 2n\langle n \rangle + \langle n \rangle^2 \rangle$$
$$= \langle n^2 \rangle - \langle 2n\langle n \rangle \rangle + \langle \langle n \rangle^2 \rangle = \langle n^2 \rangle - 2\langle n \rangle\langle n \rangle + \langle n \rangle^2$$
$$= \langle n^2 \rangle - \langle n \rangle^2 = \langle n^2 \rangle + \langle n \rangle - \langle n \rangle - \langle n \rangle^2$$
$$= \langle n(n-1) \rangle + \langle n \rangle - \langle n \rangle^2 \qquad \langle n \rangle = Np \text{ is constant!}$$

Let's calculate first
$$\langle n(n-1) \rangle = \sum_{n=2}^N n(n-1)\, P_N(n)$$

$$= N(N-1)p^2 \sum_{n=2}^N \frac{(N-2)!}{(n-2)!\,(N-n)!} p^{n-2} q^{N-n}$$

$$= N(N-1)p^2 \sum_{n=0}^{N-2} \frac{(N-2)!}{n!\,(N-n-2)!} p^n q^{N-n-2}$$

$$= N(N-1)p^2(p+q)^{N-2} = N(N-1)p^2$$

Stirling Approximation: $\ln n! \approx n\ln n - n$ and $p + q = 1$

This yields $\sigma^2 = N(N-1)p^2 + Np - N^2 p^2 = Npq$.
In a room with roughly $N = 10^{25}$ molecules and $p = 0,1$, the fluctuation is about $\sigma = \sqrt{Npq} \approx 10^{12}$.
Where is the peak of $P_N(n)$? Expectation: $\langle n \rangle$. Calculation:
Equivalent: Peak von $\ln P_N(n)$ (easier):
$$\ln P_N(n) = \ln N! - \ln n! - \ln(N-n)! + n\ln p - (N-n)\ln q$$
$$\approx N\ln N - n\ln n - (N-n)\ln(N-n) + n\ln p + (N-n)\ln q$$
$$\frac{d}{dn} P_N(n) = -\ln n + \ln(N-n) + \ln\frac{p}{q} \overset{!}{=} 0 \quad \Leftrightarrow \quad n = Np$$

Shape of the peak: Taylor Expansion von $\ln P_N(n)$:
$$\left.\frac{d^2}{dn^2}\ln P_N(n)\right|_{n=Np} = \left. -\frac{1}{n} - \frac{1}{N-n}\right|_{n=Np} = -\frac{p+q}{Npq} = -\frac{1}{\sigma^2}$$
$$\Rightarrow \ln P_N(n) \approx P_N(\langle n \rangle) - \frac{1}{2\sigma^2}(n - \langle n \rangle)^2$$
$$\Leftrightarrow P_N(n) \approx P_N(\langle n \rangle)e^{-(n-\langle n \rangle)^2/2\sigma^2} \text{ (Gaussian Distribution)}$$

2 Basic ideas

2.1 Types of Systems and States

Isolated System:

E, V, N fixed, Microcanoical Ensemble, $S = k \ln W$

Closed System:

T, V, N fixed (equilibrium with heat bath), Canonical Ensemble, $F = -kT \ln Z$

Open System:

T, V, μ fixed (equilibrium with heat bath and particle reservoir), Grand Canonical Ensemble

Explain Micro-/Macrostate and Distribution with example of $N = 3$ distinguishable particles with allowed energy states $E_i = m_i \varepsilon$, $m_i \in \mathbb{N}$ and total energy $E = 3\varepsilon$.

Microstates:

Energy level of each particle, e.g. $E_1 = 3\varepsilon, E_2 = 0\varepsilon, E_3 = 2\varepsilon$ is one microstate.

Since particles are distinguishable in this case, rearrangement of the same energy values among the particles are different microstates.

Accessible Microstates:

Only Microstates with total energy 3ε are accessible in this case. Here, there are $C_3^{3+3-1} = 10$ different accessible microstates.

Distributions:

A distribution is a string $\{n_0, n_1, n_2, \dots \}$, in which n_i the number of atoms with energy $i\varepsilon$ characterizes. In this case, there are the following three distributions possible:

d_1: $\{0,3,0,0,0 \dots \}$, including one microstate.

d_2: $\{2,0,0,1,0,0 \dots \}$, including three microstates.

d_3: $\{1,1,1,0,0,0 \dots \}$, including six microstates.

Constraints as formulas:

$N = \sum_i n_i \qquad E = \sum_i \varepsilon_i n_i$

Macrostates:

Tupel (E, V, N).

Divide problem: $W(E, V, N) = \sum_i w(d_i)$ with

$w(d_1) = \frac{3!}{3!} = 1 \qquad w(d_2) = \frac{3!}{2!1!} = 3 \qquad w(d_3) = \frac{3!}{1!1!1!} = 6$

(numerator: number of particles; denominator: distribution)

Postulate: In isolated systems equilibrium, all microstates are equally probable.

2.2 Phase Space

1D harmonic oscillator: $E = \frac{p_x^2}{2m} + \frac{m\omega^2}{2} x^2$.

Phase space is the space (x, p_x), in which the allowed states are defined by E. This yields an ellipse.
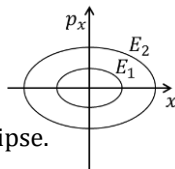
Particle in 3D $\Longrightarrow$ 6D phase space.

N particles in 3D $\Longrightarrow$ $6N$ dimensions, each point defines one microstate. For conservative forces, E is constant and defines a $6N - 1$ dimensional hypersurface. In an infinite time, each point of this surface is reached by the system. Therefore, for a measurable quantity A

$$\langle A \rangle := \frac{1}{T} \int_0^T dt\, A(t) = \sum_i p_i A_i = \frac{1}{W} \sum_i A_i$$

Here, p_i is the probability of the system to be in state i. Since all p_i are equal, the last step follows.

In general, for a system $\hat{H}\psi(\{\vec{r}_i\}, \{\vec{p}_i\}) = E\psi(\{\vec{r}_i\}, \{\vec{p}_i\})$, $W(E, V, N)$ is the degeneracy of the energy E in the sense of Quantum Mechanics.

3 Microcanonical Ensemble

3.1 Sackur-Tetrode-Equation

(Derivation for d dimensions: see 10.1).

Ideal gas: $H = \sum_{i=1}^{N} \vec{p}_i^2/2m$. The number of microstates W the should be proportional to the hypersurface on which the states have an energy E:

$$W = \Lambda \prod_{i=1}^{N} \int d^3 r_i \int d^3 p_i \, \delta\left(E - \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}\right)$$

$\Lambda = 1/N! \, h^{3N}$ gives correct answers:

    $1/N!$ eliminates over-counting of states (particles are indist.)

    $1/h^{3N}$ gives correct dimension and makes some sense

        because of the uncertainty principle $\Delta x \Delta p_x \sim h$

Using $\prod_{i=1}^{N} \int d^3 r_i = V^N$, the integral simplifies to

$$W = \frac{V^N}{N! \, h^{3N}} \prod_{i=1}^{N} \int d^3 p_i \, \delta\left(E - \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}\right)$$

Using sphere coordinates and knowing the surface of a D-dimensional sphere is $2r^{D-1} \pi^{D/2}/(D/2-1)!$, it follows ($r = 1$)

$$W = \frac{V^N}{N! \, h^{3N}} \frac{2\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!} \int_0^\infty p^{3N-1} \, dp \, \delta\left(E - \frac{p^2}{2m}\right)$$

Delta functions are transformed as: $\delta(g(x)) = \sum_i \frac{1}{|g'(x_i)|} \delta(x - x_i)$ with x_i being the zeros of g. Therefore:

$$W = \frac{V^N}{N! \, h^{3N}} \frac{2\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!} \int_0^\infty p^{3N-1} \, dp \, \frac{m}{\sqrt{2mE}} \, \delta(p \pm \sqrt{2mE})$$

$$= \frac{V^N}{N! \, h^{3N}} \frac{2\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!} \frac{m}{\sqrt{2mE}} (2mE)^{\frac{3N-1}{2}} = \frac{3NV^N}{2N! \, h^{3N}} \frac{\sqrt{2\pi mE}^{3N}}{\left(\frac{3N}{2}\right)! \, E}$$

Using $\ln x! = x \ln x - x$, it follows

$$S = k \ln W$$

$$= Nk \ln\left(V \frac{\sqrt{2\pi mE}^3}{h^3}\right) + k \ln\left(\frac{3N}{2E}\right) - Nk \ln(N) + Nk$$

$$- k \frac{3N}{2} \ln\left(\frac{3N}{2}\right) + k \frac{3N}{2}$$

$$= Nk \ln\left(\frac{V}{N}\left(\frac{mE}{3\pi\hbar^2 N}\right)^{3/2}\right) + k \ln\left(\frac{3N}{2E}\right) + \frac{5}{2} Nk$$

Because the second ln-Term is only $\sim \ln N$, whereas the others are at least $\sim N$, it can be ignored:

$$S = Nk \ln\left(\frac{V}{N}\left(\frac{mE}{3\pi\hbar^2 N}\right)^{3/2}\right) + \frac{5}{2} Nk$$

Now calculate:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3}{2}\frac{Nk}{E} \quad \Longleftrightarrow \quad E = \frac{3}{2} NkT$$

$$\frac{p}{T} = \frac{\partial S}{\partial V} = \frac{Nk}{V} \quad \Longleftrightarrow \quad pV = NkT$$

Obviously, S is extensive: $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$

3.2 De Broglie Thermal Wavelength

$\boxed{E = \frac{3}{2} NkT}$

What happens, if $S < 0$? That's possible if

$$\frac{V}{N}\left(\frac{mE}{3\pi\hbar^2 N}\right)^{3/2} = \frac{V}{N}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3 < 1$$

de Broglie thermal wavelength: $\lambda_{th} := h/\sqrt{2\pi mkT}$ (which is related to de Broglie matter wavelength $\lambda = h/p$ and $p^2/2m = kT \implies \lambda = h/\sqrt{2mkT}$). It follows $\sqrt[3]{V/N} > \lambda_{th}$: Wavelength smaller than atom-distance.

3.3 Statistical Mechanics Definition of Temperature

Assume isolated system E, V, N with two subsystems, which can only exchange energy (E_1, E_2 not fixed). Then, possible configurations (E_1, E_2) of energy are:

$$(0, E) \cdots (E_1, E - E_1) \cdots (\bar{E}_1, E - \bar{E}_1) \cdots (E, 0)$$

Corresponding number of microstates:

$$W_1(0)W_2(E) \cdots W_1(E_1)W_2(E - E_1) \cdots W_1(\bar{E}_1)W_2(E - \bar{E}_1)$$
$$\cdots W_1(E)W_2(0)$$

Let $\bar{E}_1$ be chosen such that $W_1(\bar{E}_1)W_2(E - \bar{E}_1)$ is the biggest (so dominating) term. Hence, the function $f := \ln(W_1(E_1)W_2(E_2))$ has a maximum at $E_1 = \bar{E}_1$. Therefore:

$\boxed{\begin{aligned} E_2 &= E - E_1 \\ \bar{E}_2 &:= E - \bar{E}_1 \end{aligned}}$

$$0 = \left.\frac{\partial f}{\partial E_1}\right|_{\bar{E}_1} = \left.\frac{\partial \ln W_1}{\partial E_1}\right|_{\bar{E}_1} + \left.\frac{\partial \ln W_2}{\partial E_1}\right|_{\bar{E}_1}$$

$$= \left.\frac{\partial \ln W_1}{\partial E_1}\right|_{\bar{E}_1} + \left.\frac{\partial E_2}{\partial E_1}\frac{\partial \ln W_2}{\partial E_2}\right|_{\bar{E}_2} = \left.\frac{\partial \ln W_1}{\partial E_1}\right|_{\bar{E}_1} - \left.\frac{\partial \ln W_2}{\partial E_2}\right|_{\bar{E}_2}$$

From thermodynamics is known, that in equilibrium, temperatures are equal. Therefore, the definition $\partial \ln W/\partial E = 1/kT$ makes sence:

$$0 = \frac{1}{kT_1} - \frac{1}{kT_2} \Longleftrightarrow T_1 = T_2$$

3.4 Direction of Time

Let there now be a constrained to the states, such that the one with $\bar{E}_1$ (the equilibrium state) is forbidden. If the constrained is removed, energy will be exchanged between the subsystems. At equilibrium, more microstates are accessible, therefore:

$$0 < \frac{d}{dt}\ln(W_1(E_1)W_2(E_2)) = \frac{d}{dt}\ln(W_1(E_1)) + \frac{d}{dt}\ln(W_2(E_2))$$

$$= \frac{dE_1}{dt}\frac{d}{dE_1}\ln(W_1(E_1)) + \frac{dE_2}{dt}\frac{d}{dE_2}\ln(W_2(E_2))$$

$$= \frac{dE_1}{dt}\frac{d}{dE_1}\ln(W_1(E_1)) - \frac{dE_1}{dt}\frac{d}{dE_2}\ln(W_2(E_2))$$

$$= \frac{dE_1}{dt}\left(\frac{1}{kT_1} - \frac{1}{kT_2}\right)$$

Therefore, $T_2 > T_1, \frac{dE_1}{dt} > 0$ and the other way around.

4 FD-/BE-/MB-Distribution

4.1 Fermi-Dirac-Distribution

All three distribution are true for non-interacting particles; hence the total Hamiltonian H is a sum of the single particle Hamiltonias h_i: $H = \sum_j h_j$. So solve the single particle problem first and get the possible energies ϵ_i.

Since for big systems (electron/fermi gas), the energy levels are very dense, it is convenient to group them together into cells, where g_r is the number of energy levels grouped into the r-th cell, n_r are the number of particles within this cell and ϵ_r is the average energy (representing the included dense energy levels). The constraints are now

$$\sum_r n_r = N \qquad \sum_r n_r \epsilon_r = E$$

A distribution now is referred to the groups: $\{n_1, n_2, \ldots, n_r, \ldots\}$ and the number of microstates is

$$W = \sum_{\{n_i\}} W(\{n_i\}) \approx W(\text{most probable distr.}) = W_{mp}$$

To find W_{mp}, one has to maximize $W(\{n_r\})$ using Lagrange multipliers. What is $W(\{n_r\})$? Within the r-th cell, there are n_r occupying g_r single particle states: n_r states are occupied by one fermion, $g_r - n_r$ are not occupied (Pauli principle!). Number of ways to arrange that: $g_r!/(n_r!\,(g_r - n_r)!)$. Hence:

$$W(\{n_r\}) = \prod_r \frac{g_r!}{n_r!\,(g_r - n_r)!}$$

$$\Rightarrow \ln W(\{n_r\}) \approx \sum_r (g_r \ln g_r - n_r \ln n_r - (g_r - n_r)\ln(g_r - n_r))$$

Now, for the most probable distribution, a change in n_r, symbolized by δn_r should vanish:

$$\delta \ln W(\{n_r\}) \approx \sum_r (-\delta n_r \ln n_r - \delta n_r + \delta n_r \ln(g_r - n_r) + \delta n_r)$$

$$= \sum_r \ln\left(\frac{g_r - n_r}{n_r}\right)\delta n_r \overset{!}{=} 0$$

Somehow, here was taken the derivative $\delta/\delta n_r$ and then put δn_r on the other side. Like this, you get the change of $\ln W$ in all possible ways of changing δn_r. Now, the constrictions come in:

$$\sum_r n_r = N \quad \Rightarrow \quad \alpha \sum_r \delta n_r = 0$$
$$\sum_r n_r \epsilon_r = E \quad \Rightarrow \quad \beta \sum_r \delta n_r \epsilon_r = 0$$

That is to say, the sum of changes δn_r must be zero, to maintain the constant N and likewise for the energy. α and β are Lagrange multipliers. Plugging this in yields:

$$\sum_r \left(\ln\left(\frac{g_r - n_r}{n_r}\right) + \alpha + \beta\epsilon_r\right)\delta n_r \overset{!}{=} 0$$

Since this must be true for any change δn_r, it must be true that:

$$\ln\left(\frac{g_r - n_r}{n_r}\right) + \alpha + \beta\epsilon_r = 0 \quad \Leftrightarrow \quad \frac{n_r}{g_r} = \frac{1}{e^{-\alpha - \beta\epsilon_r} + 1}$$

Here, the Lagrange multiplier turn out to be $\beta = -1/kT$ and $\alpha = \mu/kT$:

$$f_{FD}(\epsilon_r) := \frac{n_r}{g_r} = \frac{1}{e^{(\epsilon_r - \mu)/kT} + 1}$$

f_{FD} is the average number of fermions per single-particle state at energy ϵ_r. From that, those formulas follow:

$$N = \sum_r g_r f_{FD}(\epsilon_r) = \sum_{\substack{\text{all single} \\ \text{particle states } i}} f_{FD}(\epsilon_i)$$

$$E = \sum_r \epsilon_r g_r f_{FD}(\epsilon_r) = \sum_{\substack{\text{all single} \\ \text{particle states } i}} \epsilon_r f_{FD}(\epsilon_i)$$

Obviously, S is extensive: $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$

4.2 Bose-Einstein-Distribution

The only difference for Bosons is, that there are no constrictions on occupying the states. So, within the r-th cell, the n_r particles can be distributed in all possible ways on the g_r states. Hecce:

$$W(\{n_r\}) = \prod_r \frac{(g_r + n_r - 1)!}{n_r!\,(g_r - 1)!} \approx \prod_r \frac{(g_r + n_r)!}{n_r!\,g_r!}$$

Since the maximum of $W(\{n_r\})$ is the same as of $\ln W(\{n_r\})$:

$$\ln W(\{n_r\}) \approx \sum_r \left((g_r + n_r)\ln(g_r + n_r) - n_r \ln n_r - g_r \ln g_r\right)$$

$$\Rightarrow \delta \ln W(\{n_r\}) = \sum_r (\delta n_r \ln(g_r + n_r) - \delta n_r \ln n_r)$$

$$= \sum_r \ln\frac{g_r + n_r}{n_r}\delta n_r = \sum_r \left(\ln\frac{g_r + n_r}{n_r} + \alpha + \beta\epsilon_r\right)\delta n_r \overset{!}{=} 0$$

In the last step, again, the restrictions $\alpha \sum_r \delta n_r = 0$ and $\beta \sum_r \delta n_r \epsilon_r = 0$ were used. In the same way as for the Fermi-Dirac-Distribution, the bracket term is set to zero:

$$\ln\frac{g_r + n_r}{n_r} + \alpha + \beta\epsilon_r = 0 \quad \Leftrightarrow \quad f_{BE}(\epsilon_r) := \frac{n_r}{g_r} = \frac{1}{e^{-\alpha - \beta\epsilon_r} - 1}$$

Here, the Lagrange multiplier turn out to be $\beta = -1/kT$ and $\alpha = \mu/kT$:

$$f_{BE}(\epsilon_r) = \frac{n_r}{g_r} = \frac{1}{e^{(\epsilon_r - \mu)/kT} - 1}$$

Since $f_{BE} := n_r/g_r$ should be positive, it follows $e_r > \mu$.

4.3 Maxwell-Boltzmann-Distribution

All particles are either Fermions or Bosons. What, then, does one mean by "classical" particles?

For classical particles is $g_r \gg n_r$, since the states are continuous.

$$W_{FD}(\{n_r\}) = \prod_r \frac{g_r!}{n_r!\,(g_r - n_r)!}$$

$$= \prod_r \frac{\overbrace{g_r(g_r - 1)\cdots(g_r - n_r + 1)}^{n_r \text{ terms}}}{n_r!} \underset{g_r \gg n_r}{\approx} \prod_r \frac{g_r^{n_r}}{n_r!}$$

$$W_{EB}(\{n_r\}) \approx \prod_r \frac{(g_r + n_r)!}{n_r!\,g_r!}$$

$$= \prod_r \frac{\overbrace{(g_r + n_r)(g_r + n_r - 1)\cdots(g_r + 1)}^{n_r \text{ terms}}}{n_r!} \underset{g_r \gg n_r}{\approx} \prod_r \frac{g_r^{n_r}}{n_r!}$$

Hence, in the classical limit, the difference between Bosons und Fermions becomes ignorable. Consider now $W_{MB}(\{n_r\}) := \prod_r g_r^{n_r}/n_r!$ and find the maximum of $\ln W_{MB}$:

$$\ln W_{MB} = \sum_r (n_r \ln g_r - n_r \ln n_r + n_r)$$

$$\Rightarrow \quad \delta \ln W_{MB} = \sum_r (\delta n_r \ln g_r - \delta n_r \ln n_r - \delta n_r + \delta n_r)$$

$$= \sum_r \ln\left(\frac{g_r}{n_r}\right)\delta n_r = \sum_r \left(\ln\left(\frac{g_r}{n_r}\right) + \alpha + \beta\epsilon_r\right)\delta n_r \overset{!}{=} 0$$

In the last step was as usual used, that $\alpha \sum_r \delta n_r = 0$ and $\beta \sum_r \delta n_r \epsilon_r = 0$. Further:

$$\ln\left(\frac{g_r}{n_r}\right) + \alpha + \beta\epsilon_r \overset{!}{=} 0 \quad \Leftrightarrow \quad \frac{n_r}{g_r} = e^\alpha e^{\beta\epsilon_r}$$

Now, also α can be determined (β turns again out to be $-1/kT$):

$$N = \sum_r n_r = \sum_r g_r e^\alpha e^{-\epsilon_r/kT} = e^\alpha \sum_{\text{cells } r} g_r e^{-\epsilon_r/kT}$$

$$= e^\alpha \sum_{\text{states } i} e^{-\epsilon_i/kT} = e^\alpha z \quad \Leftrightarrow \quad e^\alpha = N/z$$

This, actually, is quite physically:

$$f_{MB}(\epsilon_r) := \frac{n_r}{g_r} = N\frac{e^{-\frac{\epsilon_r}{kT}}}{z} = NP(\epsilon_r)$$

4.4 Density of States

For a continuous problem, g_r becomes the density of single particle states $g(\epsilon)$. This yields:

$$E = \sum_r g_r f(\epsilon_r)\epsilon_r = \int d\epsilon\, g(\epsilon)\epsilon f(\epsilon), \qquad N = \int d\epsilon\, g(\epsilon)\epsilon f(\epsilon)$$

Here, f could be f_{FD}, f_{BE} or f_{MB}. In the particle in a box-problem (free particles with boundary condition), the states are equally spaced in k-space, namely like $k_i = n_i\pi/L$. The density of state is therefore $D_d = G_s V/(2\pi)^d$, where G_s is the spin-degeneracy and d symbolizes the dimension of the problem.

Therefore, it is convenient to evaluate $D_d d^d k = g_{dp}(\epsilon)d\epsilon$ (in d dimensions). If the dispersion relation is $\epsilon = \alpha k^p$, with some power $p \in \mathbb{R}$, then:

$$D_d d^d k = D_d S_d k^{d-1} dk = \frac{D_d S_d}{p\alpha} k^{d-p} d\epsilon = \frac{D_d S_d}{p\alpha}\left(\frac{\epsilon}{\alpha}\right)^{\frac{d-p}{p}} d\epsilon$$

Here, S_d is the surface area of an d-dimensional sphere with radius 1. Hence, the density of states in energy is

$$g(\epsilon) = \frac{D_d S_d}{p\alpha^{d/p}}\epsilon^{\frac{d-p}{p}}$$

For the most common cases, $p = 2$, $\alpha = \hbar^2/2m$ and $D = G_s V/(2\pi)^3$, this yields (in 1D, V is an length, in 2d an area):

$$
g(\epsilon) =
\begin{cases}
\dfrac{D_1 S_1}{2\alpha^{1/2}}\epsilon^{\frac{1-2}{2}} = \dfrac{\left(G_s \frac{V}{2\pi}\right)\cdot 2}{2\left(\frac{\hbar^2}{2m}\right)^{1/2}}\epsilon^{-1/2} = \dfrac{G_s V}{2\pi}\left(\dfrac{2m}{\hbar^2}\right)^{1/2}\epsilon^{-1/2}, & d = 1 \\[4mm]
\dfrac{D_2 S_2}{2\alpha^{2/2}}\epsilon^{\frac{2-2}{2}} = \dfrac{\left(G_s \frac{V}{(2\pi)^2}\right)\cdot 2\pi}{2\left(\frac{\hbar^2}{2m}\right)^{2/2}} = \dfrac{m G_s V}{2\pi\hbar^2}, & d = 2 \\[4mm]
\dfrac{D_3 S_3}{2\alpha^{3/2}}\epsilon^{\frac{3-2}{2}} = \dfrac{\left(G_s \frac{V}{(2\pi)^3}\right)\cdot 4\pi}{2\left(\frac{\hbar^2}{2m}\right)^{3/2}}\epsilon^{1/2} = \dfrac{G_s V}{4\pi^2}\left(\dfrac{2m}{\hbar}\right)^{3/2}\epsilon^{1/2}, & d = 3
\end{cases}
$$

Formula for volume $\mathcal{V}_d$ and surface area S_d of d-dimensional sphere with radius R:

$$\mathcal{V}_d = \frac{\pi^{d/2}}{\frac{d}{2}\Gamma(d/2)}R^d, \qquad S_d = \frac{\partial \mathcal{V}_d}{\partial R} = \frac{2\pi^{d/2}}{\Gamma(d/2)}R^{d-1}$$
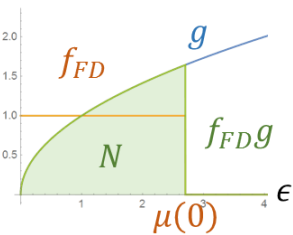
4.5 Density of States and the Distribution-Functions
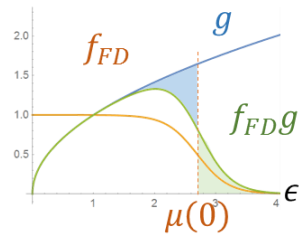
Accepting, that $\beta = 1/kT$, the equation

$$N = \sum_r g_r f(\epsilon_r) = \int_0^\infty d\epsilon\, g(\epsilon)f(\epsilon) = \int_0^\infty d\epsilon\, g(\epsilon)f(\epsilon)$$

determines $\mu(T)$. For $T = 0$, f_{FD} is a step dropping at μ and the area beneath g up to μ is N. For higher temperatures, N must be constant, so the blue and green areas must have the same size. To achieve this, $\mu(T) < \mu(0)$.

4.6 Maxwell's Distribution of Speeds

The distribution $n(v)$ can be derived using the density of states. But since $n(v)$ is a particle density, the number of particles in the states have to be multiplied:

$$n(v)dv = D(k)d^3 k\frac{N e^{-\beta\hbar^2 k^2/2m}}{z} = \left(\frac{L}{2\pi}\right)^3 4\pi k^2 dk\frac{N e^{-\beta\hbar^2 k^2/2m}}{z}$$

Using $v = p/m = \hbar k/m$ yields (using $L^3 = V$):

$$n(v)dv = \left(\frac{L}{2\pi}\right)^3 4\pi\left(\frac{mv}{\hbar}\right)^2\frac{m}{\hbar}dv\frac{e^{-\beta mv^2/2}}{z}$$

$$\Rightarrow \quad n(v) = \frac{4\pi NV}{(2\pi)^3}\left(\frac{m}{\hbar}\right)^3 v^2\frac{e^{-\beta mv^2/2}}{\frac{1}{(2\pi\hbar)^3}\int d^3 x\int d^3 p\, e^{-\beta p^2/2m}}$$

$$= 4\pi\hbar^3 N\left(\frac{m}{\hbar}\right)^3 v^2\frac{e^{-\beta mv^2/2}}{\left(\int dp_x\, e^{-\beta p_x^2/2m}\right)^3}$$

$$= 4\pi N m^3 v^2\frac{e^{-\beta mv^2/2}}{(2\pi m kT)^{3/2}} = N\frac{4\pi m^3 v^2}{(2\pi m kT)^{3/2}}e^{-mv^2/2kT}$$

Of course, the same can be achieved using the energy relation

$$n(v)dv = n(\epsilon)d\epsilon = N g(\epsilon)\frac{e^{-\beta\epsilon}}{z}d\epsilon$$

with $\epsilon = m/2\, v^2$.

5 Canonical Ensemble

5.1 Partition Function

Consider an isolated system with two subsystems, which can only exchange energy. Let now be subsystem 1 = *heat bath* and subsystem 2 = *system* with (E_B, V_B, N_B, T_B) and (E, V, N, T) with fixed volumes and particle numbers and fixed total energy $E_0 = E_B + E$. Moreover is the bath so big, that $T_B = T$ after a long time (T_B fixed). Possible configurations (E, E_B):

$$(0, E_0) \cdots (E_i, E_0 - E_i) \cdots (\bar{E}, E - \bar{E}) \cdots (E_0, 0)$$

Corresponding number of microstates:

$$W_S(0)W_B(E_0) \cdots W_S(E_i)W_B(E_0 - E_i) \cdots W_S(\bar{E})W_B(E_0 - \bar{E})$$
$$\cdots W_S(E_0)W_B(0)$$

Probability of energy level $E = E_i$ (W = total number of mircos.)

$$\mathcal{P}(E_i) = \frac{1}{W} W_S(E_i) W_B(E_0 - E_i)$$

But there are several microstates $W_S(E_i)$, which is the degeneracy of that energy E_i. Therefore, the probability of one state with E_i is:

$$P(E_i) := \frac{1}{W} W_B(E_0 - E_i) \sim W_B(E_0 - E_i)$$

To calculate W_B, consider Taylor expansion at E_0:

$$\ln W_B(E_0 - E_i) \approx \ln W_B(E_0) + \left.\frac{\partial \ln W_B(E)}{\partial E}\right|_{E_0} (E_0 - E_i - E_0)$$

$$\frac{\partial^2 \ln W_B}{\partial^2 E} \sim \frac{\partial^2 S}{\partial E^2} \sim \frac{\partial}{\partial E}\frac{1}{T_B} \sim \frac{1}{C_B} \ll 1$$
(heat capacity of bath is huge, so ignore second order)

$$= \ln W_B(E_0) - \frac{1}{kT_B}E_i = \ln W_B(E_0) - \frac{1}{kT}E_i$$

$$\Rightarrow P(E_i) \sim W_B(E_0 - E_i) \sim e^{-E_i/kT}$$

Since $P(E_i)$ is a probability, it must be normalized:

$$1 = \sum_{\substack{\text{all} \\ \text{states}}} c e^{-E_i/kT} \iff c = \left(\sum_{\substack{\text{all} \\ \text{states}}} e^{-E_i/kT}\right)^{-1} = \frac{1}{Z(T,V,N)}$$

Note, that $E_i \equiv E_i(V, N)$

5.2 Energy Distribution

$$\beta := \frac{1}{kT}$$

Mean energy (each index i represents one state):

$$\langle E \rangle = \sum_i E_i P(E_i) = \sum_i \frac{E_i}{Z} e^{-\beta E_i} = -\frac{1}{Z}\frac{\partial}{\partial \beta}\sum_i e^{-\beta E_i} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta}\ln Z = kT^2\frac{\partial}{\partial T}\ln Z \qquad \frac{\partial f}{\partial \beta} = \frac{\partial f}{\partial T}\frac{\partial T}{\partial \beta} = -kT^2\frac{\partial f}{\partial T}$$

Standard derivation:

$$\langle E^2 \rangle = \sum_i E_i^2 P(E_i) = \frac{1}{Z}\frac{\partial^2}{\partial \beta^2}\sum_i e^{-\beta E_i} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$$

$$\Rightarrow \sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = -\frac{\partial \langle E \rangle}{\partial \beta}$$

$$= kT^2\frac{\partial \langle E \rangle}{\partial T} = kT^2 C_V$$

Since C_V is extensive, σ_E^2 is also extensive, hence $\sigma_E^2 \sim N, \sigma_E \sim \sqrt{N}$. The shape is of course Gaussian $\sim e^{-(E - \langle E \rangle)^2/2\sigma_E^2}$.

5.3 Connection to Thermodynamics

In contrast to $W \equiv W(E, V, N)$, for the partition function $Z \equiv Z(T, V, N)$ is true, due to the heat bath with constant temperature T. Those are the natural variables of the Helmholtz free energy:

$$F = E - TS \implies dF = dE - TdS - SdT = -SdT - pdV + \mu dN$$

Furthermore $\langle E \rangle = kT^2 \partial/\partial T \ln Z$ was found. There should be also something like $E = kT^2 \partial/\partial T X$ in thermodynamics. What is X? Consider:

$$d\left(\frac{F}{T}\right) = \frac{1}{T}dF - \frac{F}{T^2}dT = \frac{1}{T}(-SdT - pdV + \mu dN) - \frac{F}{T^2}dT$$

$$= -\frac{1}{T^2}(ST + F)dT - \frac{p}{T}dV + \frac{\mu}{T}dN = -\frac{E}{T^2}dT - \frac{p}{T}dV + \frac{\mu}{T}dN$$

So, obviously:

$$\frac{d}{dT}\frac{F}{T} = -\frac{E}{T^2} \iff E = -T^2\frac{d}{dT}\frac{F}{T} = kT^2\frac{\partial}{\partial T}\left(-\frac{F}{kT}\right)$$

Hence $F = -kT\ln Z$.

5.4 Connection to Quantum Mechanics

$$Z = \sum_i e^{-\beta E_i} = \sum_i \underbrace{\langle i | \sum_i e^{-\beta \hat{H}} | i \rangle}_{=\mathcal{H}_{ii}} = \text{Trace}(\mathcal{H})$$

The trace of a matrix is always independent from the chosen basis $|i\rangle$.

5.5 Qualitative Description

Consider again

$$\mathcal{P}(E_i) = \frac{1}{W}W_S(E_i)W_B(E - E_i) \sim W_S(E_i)e^{-E_i/kT}$$

In a closed system, the energy is not fixed and therefore not all the (micro-)states are equally probable. States with high energy are less probably ($e^{-E_i/kT}$), however, the number of degenerated states increases with energy ($W_S(E_i)$). Therefore there is a sharp mean $\langle E \rangle$ with small fluctuations.

5.6 Example I: Classical Ideal Gas

The partition function of an classical ideal gas is given by integrals instead of sums with $H = \sum_{i=1}^N \vec{p}_i^2/2m$:

$$Z = \frac{1}{N! \, h^{3N}}\int d^3x_1 \cdots \int d^3x_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H}$$

$$= \frac{1}{N! \, h^{3N}}\left(V\int d^3p \, e^{-\beta \vec{p}^2/2m}\right)^N = \frac{1}{N!}z^n$$

The single particle partition function is

$$z = \frac{V}{h^3}\int d^3p \, e^{-\beta \vec{p}^2/2m} = \frac{V}{h^3}\left(\int dp_x \, e^{-\beta p_x^2/2m}\right)^3 = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

$$= V\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3 = \frac{V}{\lambda_{th}^3}$$

$$\Rightarrow Z = \frac{z^N}{N!} = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N \qquad \Rightarrow F = -kT\ln Z$$

$$\Rightarrow p = -\frac{\partial F}{\partial V} = \frac{NkT}{V} \qquad \langle E \rangle = -\frac{\partial}{\partial \beta}\ln Z = \frac{3}{2}NkT$$

5.7 Equipartition Theorem

Let the Hamilton be $H(\{\vec{x}_i, \vec{p}_i\}) = aq^2 + [\text{Other}]$. Here, q is any x_{ji}-coordinate (e.g. $x_{2,5}$, the y-coordiante of the 5th particle) and "[Other]" are any other terms independent of q. Then, the contribution of the aq^2-term to the energy is:

$$\frac{\int dq \int d[\text{Other}] \, aq^2 \, e^{-\beta aq^2}e^{-\beta[\text{Other}]}}{\int dq \int d[\text{Other}] \, e^{-\beta aq^2}e^{-\beta[\text{Other}]}} = \frac{\int dq \, aq^2 \, e^{-\beta aq^2}}{\int dq \, e^{-\beta aq^2}}$$

$$= -\frac{\partial}{\partial \beta}\ln\left(\int_{-\infty}^{\infty} dq \, e^{-\beta aq^2}\right) = -\frac{\partial}{\partial \beta}\ln\sqrt{\frac{\pi}{a\beta}} = \frac{1}{2}kT$$

Hence, every quadratic term in the Hamiltonian contributes $kT/2$ to the energy. This is even true for terms like $x_{2,5}p_{1,1}$.

5.8 Example II: Two-level systems

Consider N distinguishable particles, all of which can access only two energy levels (those levels might differ from particle to particle) with the energies ϵ_{li} (lower level, i-th particle) and ϵ_{ui} (upper level, i-th particle). Define a state via the energy values of each particle: $\{\epsilon_1, \ldots, \epsilon_N\}, \epsilon_i \in \{\epsilon_{li}, \epsilon_{ui}\}$. There are 2^N different states. Total energy: $E(\{\epsilon_i\}) = \sum_{(i=1)}^N \epsilon_i$. Partition function:

$$Z = \sum_{\substack{\text{all} \\ \text{states}}} e^{-\beta E(\{\epsilon_i\})} = \sum_{\epsilon_1 = \epsilon_{l1}, \epsilon_{u1}} \cdots \sum_{\epsilon_N = \epsilon_{lN}, \epsilon_{uN}} e^{-\beta \sum_{i=1}^N \epsilon_i}$$

$$= \prod_{i=1}^N \sum_{\epsilon_i = \epsilon_{li}, \epsilon_{ui}} e^{-\beta \epsilon_i} = \prod_{i=1}^N z_i$$

Here, z_i is the partition function of a single particle.

$$\implies F = -kT \ln Z = -kT \sum_{i=1}^\infty \ln z_i$$

Simplest case: All particles have the same energy levels: $\epsilon_{li} = \epsilon_l = -\epsilon/2$ and $\epsilon_{ui} = \epsilon_u = \epsilon/2$. This yields $Z = z^N$ and

$$z = e^{-\beta \epsilon/2} + e^{\beta \epsilon/2}$$

For one particle let the probability to have a Energy ε be $P(\varepsilon)$:

$$\implies P(-\epsilon/2) = e^{\beta \epsilon/2}/z \qquad P(\epsilon/2) = e^{-\beta \epsilon/2}/z$$

Note $P(-\epsilon/2) > P(\epsilon/2)$.

Low temperature case: $\beta \epsilon/2 \gg 1 \implies z \approx e^{\beta \epsilon/2}$

$$\implies P(-\epsilon/2) \approx 1 \qquad P(\epsilon/2) \approx 0$$

Hight temperature case: $\beta \epsilon/2 \ll 1 \implies z \approx e^0 + e^0 = 2$

$$\implies P(-\epsilon/2) \approx 1/2 \qquad P(\epsilon/2) \approx 1/2$$

Mean energy:

$$\langle E \rangle = -\frac{\epsilon}{2} \frac{1}{z} e^{\frac{\beta \epsilon}{2}} + \frac{\epsilon}{2} \frac{1}{z} e^{-\frac{\beta \epsilon}{2}} = -\frac{\epsilon}{2} \frac{e^{\frac{\beta \epsilon}{2}} - e^{-\frac{\beta \epsilon}{2}}}{e^{\frac{\beta \epsilon}{2}} + e^{-\frac{\beta \epsilon}{2}}} = -\frac{\epsilon}{2} \tanh\left(\frac{\epsilon}{2kT}\right)$$

5.9 Example III: Paramagnetism

Magnetisation of a material: $M = \chi H$

$$\implies B = \mu_0(H + M) = \mu_0(1 + \chi)H = \mu_0 \mu_r H$$

But experimental one finds $\chi \equiv \chi(T) \sim 1/T$ (Pierre Curie's Law) Can one find this behavior using statistical mechanics?

Assumption: Solid, array of N magnetic moments, independent, distinguishable ($Z = z^N$). In general is $\vec{\mu} = -\frac{ge}{2m}\vec{j}$ ($\vec{j}$ is angular momentum, g is Landé factor), in this case consider the spin with $g \approx 2$ and $\vec{j} = \vec{s}$. The energy of a particle within a magnetic field $\vec{B} = B\vec{e}_z$ is

$$E = -\vec{\mu}\vec{B} = -\mu_z B = \frac{e}{m} B s_z = \frac{e\hbar}{m} B m_s = 2\mu_B B m_s = \pm \mu_B B$$

(μ_B is Bohr magneton). The partition function is therefore

$$z = e^{\beta \mu_B B} + e^{-\beta \mu_B B}$$

which yields the following mean (note that $\mu_z \sim -s_z$):

$$\langle \mu_z \rangle = \mu_B e^{\beta \mu_B B}/z - \mu_B e^{-\beta \mu_B B}/z = \mu_B \frac{e^{\beta \mu_B B} - e^{-\beta \mu_B B}}{e^{\beta \mu_B B} + e^{-\beta \mu_B B}}$$

$$= \mu_B \tanh\left(\frac{\mu_B B}{kT}\right)$$

$$\implies M = \frac{N}{V} \langle \mu_z \rangle = \frac{N}{V} \mu_B \tanh\left(\frac{\mu_B B}{kT}\right)$$

For room temperature is $kT \gg \mu_B B$ (using $B \approx 1$ T). Therefore, using $\tanh x \approx x, x \ll 1$ yields (Paramagnetism: $\mu_r \approx 1$):

$$M = \frac{N}{V} \frac{\mu_B^2 B}{kT} \approx \frac{N}{V} \frac{\mu_B^2 \mu_0}{kT} H \overset{!}{=} \chi H \iff \chi = \frac{N}{V} \frac{\mu_B^2 \mu_0}{kT} \sim \frac{1}{T}$$

Mean energy (one atom):

$$\langle E \rangle = -\mu_B B \frac{e^{\beta \mu_B B}}{z} + \mu_B B \frac{e^{-\beta \mu_B B}}{z} = -\mu_B B \tanh(\beta \mu_B B)$$

(This is also the solution of $\langle E \rangle = -\partial/\partial\beta \ln z$)

If we want to consider not only the spin but a general $\vec{j}$, a one particle system has access to $2j + 1$ states ($-j < m_j < j$) with energies $E = -\mu_z B = \frac{ge}{2m} j_z B = \frac{ge\hbar}{2m} m_j B = g\mu_B m_j B$ Partition function:

$$z = \sum_{m_j=-j}^j e^{-\beta g\mu_B B m_j}$$

Using $\sum_{n=0}^N x^n = (1 - x^{N+1})/(1 - x)$ yields with $x = e^{-\beta g\mu_B B}$:

$$z = \sum_{m_j=-j}^j x^{m_j} = \sum_{m_j=1}^j x^{-m_j} + \sum_{m_j=0}^j x^{m_j} = -1 + \sum_{m_j=0}^j \left(\frac{1}{x}\right)^{m_j} + \sum_{m_j=0}^j x^{m_j}$$

$$= -1 + \frac{1 - \left(\frac{1}{x}\right)^{j+1}}{1 - \frac{1}{x}} + \frac{1 - x^{j+1}}{1 - x} = \frac{x^{-j} - x^{j+1}}{1 - x} = \frac{e^y - e^{-y(j+1)/j}}{1 - e^{-y/j}}$$

$$= e^y \frac{1 - e^{-(2j+1)y/j}}{1 - e^{-y/j}} = \frac{e^{(2j+1)y/2j}}{e^{y/2j}} \frac{1 - e^{-(2j+1)y/j}}{1 - e^{-y/j}}$$

$$= \frac{e^{(2j+1)y/2j} - e^{-(2j+1)y/2j}}{e^{y/2j} - e^{-y/2j}} = \sinh\left(\frac{2j+1}{2j}y\right)\Big/\sinh\left(\frac{y}{2j}\right)$$

In the end, $y = \beta g\mu_B jB$ was used, so that $x = e^{-y/j}$.

Note, that the above equation for $\langle \mu_z \rangle = \mu_B e^{\beta \mu_B B}/z - \mu_B e^{-\beta \mu_B B}/z$ can also be achieved with

$$\langle \mu_z \rangle = \frac{1}{z\beta} \frac{\partial z}{\partial B} = \frac{\partial}{\partial B} kT \ln z = -\frac{1}{N} \frac{\partial F}{\partial B}$$

In the last step, the Helholtz-Free-Energy $F = -kT \ln Z = -NkT \ln z$ was used. Now, the magnetization M is

$$M = \frac{N}{V} \langle \mu_z \rangle = -\frac{1}{V} \frac{\partial F}{\partial B} = \frac{NkT}{V} \frac{\partial}{\partial B} \ln z$$

$$= \frac{NkT}{V} \frac{\partial}{\partial B} \ln\left(\sinh\left(\frac{2j+1}{2j}y\right)\Big/\sinh\left(\frac{y}{2j}\right)\right)$$

$$= \frac{Ng\mu_B j}{V} \left(\frac{2j+1}{2j} \coth\left(\frac{2j+1}{2j}y\right) - \frac{1}{2j} \coth\left(\frac{y}{2j}\right)\right)$$

$$= \frac{Ng\mu_B j}{V} B_j(y)$$

Here, $B_j(y)$ is the Brillouin function.

5.10 Example IV: Classical Langevin Theory of Paramagnetism

Classically, the directions of the magnetic momentums are not quantized: Is has to be described using angles $\theta_i \in \{0, \pi\}$ and $\varphi_i \in \{0, 2\pi\}$ for the i-th particle. The energy for $\vec{B} = B\vec{e}_z$ is then:

$$E_i = -\vec{\mu}_i \vec{B} = -\mu B \cos \theta_i$$

A state is described by $\{\theta_1, \varphi_1, \ldots, \theta_N, \varphi_N\}$. The sum over all states becomes an integral:

$$Z = \int d\Omega_1 \cdots \int d\Omega_N \, e^{-\beta \mu B \sum_{i=1}^N \cos \theta_i} = \prod_{i=1}^N \int d\Omega_i \, e^{-\beta \mu B \cos \theta_i}$$

$$= \left(\int_0^{2\pi} \int_0^{\pi} d\varphi d\theta \, \sin \theta \, e^{-\beta \mu B \cos \theta} \right)^N = \underbrace{\left(\frac{4\pi}{\beta \mu B} \sinh(\beta \mu B) \right)^N}_{=z^N}$$

The magnetization is, again (using $y = \beta \mu B$):

$$M = \frac{N}{V} \langle \mu_z \rangle = -\frac{1}{V} \frac{\partial F}{\partial B} = \frac{N}{V\beta} \frac{\partial}{\partial B} \ln z = \frac{N}{V\beta} \beta \mu \frac{\partial}{\partial y} \ln \left(\frac{4\pi}{y} \sinh y \right)$$

$$= \frac{N\mu}{V} \left(\coth y - \frac{1}{y} \right) = \frac{N\mu}{V} L(y) \qquad L(y) \to \text{Langevin function}$$

For $y = \mu B / kT \ll 1$, Curie's Law can be derived again.

5.11 Example V: Harmonic Oscillators

For N harmonic oscillators, the partition function is:

$$Z = \sum_{n_1=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} e^{-\beta \sum_{i=1}^N \hbar \omega_i \left(n_i + \frac{1}{2} \right)} = \prod_{i=1}^N \sum_{n_i=0}^{\infty} e^{-\beta \hbar \omega_i \left(n_i + \frac{1}{2} \right)} = \prod_{i=1}^N z_i$$

The Helmholtz Free Energy is: $F = -kT \ln Z = -kT \sum_{i=1}^N \ln z_i$

Now, focus on just one particle (use $\sum_{n=0}^{\infty} x^n = 1/(1-x)$):

$$z = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega \left(n + \frac{1}{2} \right)} = e^{-\beta \frac{\hbar \omega}{2}} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega n} = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}}$$

Further, the mean energy is

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln z = \frac{\hbar \omega}{2} + \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} = \hbar \omega \left(\frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right)$$

For $kT \gg \hbar \omega$, $e^{\beta \hbar \omega} \approx 1 + \beta \hbar \omega$ yields $\langle E \rangle \approx \hbar \omega / 2 + kT \approx kT$. Hence, the mean excitation is

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1}$$

Heat Capacity:

$$C = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial}{\partial T} \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1} = k \left(\frac{\hbar \omega}{kT} \right)^2 \frac{e^{\hbar \omega / kT}}{(e^{\hbar \omega / kT} - 1)^2} = k \, E \left(\frac{\hbar \omega}{kT} \right)$$

Here, $E(x) = x^2 e^x / (e^x - 1)^2$ is the Einstein function.

For low temperature $\hbar \omega / kT \gg 1$:

$$C \approx k \frac{\hbar \omega}{kT} e^{-\frac{\hbar \omega}{kT}} \to 0$$

For high temperature $\hbar \omega / kT \ll 1$:

$$e^{\hbar \omega / kT} \approx 1 - \hbar \omega / kT$$

$$\implies \quad C \approx k \left(\frac{\hbar \omega}{kT} \right)^2 \frac{1}{(\hbar \omega / kT)^2} = k \qquad \text{(one particle!)}$$

6 Heat Capacity of Solids

6.1 Einstein's Model (1907)

Assumptions:

N atoms form $3N$ harmonic oscillators in a 3-dimensional solid. All oscillators have the same frequency ω_E.

Then, the heat capacity is (see 5.11):

$$C = \sum_{n=1}^{3N} k \left(\frac{\hbar\omega_E}{kT}\right)^2 \frac{e^{\hbar\omega_E/kT}}{(e^{\hbar\omega_E/kt} - 1)^2} = 3Nk \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

Here, $\theta_E = \hbar\omega_E/k$ is called the Einstein temperature. This was the most accurate theory at this time, but for low temperatures, it drops too rapidly.

6.2 Debye's Model (1912)

In Debye's model, the frequencies of the oscillators are not the same. Since all the N atoms in the lattice are coupled by "springs", they have different normal modes (like two particles with one spring connected have two modes, three have three modes etc.). The normal modes are still independent, so it is possible to sum them up to get the energy:

$$E = \sum_{i=1}^{3N} \hbar\omega_i \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega_i/kT} - 1}\right)$$

For many particles, ω_i forms approximately a continuum with a density $D(\omega)$ and E becomes:

$$E = \int_0^\infty d\omega \, D(\omega) \, \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/kT} - 1}\right)$$

It is found, that for small ω, $D(\omega)$ goes like ω^2. Hence, Debye assumes $D(\omega) = A\omega^2 \, \theta(\omega - \omega_D)$, which implies the condition

$$\int_0^\infty d\omega \, D(\omega) = A \int_0^{\omega_D} d\omega \, \omega^2 \overset{!}{=} 3N \quad \Leftrightarrow \quad A = \frac{9N}{\omega_D^3}.$$

Now, the energy becomes:

$$E = \int_0^{\omega_D} d\omega \, A\omega^2 \, \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/kT} - 1}\right)$$

$$= \frac{A\hbar}{2} \int_0^{\omega_D} d\omega \, \omega^3 + A\hbar \int_0^{\omega_D} d\omega \, \frac{\omega^3}{e^{\hbar\omega/kT} - 1}$$

$$= \frac{9}{8} N\hbar\omega_D + A\hbar \left(\frac{kT}{\hbar}\right)^4 \int_0^{\hbar\omega_D/kT} dx \, \frac{x^3}{e^x - 1} \overset{kT \ll \hbar\omega_D}{\approx} \frac{9}{8} N\hbar\omega_D$$

$$+ A\hbar \left(\frac{kT}{\hbar}\right)^4 \int_0^\infty dx \, \frac{x^3}{e^x - 1} = \frac{9}{8} N\hbar\omega_D + \frac{9N\pi^4\hbar}{15\omega_D^3} \left(\frac{kT}{\hbar}\right)^4$$

Now, the heat capacity goes like $C = \partial E/\partial T \sim T^3$ with fulfills the experimental results.

Physically speaking, in the Einstein model, $e^{\hbar\omega_E/kT}$ declines suddenly, when $\hbar\omega_E \ll kT$. But in Debye model, there are different ω's, also bigger ones than ω_E. And those prevent the heat capacity to drop so fast.

7 Interacting Systems

7.1 Partition Function of Non-Ideal Gas

Assume potential of shape like the Lennard-Jones potential. Then, the Hamiltonian is

$$H(\{\vec{x}_i, \vec{p}_i\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + W(\{\vec{x}_i\}), \qquad W(\{\vec{x}_i\}) = \sum_{i>j} U(|\vec{x}_i - \vec{x}_j|).$$

Here, $U(|\vec{x}_i - \vec{x}_j|) = U(x_{ij})$ might be the Lennard-Jones potential. Use for simplicity $\int Dx := \int d^3x_1 \cdots \int d^3x_N$:

$$
\begin{aligned}
Z &= \frac{1}{N! \, h^{3N}} \int Dx \int Dp \, e^{-\beta H} \\
&= \underbrace{\frac{V^N}{N! \, h^{3N}} \int Dp \, e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}}}_{=Z_{\text{ideal}} \equiv Z_i} \frac{1}{V^N} \int Dx \, e^{-\beta W} \\
&= \frac{Z_i}{V^N} \int Dx \prod_{i>j} \underbrace{e^{-\beta U(x_{ij})}}_{=1+\lambda_{ij}} \\
&= \frac{Z_i}{V^N} \int Dx \, (1+\lambda_{12})(1+\lambda_{13}) \cdots (1+\lambda_{1N})(1+\lambda_{23}) \cdots \\
&= \frac{Z_i}{V^N} \int Dx \left(1 + \sum_{i>j} \lambda_{ij} + \mathcal{O}(\lambda^2) \right) \\
&\approx Z_i \left(1 + \frac{1}{V^N} \sum_{i>j} \int Dx \, \lambda_{ij} \right) = Z_i \left(1 + \frac{N(N-1)}{2V^N} \int Dx \, \lambda_{12} \right) \\
&= Z_i \left(1 + \frac{N(N-1)}{2V^N} V^{N-2} \iint d^3x_1 \, d^3x_2 \, \lambda_{12} \right) \\
&\approx Z_i \left(1 + \frac{N^2}{2V^2} \iint d^3R \, d^3r \, \lambda_{12} \right) = Z_i \left(1 + \frac{N^2}{2V} \int d^3r \, \lambda(r) \right) \\
&\approx Z_i \left(1 + \frac{N}{2V} \int d^3r \, \lambda(r) \right)^N = Z_i \left(1 + \frac{n}{2} I(\beta) \right)^N
\end{aligned}
$$

Here, the center of mass coordinates $\vec{R}$ and relative coordinates $\vec{r}$ have been introduced. The step in the end can be done, since $1 + ax \approx (1 + x)^a$, if x is small. Further more, $n = N/V$ and

$$I(\beta) := \int d^3r \, \lambda(r) = 4\pi \int_0^\infty dr \, r^2 \left(e^{-\beta U(r)} - 1 \right)$$

was used. Now it is possible, to calculate the Helmholtz free energy and other quantities:

$$
\begin{aligned}
F &= -kT \ln Z = -kT \ln Z_i - NkT \ln \left(1 + \frac{n}{2} I(\beta) \right) \\
&\approx -kT \ln Z_i - NkT \frac{n}{2} I(\beta) \\
\Rightarrow \quad p &= -\frac{\partial F}{\partial V} = \frac{NkT}{V} + \frac{NkT}{2} I(\beta) \frac{\partial}{\partial V}\left(\frac{N}{V}\right) = \frac{N}{V} kT - \left(\frac{N}{V}\right)^2 \frac{kT}{2} I(\beta) \\
\Leftrightarrow \quad \frac{p}{kT} &= n - \frac{1}{2} I(\beta) n^2
\end{aligned}
$$

The prefactors of an expansion $B_1(T) n + B_2(T) n^2 + \cdots$ are called "Virial coefficients". Hence:

$$B_2(T) = -\frac{1}{2} I(T) = -2\pi \int_0^\infty dr \, r^2 \left(e^{-\beta U(r)} - 1 \right)$$

7.2 The Van-der-Waals-Equation of State

Now, consider:

$$U(r) := \begin{cases} \infty, & r < r_c \\ -U_0 \mathcal{F}(r/r_c), & \text{else} \end{cases}$$

$\mathcal{F}$ being an arbitrary function.

$$
\begin{aligned}
\Rightarrow B(T) &= 2\pi \int_0^{r_c} dr \, r^2 - 2\pi \int_{r_c}^\infty dr \, r^2 \left(e^{U_0 \mathcal{F}(r/r_c)/kT} - 1 \right) \\
&\underset{kT \gg U_0 \mathcal{F}}{\approx} \frac{2\pi}{3} r_c^3 - \frac{2\pi U_0}{kT} \int_{r_c}^\infty dr \, r^2 \mathcal{F}(r/r_c) = 4 \frac{4\pi}{3} \left(\frac{r_c}{2}\right)^3 - \frac{a'}{kT} \\
&= b' - a'/kT
\end{aligned}
$$

Here, b' is four times the volume of one atom (leading to repulsion) and a' is a constant for the attraction.

Using $N/V = N_A/\mathcal{V}$, $\mathcal{V}$ being the volume of one mole, yields:

$$
\begin{aligned}
\Rightarrow \quad \frac{p}{kT} &= \frac{N}{V} + \left(b' - \frac{a'}{kT} \right) \frac{N^2}{V^2} = \frac{N_A}{\mathcal{V}} + b' \frac{N_A^2}{\mathcal{V}^2} - \frac{a'}{kT} \frac{N_A^2}{\mathcal{V}^2} \\
&= \frac{N_A}{\mathcal{V}} \left(1 + \frac{b}{\mathcal{V}} \right) - \frac{a}{kT} \frac{1}{\mathcal{V}^2} \approx \frac{N_A}{\mathcal{V}} \frac{1}{1 - \frac{b}{\mathcal{V}}} - \frac{a}{kT} \frac{1}{\mathcal{V}^2} \\
\Leftrightarrow \quad \frac{1}{kT}\left(p + \frac{a}{\mathcal{V}^2} \right) &= \frac{N_A}{\mathcal{V} - b} \quad \Leftrightarrow \quad \left(p + \frac{a}{\mathcal{V}^2} \right)(\mathcal{V} - b) = RT
\end{aligned}
$$

Here, $b := b' N_A$ and $a := a' N_A^2$ were used.

7.3 The Critical Point

At the critical point is true that $\frac{\partial p}{\partial \mathcal{V}} = \frac{\partial^2 p}{\partial \mathcal{V}^2} = 0$

Hence:

$$
\begin{aligned}
p &= \frac{RT}{\mathcal{V} - b} - \frac{a}{\mathcal{V}^2} \\
\Rightarrow \frac{\partial p}{\partial \mathcal{V}} &= -\frac{RT}{(\mathcal{V} - b)^2} + \frac{2a}{\mathcal{V}^3} \overset{!}{=} 0 \\
&\Leftrightarrow 2a(\mathcal{V} - b)^2 = RT\mathcal{V}^3 \\
\Rightarrow \frac{\partial^2 p}{\partial \mathcal{V}^2} &= \frac{2RT}{(\mathcal{V} - b)^3} - \frac{6a}{\mathcal{V}^4} \overset{!}{=} 0 \quad \Leftrightarrow \quad 6a(\mathcal{V} - b)^3 = 2RT\mathcal{V}^4
\end{aligned}
$$

Dividing those equations yields:

$$
\begin{aligned}
3(\mathcal{V} - b) &= 2\mathcal{V} \quad \Leftrightarrow \quad \mathcal{V}_c = 3b \\
\Rightarrow \quad T_c &= \frac{8a}{27Rb}, \quad p_c = \frac{a}{27b^2}
\end{aligned}
$$

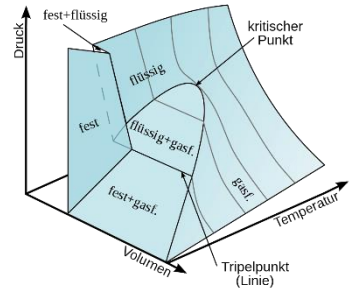Furthermore, for any gas must be universally true:

$$\frac{p_c \mathcal{V}_c}{RT_c} = \frac{3}{8}$$

Moreover, $a = 3\mathcal{V}_c^2 p_c$ and $b = \mathcal{V}_c/3$ and hence:

$$
\begin{aligned}
\left(p + 3p_c \frac{\mathcal{V}_c^2}{\mathcal{V}^2} \right)\left(\mathcal{V} - \frac{\mathcal{V}_c}{3} \right) &= RT \\
\Leftrightarrow \quad \left(\frac{p}{p_c} + 3 \frac{\mathcal{V}_c^2}{\mathcal{V}^2} \right)\left(\frac{\mathcal{V}}{\mathcal{V}_c} - \frac{1}{3} \right) &= \frac{RT}{p_c \mathcal{V}_c} \frac{T_c}{T_c} = \frac{8}{3} \frac{T}{T_c}
\end{aligned}
$$

Defining $p_R := p/p_c$ etc. yields:

$$\left(p_R + \frac{3}{\mathcal{V}_R^2} \right)(3\mathcal{V}_R - 1) = 8T_R$$

7.4 The Ising-Model for Ferromagnetism

Hamilton for Paramagnetism (see 5.9) for N particles:

$$H_{\mathrm{para}} = -\underbrace{\mu_B B_0}_{=B} \sum_{i=1}^{N} s_i$$

Here, s_i is $+1$ or -1. Ferromagnetism: Interaction between nearest neighbors with $J > 0$:

$$H_{\mathrm{ferro}} \equiv H = -J \sum_{\langle ij \rangle} s_i s_j - B \sum_{i=1}^{N} s_i$$

$\langle ij \rangle$ means, summing only over nearest neighbors.
Mean Field Theory: Each nearest neighbor k has an average value of $\langle s_k \rangle$, which is the same for every atom, hence independent of k: $m := \langle s_k \rangle$. Hence, z being the number of nearest neighbors:

$$H = -Jzm \sum_{i=1}^{N} s_i - B \sum_{i=1}^{N} s_i = -(Jzm + B) \sum_{i=1}^{N} s_i$$

Now, H has the same form as H_{para}! Using the solution from 5.9:
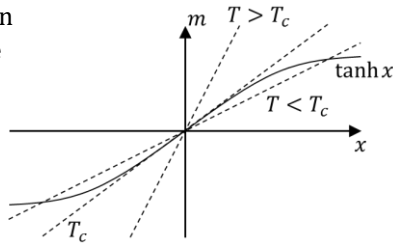
$$\frac{\langle \mu_z \rangle}{\mu_B} = m = \tanh\left(\frac{Jzm + B}{kT}\right)$$

Consider $B = 0$, will there be spontaneous magnetization?

$$m = \tanh\left(\frac{Jzm}{kT}\right) = \tanh(x), \qquad m = \frac{kT}{Jz}x$$

Now, the intersections between $\tanh x$ and the straight line are solutions. The slope of $\tanh x$ at $x = 0$ is 1, hence

$$\frac{kT_c}{Jz} = 1 \Leftrightarrow T_c = \frac{Jz}{k}$$

Behavior of $m(T)$ at T_c:

$$m = \tanh\left(\frac{T_c}{T}m\right) \approx \frac{T_c}{T}m - \frac{1}{3}\left(\frac{T_c}{T}\right)^3 m^3$$

For $m \neq 0$:

$$1 \approx \frac{T_c}{T} - \frac{1}{3}\left(\frac{T_c}{T}\right)^3 m^2$$

$$\Leftrightarrow m = \pm\sqrt{\frac{3T^2}{T_c^3}(T_c - T)} \underset{T \approx T_c}{\approx} \pm\sqrt{\frac{3}{T_c}(T_c - T)} \sim (T_c - T)^{1/2}$$

Behavior of $B(m)$ at isotherm $T = T_c$:

$$m = \tanh\left(m + \frac{B}{kT_c}\right) \approx m + \frac{B}{kT_c} - \frac{1}{3}\left(m + \frac{B}{kT_c}\right)^3$$

$$\Leftrightarrow \frac{B}{kT_c} \approx \frac{m^3}{3} + \frac{m^2 B}{kT_c} + \frac{mB^2}{kT_c} + \frac{B^3}{k^2 T_c^3}$$

Since in the leading term, $B \sim m^3$, the other terms are $\sim m^5$, $\sim m^7$ and $\sim m^9$ and can be ignored:

$$B \approx \frac{kT_c}{3}m^3$$

7.5 More formal Approach on the Ising-Model

Again, m is the average value of s_k, let's assume, the difference $s_k - m$ is small:

$$H = -J \sum_{\langle ij \rangle} s_i s_j - B \sum_{i=1}^{N} s_i$$

$$= -J \sum_{\langle ij \rangle} (s_i - m + m)(s_j - m + m) - B \sum_{i=1}^{N} s_i$$

$$\approx -J \sum_{\langle ij \rangle} \left((s_i - m)m + (s_j - m)m + m^2\right) - B \sum_{i=1}^{N} s_i$$

$$= -J \sum_{\langle ij \rangle} \left((s_i + s_j)m - m^2\right) - B \sum_{i=1}^{N} s_i$$

$$= -2mJ \sum_{\langle ij \rangle} s_i + Jm^2 \sum_{\langle ij \rangle} 1 - B \sum_{i=1}^{N} s_i$$

$$= -Jzm \sum_{i} s_i + Jm^2 \frac{zN}{2} - B \sum_{i=1}^{N} s_i$$

$$= -(Jzm + B) \sum_{i} s_i + Jm^2 \frac{zN}{2}$$

Now, the Partition Function is $Z = z^N$ with:

$$z = e^{-\beta Jm^2 z/2} \sum_{s=-1,1} e^{\beta(Jzm + B)s} = 2e^{-\beta Jm^2 z/2} \cosh\left(\beta(Jzm + B)\right)$$

Hence, the expected (average) m of this particle is:

$$m = +1 \cdot \frac{e^{-\beta Jm^2 z/2}e^{\beta(Jzm + B)}}{z} - 1 \cdot \frac{e^{-\beta Jm^2 z/2}e^{-\beta(Jzm + B)}}{z}$$

$$= \tanh\left(\frac{Jzm}{kT} + \frac{B}{kT}\right)$$

Now, it is possible to find the Helmholtz free energy $F = -kT \ln Z$ and doing so yields, that there is a symmetry breaking at $T = T_c$; $m = 0$ is no minimum for $T > T_c$ and hence no physical solution.

8 Grand Canonical Ensemble

8.1 Grand Partition Function

As for the Partition Function, consider a system inside a heat bath, which is now also allowed to exchange particles (heat bath becomes also a particle bath). Then, the probability, that the system has N particles and the energy $E_i(N)$ is:

$$\mathcal{P}(E_i(N), N) = \frac{1}{W} W_B(E_0 - E_i(N), N_0 - N) \cdot W_S(E_i(N), N)$$

Here, W is the total number of microstates, W_B the number of microstates within the bath and W_S within the system. The total energy and particle number is $E_0 = E_B + E_i(N)$ and $N_0 = N_B + N$. Then, the probability of *a state* with energy $E_i(N)$ is:

$$P(E_i(N), N) = \frac{1}{W} W_B(E_0 - E_i(N), N_0 - N)$$

Consider a Taylor expansion at $E_B = E_0 - E_i(N) \approx E_0$ and $N_B = N_0 - N \approx N$:

$$\ln\big(W_B(E_0 - E_i(N), N_0 - N)\big)$$
$$\approx \ln\big(W_B(E_0, N_0)\big) + \frac{\partial \ln(W_B(E_B, N_B))}{\partial E_B}\bigg|_{E_B = E_0} (E_0 - E_i(N) - E_0)$$
$$+ \frac{\partial \ln(W_B(E_B, N_B))}{\partial N_B}\bigg|_{E_B = N_0} (N_0 - N - N_0)$$
$$= \ln\big(W_B(E_0, N_0)\big) - \frac{E_i(N)}{kT_B} + \frac{\mu_B N}{kT_B}$$
$$= \ln\big(W_B(E_0, N_0)\big) - \frac{E_i(N)}{kT} + \frac{\mu N}{kT}$$

Here, $S_B = k \ln W_B$ and $\partial W_B/\partial E_B = T_B$ and $\partial W_B/\partial N_B = -\mu/T$ was used. This yields:

$$W_B(E_0 - E_i(N), N_0 - N) \sim e^{-\beta E_i(N)} e^{\beta \mu N}$$
$$\implies P(E_i(N), N) = \frac{e^{-\beta E_i(N)} e^{\beta \mu N}}{Q(T, V, \mu)}$$

P is called the Gibbs or Grand Canonical Distribution and Q is the Grand Partition Function:

$$Q(T, V, \mu) := \sum_{N=0}^{N_0 \approx \infty} \sum_{\substack{N \text{ particle} \\ \text{states } i}} e^{-\beta E_i(N)} e^{\beta \mu N}$$

8.2 Particle Number and Energy Distribution

Mean particle number:

$$\langle N \rangle = \sum_{N=0}^{\infty} \sum_{\substack{N \text{ particle} \\ \text{states } i}} N\, P(E_i(N), N) = \frac{1}{\beta Q} \frac{\partial Q}{\partial \mu} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Q$$

$$\langle (\Delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2 Q} \frac{\partial^2 Q}{\partial \mu^2} - \frac{1}{\beta^2 Q^2} \left(\frac{\partial Q}{\partial \mu} \right)^2$$
$$= \frac{1}{\beta^2} \frac{\partial}{\partial \mu} \left(\frac{1}{Q} \frac{\partial Q}{\partial \mu} \right) = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu}$$

Since $\langle N \rangle$ is the only extensive quantity in this expression, $\langle (\Delta N)^2 \rangle \sim \langle N \rangle$. Hence, the standard deviation is $\sigma \sim \sqrt{N}$ and

$$\sigma/\langle N \rangle \sim 1/\sqrt{\langle N \rangle}$$

Mean Energy:

$$\frac{\partial}{\partial \beta} \ln Q = \frac{1}{Q} \sum_{N,i} (\mu N - E_i(N)) e^{\beta \mu N} e^{-\beta E_i(N)} = \mu \langle N \rangle - \langle E \rangle$$
$$\iff \langle E \rangle = \mu \langle N \rangle - \frac{\partial}{\partial \beta} \ln Q$$

8.3 Connection to Thermodynamics

Consider:

$$\frac{\partial}{\partial \beta} \left(-\frac{1}{\beta} \ln Q \right) = \frac{1}{\beta^2} \ln Q - \frac{1}{\beta} \frac{\partial}{\partial \beta} \ln Q$$
$$\iff \langle E \rangle - \mu \langle N \rangle = -\frac{\partial}{\partial \beta} \ln Q = \beta \frac{\partial}{\partial \beta} \left(-\frac{1}{\beta} \ln Q \right) - \frac{1}{\beta} \ln Q$$
$$\iff \langle E \rangle - \mu \langle N \rangle + T \frac{\partial}{\partial T} (-kT \ln Q) = -kT \ln Q$$

In thermodynamics, the Grand Potential is given by
$$\Omega = E - \mu N - TS = -pV$$
which yields $d\Omega = -S dT - p dV - N d\mu$ and hence:
$$\Omega = E - \mu N + T \frac{\partial \Omega}{\partial T}$$

So, obviously is
$$\Omega(T, V, \mu) = -kT \ln Q(T, V, \mu)$$
And furthermore, if one plugs in $E = TS - pV + \mu N$:
$$\Omega = E - TS - \mu N = -pV = -kT \ln Q$$
$$\iff \frac{pV}{kT} = \ln Q$$

8.4 Classical Ideal Gas

From 5.6 is known, that the partition function is
$$Z = \sum_i e^{-\beta E_i(N)} = \frac{z^N}{N!}$$
with $z = V/\lambda_{th}^3$ and $\lambda_{th} = h/\sqrt{2\pi m k T}$. Hence:
$$Q = \sum_N \sum_i e^{-\beta E_i(N)} e^{\beta \mu N} = \sum_N Z(N) e^{\beta \mu N} = \sum_N \frac{(z e^{\beta \mu})^N}{N!}$$
$$= \text{Exp}(z e^{\beta \mu})$$

Hence, the Grand Potential is:
$$\Omega = -kT \ln Q = -zkT e^{\beta \mu} = -\gamma V (kT)^{5/2} e^{\mu/kT}$$
with $\gamma = (2\pi m/h)^{3/2}$. Furthermore, the ideal gas law follows:
$$p = -\frac{\partial \Omega}{\partial V} = \gamma (kT)^{5/2} e^{\mu/kT}$$
$$\langle N \rangle = kT \frac{\partial}{\partial \mu} \ln Q = -\frac{\partial \Omega}{\partial \mu} = z e^{\mu/kT} = \gamma V (kT)^{3/2} e^{\mu/kT}$$
$$\implies \frac{p}{N} = \frac{kT}{V} \iff pV = NkT$$

As well as the internal energy:
$$\langle E \rangle = \mu \langle N \rangle - \frac{\partial}{\partial \beta} \ln Q = \mu z e^{\mu/kT} + \frac{3}{2} \frac{z}{\beta} e^{\beta \mu} - \mu z e^{\beta \mu}$$
$$= \mu z e^{\mu/kT} + \frac{3}{2} kT z e^{\mu/kT} - \mu z e^{\mu/kT} = \frac{3}{2} \langle N \rangle kT$$

Finally, the entropy is just the Sackur-Tetrode-Equation:
$$S = -\frac{\partial \Omega}{\partial T} = \gamma V \frac{\partial}{\partial T} (kT)^{5/2} e^{\mu/kT}$$
$$= \gamma V \left(\frac{5}{2} k (kT)^{3/2} e^{\mu/kT} - (kT)^{5/2} \frac{\mu}{kT^2} e^{\mu/kT} \right)$$
$$= \gamma V \left(\frac{5}{2} k - \frac{\mu}{T} \right) (kT)^{3/2} e^{\mu/kT} = \frac{5}{2} k \langle N \rangle - \frac{\mu}{T} \langle N \rangle$$
$$= \frac{5}{2} k \langle N \rangle - k \langle N \rangle \frac{\mu}{kT} = \frac{5}{2} k \langle N \rangle + k \langle N \rangle \ln \left(\frac{1}{e^{\mu/kT}} \right)$$
$$= \frac{5}{2} k \langle N \rangle + k \langle N \rangle \ln \left(\frac{V}{z \lambda_{th}^3 e^{\mu/kT}} \right) = \frac{5}{2} k \langle N \rangle + k \langle N \rangle \ln \left(\frac{V}{\langle N \rangle \lambda_{th}^3} \right)$$
$$= k \langle N \rangle \ln \left(\frac{V}{\langle N \rangle} \left(\frac{mkT}{2\pi \hbar^2} \right)^{3/2} \right) + \frac{5}{2} k \langle N \rangle$$

8.5   Bose-Einstein-/Fermi-Dirac-Distributon

Define for non-interacting Bosons/Fermions an inifite number of single particle states with energies

$$\epsilon_1 \leq \epsilon_2 \leq \cdots \leq \epsilon_i \leq \cdots$$

Let the i-th state be occupied by n_i particles, then one state can be defined as a tupel $(n_1, n_2, \ldots, n_i, \ldots)$, where $\sum_i n_i = N$ is not fixed. For Fermions: $n_i \in \{0,1\}$, for Bosons $n_i \in \mathbb{N}_0$. Now, Q_F is for Fermions, Q_B for Bosons:

$$Q_{F,B} = \sum_N \sum_i e^{-\beta E_i(N)} e^{\beta \mu N} = \sum_{\substack{\text{all possible} \\ \text{states}}} e^{-\beta E_i(N)} e^{\beta \mu N}$$

$$= \sum_{n_1=0}^{1,\infty} \sum_{n_2=0}^{1,\infty} \cdots \, e^{-\beta \sum_{i=1}^{\infty} n_i \epsilon_i} \, e^{-\beta \mu \sum_{i=1}^{\infty} n_i}$$

$$= \sum_{n_1=0}^{1,\infty} \sum_{n_2=0}^{1,\infty} \cdots \, e^{-\beta \sum_{i=1}^{\infty}(\epsilon_i - \mu) n_i} = \sum_{n_1=0}^{1,\infty} \sum_{n_2=0}^{1,\infty} \cdots \prod_{i=1}^{\infty} e^{-\beta(\epsilon_i - \mu) n_i}$$

$$= \prod_{i=1}^{\infty} \sum_{n_i=0}^{1,\infty} e^{-\beta(\epsilon_i - \mu) n_i} = \prod_{i=1}^{\infty} \left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right)^{\pm 1}$$

(sum to 0 and + for Fermions, sum to ∞ and $-$ for Bosons)

$$\Rightarrow \quad \Omega_{F,B} = -kT \ln Q_{F,B} = \mp kT \sum_{i=1}^{\infty} \ln\left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right) \overset{!}{=} -pV$$

$$\Rightarrow \quad \frac{pV}{kT} = \pm \sum_{i=1}^{\infty} \ln\left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right)$$

$$\Rightarrow \quad \langle N \rangle = -\frac{\partial \Omega}{\partial \mu} = \sum_{i=1}^{\infty} \frac{e^{-\beta(\epsilon_i - \mu)}}{1 \pm e^{-\beta(\epsilon_i - \mu)}} = \sum_{i=1}^{\infty} \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1}$$

$$= \sum_{i=1}^{\infty} f_{FD,BE}(\epsilon_i)$$

For a certain $\langle N \rangle$, this equation determines the relation $\mu(T)$. Of cause, $f_{FD,BE} \geq 0$, so for Bosons is $\mu < \epsilon_i \; \forall i$ neccessaray. Since $\epsilon_i \geq \epsilon_1 \approx 0$, that means, the for Bosons μ is typically negative. Using the density of states in energy $g(\epsilon)$, the sum can be written as an integral:

$$\langle N \rangle = \int_0^\infty d\epsilon \, g(\epsilon) \, f_{FD,BE}(\epsilon) \qquad \langle E \rangle = \int_0^\infty d\epsilon \, g(\epsilon) \epsilon \, f_{FD,BE}(\epsilon)$$

9 The Ideal Quantum Gas

9.1 Formulas for this section

Recall the density of states from 4.4, where γ is a constant, depending on the dimensions d and the power of the dispersion relation q:

$$g(\epsilon) = \gamma \epsilon^{(d-q)/q} = \gamma \epsilon^{d/q-1} \qquad \epsilon \sim k^q$$

Recall as well the integrals of the bottom of 8.5:

$$N = \int_0^\infty d\epsilon\, g(\epsilon)\, f_{FD,BE}(\epsilon) \qquad E = \int_0^\infty d\epsilon\, g(\epsilon)\epsilon\, f_{FD,BE}(\epsilon)$$

9.2 Pressure-Volume-Energy Relation

From 8.3 is known, that $pV/kT = \ln Q$, where Q is the Grand Partition Function. Recall Q for bosons/fermions from 8.5, where the upper sign if for fermions, the lower for bosons:

$$pV = kT \ln Q = \pm kT \sum_{i=1}^\infty \ln\left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right)$$

$$= \pm kT \int_0^\infty d\epsilon\, g(\epsilon) \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right)$$

$$= \pm \gamma kT \int_0^\infty d\epsilon\, \epsilon^{d/q-1} \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right)$$

$$= \frac{q}{d}\gamma kT \int_0^\infty d\epsilon\, \epsilon^{d/q} \frac{\beta e^{-\beta(\epsilon-\mu)}}{1 \pm e^{-\beta(\epsilon-\mu)}}$$

$$= \frac{q}{d}\gamma \int_0^\infty d\epsilon\, \epsilon^{d/q} \frac{1}{e^{\beta(\epsilon-\mu)} \pm 1} = \frac{q}{d}E$$

In the second last step, integration by parts was conducted.

9.3 Zero Temperature Physics (Fermions)

For $T = 0$, $\mu(T) = E_F$, and f_{FD} becomes a step function:

$$N = \int_0^\infty d\epsilon\, g(\epsilon)\, f_{FD}(\epsilon) = \int_0^{E_F} d\epsilon\, g(\epsilon) = \frac{q}{d}\gamma E_F^{d/q}$$

$$= \frac{q}{d}g(E_F)E_F \qquad \Leftrightarrow \qquad E_F = \left(\frac{dN}{q\gamma}\right)^{\frac{q}{d}} = \left(\frac{dN}{q\tilde\gamma V}\right)^{\frac{q}{d}}$$

Last step: Recall $\gamma \sim V \implies \tilde\gamma := \gamma/V$. For the energy follows:

$$E = \int_0^\infty d\epsilon\, g(\epsilon)\epsilon\, f_{FD}(\epsilon) = \gamma \int_0^{E_F} d\epsilon\, \epsilon^{d/q} = \frac{\gamma}{d/q+1}E_F^{d/q+1}$$

$$= \frac{q}{d+q}g(E_F)E_F^2 = \frac{d}{d+q}N E_F$$

Recall from 9.2:

$$pV = \frac{q}{d}E = \frac{q}{d}\frac{\gamma}{d/q+1}E_F^{d/q+1} = \frac{q^2\gamma}{d(d+q)}\left(\frac{dN}{q\tilde\gamma V}\right)^{\frac{q}{d}+1} \sim \left(\frac{N}{V}\right)^{\frac{q}{d}+1}$$

This is called the "degenerate pressure".

9.4 Low Temperature Physics (Fermions)

For $kT \ll E_F$, the Sommerfeld expansion is valid:

$$\int_0^\infty d\epsilon \frac{F(\epsilon)}{e^{(\epsilon-\mu)/kT}+1} \approx \int_0^\mu d\epsilon\, F(\epsilon) + \frac{\pi^2}{6}(kT)^2 F'(\mu)$$

Hence:

$$N = \int_0^\infty d\epsilon \frac{g(\epsilon)}{e^{(\epsilon-\mu)/kT}+1} \approx \gamma\frac{q}{d}\mu^{d/q} + \frac{\pi^2}{6}(kT)^2\gamma\frac{d-q}{q}\mu^{d/q-2}$$

$$= \gamma\frac{q}{d}\mu^{d/q}\left(1 + \frac{\pi^2}{6}(kT)^2\frac{d}{q}\frac{d-q}{q}\mu^{-2}\right)$$

$$= \gamma\frac{q}{d}E_F^{d/q}\left(\frac{\mu}{E_F}\right)^{d/q}\left(1 + \frac{\pi^2}{6}\frac{d(d-q)}{q^2}\left(\frac{kT}{\mu}\right)^2\right)$$

$$= N\left(\frac{\mu}{E_F}\right)^{d/q}\left(1 + \frac{\pi^2}{6}\frac{d(d-q)}{q^2}\left(\frac{kT}{\mu}\right)^2\right)$$

$$\Leftrightarrow \quad \mu = E_F\left(1 + \frac{\pi^2}{6}\frac{d(d-q)}{q^2}\left(\frac{kT}{\mu}\right)^2\right)^{-q/d} \approx E_F\left(1 - \frac{\pi^2}{6}\frac{d-q}{q}\left(\frac{kT}{E_F}\right)^2\right)$$

Last step is possible because $(1 \pm x)^\alpha \approx 1 \pm \alpha x$.

Next, calculate the energy ($E_0 := E(T=0)$ from 9.3):

$$E = \int_0^\infty d\epsilon \frac{g(\epsilon)\epsilon}{e^{(\epsilon-\mu)/kT}+1} = \gamma\int_0^\mu d\epsilon \frac{\epsilon^{d/q}}{e^{(\epsilon-\mu)/kT}+1}$$

$$\approx \frac{\gamma}{d/q+1}\mu^{d/q+1} + \frac{\pi^2}{6}(kT)^2\gamma\frac{d}{q}\mu^{d/q-1}$$

$$= \frac{\gamma q}{d+q}\mu^{d/q+1}\left(1 + \frac{\pi^2}{6}(kT)^2\frac{d+q}{q}\frac{d}{q}\mu^{-2}\right)$$

$$= \frac{\gamma q}{d+q}E_F^{d/q+1}\left(\frac{\mu}{E_F}\right)^{d/q+1}\left(1 + \frac{\pi^2}{6}\frac{d(d+q)}{q^2}\left(\frac{kT}{\mu}\right)^2\right)$$

$$= E_0\left(1 - \frac{\pi^2}{6}\frac{d-q}{q}\left(\frac{kT}{E_F}\right)^2\right)^{d/q+1}\left(1 + \frac{\pi^2}{6}\frac{d(d+q)}{q^2}\left(\frac{kT}{\mu}\right)^2\right)$$

$$\approx E_0\left(1 - \frac{\pi^2}{6}\frac{d^2-q^2}{q^2}\left(\frac{kT}{E_F}\right)^2\right)\left(1 + \frac{\pi^2}{6}\frac{d(d+q)}{q^2}\left(\frac{kT}{E_F}\right)^2\right)$$

$$= E_0\left(1 + \frac{\pi^2}{6}\left(\frac{d(d+q)}{q^2} - \frac{d^2-q^2}{q^2}\right)\left(\frac{kT}{E_F}\right)^2 + \mathcal{O}\left(\left(\frac{kT}{E_F}\right)^4\right)\right)$$

$$\approx E_0\left(1 + \frac{\pi^2}{6}\frac{d+q}{q}\left(\frac{kT}{E_F}\right)^2\right) = E_0 + \frac{\pi^2}{6}g(E_F)(kT)^2$$

In the last step, $E_0 = q/(d+q)\,g(E_F)E_F^2$ from 9.3 was used.

9.5 Bose-Einstein Condensation (Bosons)

As stated in 8.5, μ has to be bigger than the single particle energy ground state ϵ_0, which is typically close to zero. Hence, the number of particles is

$$N = \int_{\epsilon_0}^\infty d\epsilon \frac{g(\epsilon-\epsilon_0)}{e^{(\epsilon-\mu)/kT}-1}$$

That is to say, the density of states is somehow shifted, such that $g(\epsilon-\epsilon_0) = 0, \epsilon < \epsilon_0$. This equation defines the temperature dependence of $\mu \equiv \mu(T)$. But for small T, μ has to become positive, such that this equation is fulfilled. Since it is not allowed to be positive, for $T < T_c$ follows $\mu = 0$. But this would lead to a lack of particles, the integral would be smaller than N. Since the integral starts only at $\epsilon = \epsilon_0$, it misses the N_0 particles in the ground state. For high temperature, $N_0/N \approx 0$. But for lower temperatures, N_0 cannot be neglected anymore:

$$N = N_0(T) + \int_{\epsilon_0}^\infty d\epsilon \frac{g(\epsilon-\epsilon_0)}{e^{(\epsilon-\mu)/kT}-1}$$

Now, as long as $T > T_c$, $\mu < 0 \implies N_0/N \approx 0$.

First, calculate T_c:
Here, $T \to T_c$, $\mu \to 0$ and $N_0/N \approx 0$, $\epsilon_0 \approx 0$. Use the substitution $x := \beta_c\epsilon$:

$$N = \gamma\int_0^\infty d\epsilon \frac{\epsilon^{d/q-1}}{e^{\beta_c\epsilon}-1} = \gamma(kT_c)^{d/q}\underbrace{\int_0^\infty d\epsilon \frac{x^{d/q-1}}{e^x-1}}_{=I_{dq}}$$

$$\Leftrightarrow \qquad kT_c = \left(\frac{N}{\gamma I_{dq}}\right)^{q/d}$$

But attention! The integral I_{dq} converges only for $d/q > 1$, hence only in those cases is the Bose-Einstein condensation possible! In other cases, there is no Bose-Einstein condensation, or $T_c = 0$, if one still wishes to speak about T_c.

Next, calculate $N_0(T)$:
For $T < T_c$, still $\mu = 0$ is true:

$$N = N_0(T) + \gamma\int_0^\infty d\epsilon \frac{\epsilon^{d/q-1}}{e^{\beta\epsilon}-1} = N_0(T) + \gamma\left(\frac{kTT_c}{T_c}\right)^{d/q}I_{dq}$$

$$= N_0(T) + N\left(\frac{T}{T_c}\right)^{d/q} \quad \Leftrightarrow \quad N_0(T) = N\left(1 - \left(\frac{T}{T_c}\right)^{d/q}\right)$$

Hence, all the bosons, which are not covered anymore by the integral after $T < T_c$ go into the ground state.

9.6 Formal Equations for Ideal Quantum Gas

Consider the substitution $\xi := e^{\beta\mu}$ and $x := \beta\epsilon$:

$$N = \int_0^\infty d\epsilon \, \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)} \pm 1} = \gamma \int_0^\infty d\epsilon \, \frac{\epsilon^{d/q-1}}{\xi^{-1}e^{\beta\epsilon} \pm 1}$$

$$= \gamma(kT)^{d/q} \int_0^\infty dx \, \frac{x^{d/q-1}}{\xi^{-1}e^x \pm 1} = \gamma(kT)^{d/q}\Gamma(d/q)f_{d/q}^{\pm}(\xi)$$

In the same way deal with the energy:

$$E = \int_0^\infty d\epsilon \, \frac{g(\epsilon)\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1} = \gamma \int_0^\infty d\epsilon \, \frac{\epsilon^{d/q}}{\xi^{-1}e^{\beta\epsilon} \pm 1}$$

$$= \gamma(kT)^{d/q+1} \int_0^\infty d\epsilon \, \frac{x^{d/q+1-1}}{\xi^{-1}e^x \pm 1}$$

$$= \gamma(kT)^{d/q+1}\Gamma(d/q + 1)f_{d/q+1}^{\pm}(\xi)$$

Hence, the equation of state looks like:

$$\frac{pV}{N} = \frac{q}{d}\frac{E}{N} = \frac{kTf_{d/q+1}^{\pm}(\xi)}{f_{d/q}^{\pm}(\xi)} \quad \Longleftrightarrow \quad \frac{pV}{NkT} = \frac{f_{d/q+1}^{\pm}(\xi)}{f_{d/q}^{\pm}(\xi)}$$

Here and above, f_n^+ is the Fermi-Dirac integral and f_n^- the Bose-Einstein integral (often $f_n^+ = f_n$ and $f_n^- = g_n$ is written):

$$f_n^{\pm}(\xi) := \frac{1}{\Gamma(n)} \int_0^\infty dx \, \frac{x^{n-1}}{\xi^{-1}e^x \pm 1} = \frac{1}{\Gamma(n)} \int_0^\infty dx \, \frac{x^{n-1}\xi e^{-x}}{1 \pm \xi e^{-x}}$$

$$= \frac{1}{\Gamma(n)} \int_0^\infty dx \, x^{n-1}\xi e^{-x} \sum_{m=0}^\infty (\mp \xi e^{-x})^m$$

$$= \frac{1}{\Gamma(n)} \sum_{m=0}^\infty (\mp 1)^m \xi^{m+1} \int_0^\infty dx \, x^{n-1}e^{-(m+1)x}$$

$$= \frac{1}{\Gamma(n)} \sum_{m=0}^\infty \frac{(\mp 1)^m \xi^{m+1}}{(m+1)^n} \int_0^\infty dy \, y^{n-1}e^{-y} = \sum_{m=1}^\infty (\mp 1)^{m+1}\frac{\xi^m}{m^n}$$

Here, the substitution $y = (m + 1)x$ was used.

9.7 High Temperature Physics

In high temperature, Fermi and Bose gas obey the ideal gas law. Here, the first correction term is evaluated.

For $kT \gg E_F$, μ is negative and $\xi = e^{\beta\mu} < 1$, hence:

$$N = \gamma(kT)^{d/q}\Gamma(d/q)f_{d/q}^{\pm}(\xi)$$

$$= \gamma(kT)^{d/q}\Gamma(d/q) \sum_{m=1}^\infty (\mp 1)^{m+1}\frac{\xi^m}{m^{d/q}} \approx \gamma(kT)^{d/q}\Gamma(d/q)\xi$$

$$\Longleftrightarrow \quad \xi \approx \frac{N}{\gamma(kT)^{d/q}\Gamma(d/q)}$$

Using $f_n^{\pm}(\xi) \approx \xi \mp \xi^2/2^n$ and $(1 + x)^a \approx 1 + ax$:

$$\frac{pV}{NkT} = \frac{f_{d/q+1}^{\pm}(\xi)}{f_{d/q}^{\pm}(\xi)} \approx \frac{\xi \mp \dfrac{\xi^2}{2^{d/q+1}}}{\xi \mp \dfrac{\xi^2}{2^{d/q}}} = \frac{1 \mp \dfrac{\xi}{2^{d/q+1}}}{1 \mp \dfrac{\xi}{2^{d/q}}}$$

$$\approx \left(1 \mp \frac{\xi}{2^{d/q+1}}\right)\left(1 \pm \frac{\xi}{2^{d/q}}\right)$$

$$= 1 + \left(\mp \frac{1}{2^{d/q+1}} \pm \frac{1}{2^{d/q}}\right)\xi + \mathcal{O}(\xi^4)$$

$$\approx 1 + \left(\mp \frac{1}{2^{d/q+1}} \pm \frac{1}{2^{d/q}}\right)\frac{N}{\gamma(kT)^{d/q}\Gamma(d/q)}$$

Recall $\gamma \sim V$, hence define $\tilde{\gamma} := \gamma/V$ and get:

$$\frac{p}{kT} = \frac{N}{V} + \underbrace{\left(\mp \frac{1}{2^{d/q+1}} \pm \frac{1}{2^{d/q}}\right)\frac{1}{\tilde{\gamma}(kT)^{d/q}\Gamma(d/q)}}_{=B_2(T)}\left(\frac{N}{V}\right)^2$$

As in 7.1, $B_2(T)$ is the second virial coefficient.

10 Appendixes

10.1 Sackur-Tetrode-Equation in d dimensions

(see also 3.1)

Let $W^<(E, V, N)$ be the number of microstates with an energy of less than E. The surface of a D dimensional sphere $S_D(R) = \frac{2\pi^{D/2}}{\Gamma(D/2)} R^{D-1}$ will be needed:

$$W^< = \frac{1}{h^{dN} N!} \underbrace{\iint \cdots \iint}_{\sum_{i=1}^{N} p_i^2/2m < E} d^d r_1 d^d p_1 \cdots d^d r_N d^d p_N$$

$$= \frac{V^N}{h^{dN} N!} \underbrace{\int \cdots \int}_{p < \sqrt{2mE}} d^d p_1 \cdots d^d p_N$$

$$= \frac{V^N}{h^{dN} N!} \frac{2\pi^{dN/2}}{\Gamma(dN/2)} \int_0^{\sqrt{2mE}} dp \, p^{dN-1}$$

$$= \frac{2\pi^{dN/2} V^N}{h^{dN} N! \, \Gamma(dN/2)} \frac{1}{dN} \sqrt{2mE}^{dN}$$

$$= \frac{2\pi^{dN/2} V^N}{dN h^{dN} N! \, \Gamma(dN/2)} (2mE)^{dN/2}$$

Now, conduct an Taylor expansion:

$$W(E, V, N, \Delta E) := W^<(E + \Delta E, V, N) - W^<(E, V, N)$$

$$\approx \frac{\partial W^<(E)}{\partial E} \Delta E = \frac{\pi^{dN/2} V^N (2mE)^{dN/2}}{h^{dN} N! \, \Gamma(dN/2)} \frac{\Delta E}{E}$$

Hence, the entropy is, using $\Gamma(dN/2) = (dN/2 - 1)!$:

$$S = k \ln W = k \left(-\ln(N!) - \ln\left(\left(\frac{dN}{2} - 1 \right)! \right) + \ln\left(\frac{\pi^{dN/2} V^N (2mE)^{dN/2}}{h^{dN}} \right) + \ln \frac{\Delta E}{E} \right)$$

$$\approx -Nk \ln N + Nk - k\left(\frac{dN}{2} - 1 \right) \ln\left(\frac{dN}{2} - 1 \right) + k\left(\frac{dN}{2} - 1 \right)$$

$$+ Nk \ln\left(\frac{\pi^{d/2} V (2mE)^{d/2}}{h^d} \right) + \ln \frac{\Delta E}{E}$$

$$\approx -Nk \ln N + Nk - k\frac{dN}{2} \ln\left(\frac{dN}{2} \right) + k\frac{dN}{2} + Nk \ln\left(\frac{\pi^{d/2} V (2mE)^{d/2}}{h^d} \right) + \ln \frac{\Delta E}{E}$$

$$= -Nk \ln\left(N \left(\frac{dN}{2} \right)^{d/2} \right) + Nk\left(\frac{d}{2} + 1 \right) + Nk \ln\left(\frac{\pi^{d/2} V (2mE)^{d/2}}{h^d} \right) + \ln \frac{\Delta E}{E}$$

$$= Nk\left(\frac{d}{2} + 1 \right) + Nk \ln\left(\frac{1}{N \left(\frac{dN}{2} \right)^{d/2}} \frac{\pi^{d/2} V (2mE)^{d/2}}{h^d} \right) + \ln \frac{\Delta E}{E}$$

$$\approx Nk\left(\frac{d}{2} + 1 \right) + Nk \ln\left(\frac{V}{N} \left(\frac{mE}{d\pi\hbar^2 N} \right)^{d/2} \right)$$

Since N is huge, the last term is negligible.

The temperature can be calculate as follows:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{d}{2} \frac{Nk}{E} \quad \Leftrightarrow \quad E = \frac{d}{2} NkT$$

Hence, the Sackur-Tetrode-Equation becomes:

$$S = Nk\left(\frac{d}{2} + 1 \right) + Nk \ln\left(\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{d/2} \right)$$

$$= Nk\left(\frac{d}{2} + 1 \right) + Nk \ln\left(\frac{V}{N} \frac{1}{\lambda_{th}^d} \right)$$