

5 Statistical Mechanics of Real Systems

5.1 Virial Theorem

We now consider a real gas of interacting atoms.

Here N will be (as usual) the number of interacting (gas) particles. The Hamiltonian therefore is

$$\mathbb{H} = \mathbb{H}_{\text{kin}} + \mathbb{H}_{\text{pot}} \quad (5.1)$$

$$\mathbb{H}_{\text{kin}} = \sum_{j=1}^N \frac{p_j^2}{2m_j} \quad (5.2)$$

$$\mathbb{H}_{\text{pot}} = \sum_{j=1}^N \sum_{k=j+1}^N [(\tilde{q}_j - \tilde{q}_k)^2]^{\frac{n}{2}} a_{jk} \quad (5.3)$$

Here the parameter a_{jk} gives the strength of the potential. With this, different scenarios can be considered.

- Gravitation, where $n = -1$ and $a_{jk} \propto -m_j m_k$
- One-component plasma, where $n = -1$ and $a_{jk} \propto q^2$
- Two-component plasma, where $n = -1$ and $a_{jk} \propto q_j q_k$

This model is very general, as this is a power law interaction model and n can be any arbitrary number. So solving this problem could be applied to many, many more examples. The partition function Z again is

$$Z = \frac{1}{N!} \prod_{j=1}^N \left[\int_V d^3 q_j \int \frac{d^3 p_j}{h^3} \right] e^{-\beta(\mathbb{H}_{\text{kin}} + \mathbb{H}_{\text{pot}})} \quad (5.4)$$

An important note is that Z cannot be calculated analytically, only by approximation. At this point is useful to rescale T, p and q , using a rescaling factor of λ .

For this it according to

$$T = \tilde{T} \lambda^n \quad (5.5)$$

$$p = \tilde{p} \lambda \quad (5.6)$$

$$q = \tilde{q} \lambda^{\frac{n}{2}} \quad (5.7)$$

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This rescaling ^{is} was constructed so that the Hamiltonian stays invariant under this rescaling, so do the number of particles.

write down the rescaling!
(see lecture notes!)

$$\frac{H}{T} = \frac{H_{kin} + H_{pot}}{T} \quad (5.8)$$

$$\frac{\tilde{H}}{\tilde{T}} = \frac{H_{kin} + H_{pot}}{T} \quad (5.9)$$

But the integration boundaries however do change. ^{as}

$$\int_0^L dq = \int_0^{\frac{L}{\lambda}} \lambda d\tilde{q} \quad (5.10)$$

$$= \int_0^{\tilde{L}} \lambda d\tilde{q} \quad (5.11)$$

$$L = \lambda \tilde{L} \quad (5.12)$$

$$V = \lambda^3 \tilde{V} \quad (5.13)$$

$$(5.14)$$

Here L is the length of a cube with volume V . Now the partition function in rescaled coordinates becomes

$$Z(V, T, N) = \frac{1}{N!} \prod_{j=1}^N \left[\int_{\tilde{V}} d^3 \tilde{q}_j \lambda^3 \int \frac{d^3 \tilde{p}_j}{h^3} \lambda^{\frac{3n}{2}} \right] e^{-\frac{H_{kin}(\tilde{p}) + H_{pot}(\tilde{q})}{k_B \tilde{T}}} \quad (5.15)$$

$$= \lambda^{3N(1+\frac{n}{2})} Z(\tilde{V}, \tilde{T}, N) \quad (5.16)$$

This λ factor has no physical meaning, it is just a scaling factor. Now from the three variables V, T, N three new variables $VT^{-\frac{3}{n}}, T$ and N are defined; with those the partition function becomes ^{can be written as}

$$Z(V, T, N) \equiv h(VT^{-\frac{3}{n}}, T, N) \quad (5.17)$$

$$= h(\lambda^3 \tilde{V} \tilde{T}^{-\frac{3}{n}} \lambda^{-3}, \lambda^n \tilde{T}, N) = h(\tilde{V} \tilde{T}^{-3/n}, \tilde{T}, N) \quad (5.18)$$

Here h is an unknown function. With that λ only appears as a pre-factor to \tilde{T} .

$$\frac{1}{\lambda^{3N(1+\frac{n}{2})}} \text{ Since } Z \text{ is proportional to } \lambda^{3N(1+\frac{n}{2})} \quad (5.19)$$

Therefore the partition function has to be

$$Z \propto (\lambda^n \tilde{T})^{\frac{3N(1+\frac{n}{2})}{n}} \quad (5.20)$$

$$Z(N, \tilde{V}, \tilde{T}) = (\lambda^n \tilde{T})^{\frac{3N(1+\frac{n}{2})}{n}} \phi(\tilde{V} \tilde{T}^{-\frac{3}{n}}, N) \quad (5.21)$$

Here ϕ is an unknown function. This formula for Z is exact, as no approximation were made. Now this λ was used to reveal certain symmetry relations but can well be set to

The scaling factor

$\lambda = 1$ now. With that Z becomes

$$Z(N, V, T) = T^{\frac{3N(1+\frac{n}{2})}{n}} \phi(VT^{-\frac{3}{n}}, N) \quad \text{We conclude that the free energy reads } (5.22)$$

$$F = -k_B T \left[\frac{3N}{n} \left(1 + \frac{n}{2} \right) \ln(T) + \ln(\phi(VT^{-\frac{3}{n}})) \right] \quad (5.23)$$

$$P = - \frac{\partial F}{\partial V} \Big|_T = - \frac{\partial F}{\partial V} \Big|_T \quad (5.24)$$

$$= k_B T T^{-\frac{3}{n}} \frac{\phi'(VT^{-\frac{3}{n}})}{\phi(VT^{-\frac{3}{n}})} \quad (5.25)$$

$$S = - \frac{\partial F}{\partial T} \Big|_V = - \frac{\partial F}{\partial T} \Big|_V \quad (5.26)$$

$$= - \frac{F}{T} + k_B T \frac{3N}{n} \left(1 + \frac{n}{2} \right) \frac{1}{T} - k_B T \frac{3}{n} T^{-\frac{3}{n}-1} V \frac{\phi'(VT^{-\frac{3}{n}})}{\phi(VT^{-\frac{3}{n}})} \quad (5.27)$$

$$= - \frac{F}{T} + k_B \frac{3N}{n} \left(1 + \frac{n}{2} \right) - \frac{3V}{nT} P \quad (5.28)$$

$$F = U - TS \quad \text{we obtain } (5.29)$$

$$U = k_B T \frac{3N}{n} \left(1 + \frac{n}{2} \right) - \frac{3}{n} VP \quad (5.30)$$

by comparison with Eq 5.25 we obtain and from (show intermedi. step)

This is an exact relation between U, T, N, V and P for an interacting system. It is not an equation of state, as it depends on 5, not state variables. This is called the virial theorem. For $n = -1$ (gravitational or Coulombic systems this becomes)

$$U = - \frac{3k_B T N}{2} + 3VP \quad (5.31)$$

and for $n=0$ we obtain ... (5.32)

5.2 Virial Expansion

a perturbative analysis of a real gas.

This virial expansion is really a kind of Taylor expansion. This chapter is also about perturbation theory. The partition function for an interacting gas is as usual

$$Z(N, T, V) = \frac{1}{N!} \prod_{j=1}^N \left[\int \frac{d^3 p_j d^3 q_j}{(2\pi\hbar)^3} \right] e^{-\beta \mathbb{H}_{\text{kin}} + \mathbb{H}_{\text{pot}}} \quad (5.33)$$

$$\mathbb{H}_{\text{kin}} = \sum_{l=1}^N \frac{\vec{p}_l^2}{2m} \quad (5.34)$$

$$\mathbb{H}_{\text{pot}} = \sum_{l=1}^N \sum_{k=l+1}^N w(q_l - q_k) \quad (5.35)$$

where $w(q)$ is an arbitrary pair potential

First of all the momenta can be integrated out exactly.

$$Z_N(V, T) = \frac{1}{N!} \prod_j \int \frac{d^3 q_j}{\lambda_t^3} e^{-\beta \sum_{k>l}^N w(q_l - q_k)} \quad (5.36)$$

Here λ_t is again the thermal wavelength. The trick with this expansion is to switch over to the grand-canonical ensemble.

$$\mathbb{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta N \mu} Z_N(V, T) \quad (5.37)$$

The In section xy the grand canonical equation of state

In the chapter from statistical mechanics the product of volume and pressure was

$$PV = k_B T \ln(\mathbb{Z}(\mu, V, T)) \quad (5.38)$$

further and also

$$N = \frac{1}{\beta} \frac{\partial \ln(\mathbb{Z}(\mu, V, T))}{\partial \mu} \quad (5.39)$$

$z = e^{\beta \mu}$ is called the fugacity and with this the grand-canonical partition function from equation (5.37) can be written as a power series in z :

$$\mathbb{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta N \mu} Z_N(V, T) \quad (5.40)$$

$$= \sum_{N=0}^{\infty} z^N Z_N(V, T) \quad (5.41)$$

With that the equation of state can also be written as a power series.

$$\frac{PV}{k_B T} = \ln(\mathbb{Z}) \quad (5.42)$$

$$\equiv V \sum_{l=1}^{\infty} \left(\frac{Z}{\lambda_t^3} \right)^l b_l \quad (5.43)$$

$$= \ln \left[\sum_{N=0}^{\infty} z^N Z_N \right] \quad (5.44)$$

With $Z_0 \equiv 1$ the first few terms can be written as

$$= \ln[1 + zZ_1 + z^2 Z_2 + z^3 Z_3 + \dots] \quad (5.45)$$

using the Taylor expansion for $\ln(1 + \epsilon)$ this yields

$$= zZ_1 + z^2 \left(Z_2 - \frac{1}{2} Z_1^2 \right) + z^3 \left(Z_3 - Z_1 Z_2 + \frac{1}{3} Z_1^3 \right) + O(z^4) \quad (5.46)$$

By comparison with the definition from equation (5.43) the coefficients of b_l can just be read off as

$$b_1 = \frac{\lambda_t^3}{V} Z_1 \quad (5.47)$$

$$b_2 = \frac{\lambda_t^6}{V} \left(Z_2 - \frac{1}{2} Z_1^2 \right) \quad (5.48)$$

$$b_3 = \frac{\lambda_t^9}{V} \left(Z_3 - Z_1 Z_2 + \frac{1}{3} Z_1^3 \right) \quad (5.49)$$

$$b_4 = \dots \quad (5.50)$$

Using the Mayer function $f_{12} = e^{-\beta w(q_1 - q_2)} - 1$ the Z_n become

$$Z_1 = \int \frac{d^3 q}{\lambda_t^3} e^0 \quad (5.51)$$

$$= \frac{V}{\lambda_t^3} \quad (5.52)$$

$$Z_2 = \frac{1}{2! \lambda_z^6} \int d^3 q_1 d^3 q_2 e^{-\beta w(q_1 - q_2)} \quad (5.53)$$

$$= \frac{1}{2! \lambda_z^6} \int d^3 q_1 d^3 q_2 (1 + f_{12}) \quad (5.54)$$

$$Z_3 = \frac{1}{3! \lambda_z^9} \int d^3 q_1 d^3 q_2 d^3 q_3 (1 + f_{12})(1 + f_{23})(1 + f_{13}) \quad (5.55)$$

and finally the coefficients b_l can be calculated as follow as

$$b_1 = 1 \quad (5.56)$$

$$b_2 = \frac{1}{2} \int \frac{d^3 q_1 d^3 q_2}{V} f_{12} \quad (5.57)$$

$$b_3 = \frac{1}{6} \int \frac{d^3 q_1 d^3 q_2 d^3 q_3}{V} [(1 + f_{12})(1 + f_{23})(1 + f_{13}) - 3(1 + f_{12}) + 2] \quad (5.58)$$

$$= \frac{1}{6} \int \frac{d^3 q_1 d^3 q_2 d^3 q_3}{V} [f_{12} f_{23} f_{13} + f_{12} f_{23} + f_{12} f_{13} + f_{23} f_{13} + f_{12} + f_{13} + f_{23}] \quad (5.59)$$

$$= \frac{1}{6} \int \frac{d^3 q_1 d^3 q_2 d^3 q_3}{V} [f_{12} f_{23} f_{13} + 3f_{12} f_{23}] \quad (5.60)$$

With this N becomes

$$N = \frac{1}{\beta} \frac{\partial \ln(Z(\mu))}{\partial \mu} \quad (5.61)$$

$$= \frac{1}{\beta} \frac{\partial z}{\partial \mu} \frac{\partial \ln(Z(\mu))}{\partial z} \quad (5.62)$$

$$= z \frac{\partial \ln(Z(z))}{\partial z} \quad (5.63)$$

we define the concentration as

$$c = \frac{N}{V} \quad (5.64)$$

$$= \sum_{l=1}^{\infty} l \left(\frac{z}{\lambda_t^3} \right)^l b_l \quad (5.65)$$

$$c \approx b_1 \frac{z}{\lambda_t^3} + b_2 2 \left(\frac{z}{\lambda_t^3} \right)^2 + \dots \quad (5.66)$$

$$\frac{z}{\lambda_t^3} \approx c - 2b_2 c^2 + O(c^3) \quad \text{small } z! \quad (5.67)$$

$$\frac{P}{k_B T} = \frac{Z}{\lambda_t^3} + \left(\frac{Z}{\lambda_t^3} \right)^2 b_2 + O\left(\left(\frac{z}{\lambda_t^3} \right)^3 \right) \quad (5.68)$$

$$= c - b_2 c^2 + O(c^3) \quad (5.69)$$

The leading term is the ideal gas law and the correction term is proportional to $-b_2 c^2$. With the model of hard spheres with diameter d this becomes

$$b_1 = 1 \quad (5.70)$$

$$b_2 = \frac{1}{2} \int \frac{d^3 q_1 d^3 q_2}{v} (e^{-\beta w(q_1 - q_2)} - 1) \quad (5.71)$$

$$= -\frac{1}{2} \frac{4\pi}{3} d^3 \quad (5.72)$$

$$= -\frac{1}{2} v_{ex} \quad (5.73)$$

Here $v_{ex} = \frac{4\pi}{3} d^3$ is the excluded volume. And with all of that $\frac{P}{k_B T}$ becomes

$$\frac{P}{k_B T} = c + \frac{1}{2} v_{ex} c^2 + O(c^3) \quad (5.74)$$

So the first correction to the ideal gas law is proportional to the excluded volume of the hard-sphered particles.

5.2.1 Side Note on the Inversion of Power Series

$$c = \sum_{l=1}^{\infty} d_l z^l \quad z^l \text{ small } z! \quad (5.75)$$

Starting from the Ansatz

$$Z = \sum_{l=1}^{\infty} n_l c^l \quad (5.76)$$

and inserting it c becomes

$$c = d_1 Z + d_2 Z^2 + d_3 Z^3 + \dots \quad (5.77)$$

$$= d_1 (n_1 c + n_2 c^2 + \dots) + d_2 (n_1 c + n_2 c^2 + \dots)^2 + \dots \quad (5.78)$$

$$= d_1 n_1 c + (d_1 n_2 + d_2 n_1^2) c^2 + \dots \quad (5.79)$$

$$(5.80)$$

By equating the coefficients this yields

$$d_1 n_1 \stackrel{!}{=} 1 \quad \rightarrow \quad n_1 = 1/d_1 \quad (5.81)$$

$$d_1 n_2 + d_2 n_1^2 \stackrel{!}{=} 0 \quad \rightarrow \quad n_2 = \dots \quad (5.82)$$

5.3 Van-der-Waals Equation of State.

The typical pair potential $w(r)$ (figure 5.1) of a real gas is

$$w(r) = \begin{cases} \infty & |r| < D \\ -w_0 \left(\frac{D}{r}\right)^s & |r| > D \end{cases} \quad (5.83)$$

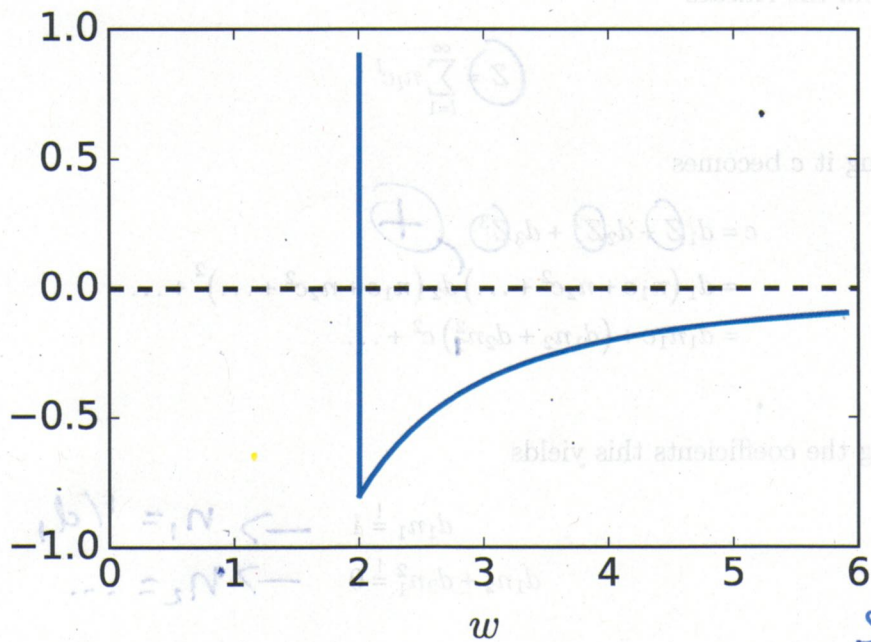


Figure 5.1: Typical pair potential (Here for example: $D = 2$, $s = 2$)

The first non-trivial virial coefficient is the second one, which becomes

$$a_2 = \frac{1}{2} \int_0^\infty dr 4\pi r^2 (1 - e^{-\beta w(r)}) \quad (5.84)$$

$$= 2\pi \int_0^D dr r^2 + 2\pi \int_D^\infty dr r^2 \left(1 - e^{-\frac{w_0}{k_B T} \left(\frac{D}{r}\right)^s}\right) \quad (5.85)$$

The second integral can not be solved in closed form as it will result in a gamma function. So rather weak attraction can be assumed and

$$\frac{w_0}{k_B T} < 1 \quad (5.86)$$

$$a_2 = \frac{2\pi}{3} D^3 - 2\pi D^s \frac{w_0}{k_B T} \int_D^\infty dr r^{2-s} \quad (5.87)$$

For $s > 3$ the integral converges and it can be written as

$$a_2 = \frac{2\pi}{3} D^3 - \frac{2\pi}{s-3} D^3 \frac{w_0}{k_B T} \quad (5.88)$$

with

omit \rightarrow $a' = \frac{2\pi}{s-3} D^3 w_0 \quad (5.89)$

$$b' = \frac{2\pi}{3} D^3 \quad (5.90)$$

this becomes

$$a_2 \equiv b' - \frac{a'}{k_B T} \quad (5.91)$$

$$(5.92)$$

Which is now the second virial coefficient. It can be plugged into the virial expansion.

$$\frac{P}{k_B T} = c + a_2 c^2 \quad (5.93)$$

$$= c + \left(b' - \frac{a'}{k_B T} \right) c^2 \quad (5.94)$$

$$P = ck_B T + (b' k_B T - a') c^2 \quad (5.95)$$

$$P + a' c^2 = ck_B T (1 + b' c) \quad (5.96)$$

with the expansion for $\frac{1}{1-\epsilon} \approx 1 + \epsilon + O(\epsilon^2)$ this becomes

$$\approx \frac{ck_B T}{1 - b' c} \quad (5.97)$$

$$P + a' c^2 = \frac{ck_B T}{1 - b' c} \quad (5.98)$$

$$(P + a' c^2)(1 - b' c) = ck_B T \quad (5.99)$$

$$(5.100)$$

With $c = \frac{N}{V}$ this becomes the Van-der-Waals equation of state.

$$\left(P + \frac{a' N^2}{V^2} \right) (V - b' N) = N k_B T \quad (5.101)$$

5.3.1 Conclusions

- In the ideal limit ($w_0 \rightarrow 0$ and $V \rightarrow \infty$) $a' = b' = 0$ the Van-der-Waals equation of state becomes the ideal equation of state.
- The real volume $V_{\text{real}} = V - b' N$ is reduced by the volume of particles.
- The real pressure $P_{\text{real}} = P + \frac{a' N^2}{V^2}$ is increased by the attraction between the particles, as $a_2 \propto w_0 D^3$.

$\left(P + \frac{a' N^2}{V^2} \right) (V - b' N) = N k_B T$ can be rewritten as

Eq 5.01

$$P = \frac{N k_B T}{V - b' N} - \frac{a' N^2}{V^2} \quad (5.102)$$

which is and plotted in figure 5.2.

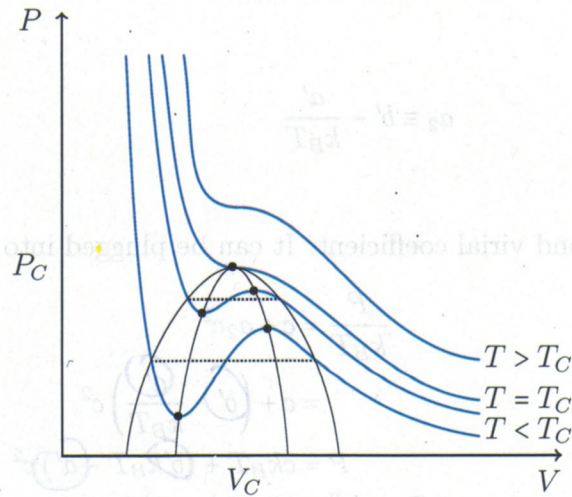


Figure 5.2: P-V diagram of the Van-der-Waals equation

So there is a finite range of volume for $T < T_c$ within which the volume goes up when the pressure increases. As a negative compressibility is unphysical, the Maxwell construction is used.

$$dF = -SdT - PdV \quad (5.103)$$

With a constant T this becomes

$$= -PdV. \quad (5.104)$$

Hence the free energy difference between two volumes V_1 and V_2 along an isotherm is

$$\Delta F = - \int_{V_1}^{V_2} P(V) dV \quad (5.105)$$

The ΔG for two system parts with the same P_0 is

$$\Delta G = \Delta F + P_0 \Delta V \quad (5.106)$$

$$= \int_{V_1}^{V_2} (P_0 - P(V)) dV \quad (5.107)$$

$$= 0 \quad (5.108)$$

This is the equilibrium condition at phase coexistence.

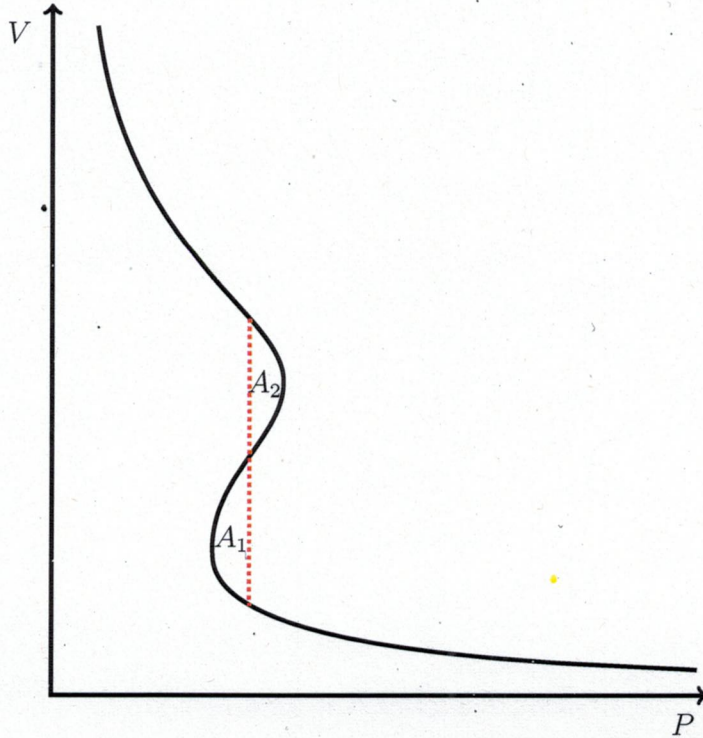


Figure 5.3: V-P-diagram. The two areas A_1 and A_2 must be equal: only then the integral becomes zero.

The region with $\frac{dP}{dV} > 0$ is never observed, because the system splits into two volumes V_1 and V_2 at pressure P_0 . These so called binodals limit the two-plane coexistence region. Below the critical temperature $T < T_c$ there are two planes and there are volumes, where the slope is zero, there is a volume where the curvature is zero. At the critical point the slope and the curvature are zero. This is how the critical point can be found. So from equation (5.102) the volume, temperature (up to a factor of k_B) and the pressure at the critical (c) point Q_c are $V_{\text{critical}} = 3b'N$, $k_B T_c = \frac{8}{27} \frac{a'}{b'}$ and $P_{\text{critical}} = \frac{a'}{27b'^2}$.

So what does ~~all~~ of this mean? The equation ~~predicts~~ a critical point at V_c, P_c, T_c .

incomplete!

6 Quantum Statistics

Suggested

6.1 Quantum Theory

discovers led

There are a ~~small~~ number of experimental ~~insights~~ that ~~lead~~ to the development of quantum theory. One of them is the photo electric effect, where an electron is emitted from a metal surface, when hit by radiation, which ~~gave the impression~~ that the energy is quantized by h with $E = h\nu$. The second one was the electron diffraction experiment which resulted in $\lambda = \frac{h}{p}$.

In classical mechanics Newtons equation of motion describes the energy E of a system $E = \frac{p^2}{2m}$. This can also be applied to waves. The simplest possible wave is a planar wave

$$\Psi(x, t) \propto e^{i(kx - \omega t)} \quad (6.1)$$

with the momentum

$$p = \frac{h}{\lambda} \quad (6.2)$$

$$= \hbar k \quad (6.3)$$

$$k = \frac{2\pi}{\lambda} \quad (6.4)$$

and $\hbar = \frac{h}{2\pi}$

with $\omega = 2\pi\nu$ the energy can be written as

$$E = h\nu \quad (6.5)$$

$$= \hbar\omega \quad (6.6)$$

$$E = \frac{p^2}{2m} \quad (6.7)$$

And from ~~this~~ the Schrödinger equation emerges.

$$i\hbar \frac{\partial \Psi}{\partial t} \quad (6.8)$$

$$= -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} \quad (6.9)$$

With an external potential V the energy becomes

$$E = \frac{p^2}{2m} + V(x). \quad (6.10)$$

And the stationary Schrödinger equation is

$$E_n \Psi_n(x) = \hat{H} \Psi_n(x). \quad (6.11)$$

With the Hamiltonian \hat{H} .

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (6.12)$$

$$\Psi(x) \Psi^*(x) = |\Psi(x)|^2 \quad \text{means what?} \quad (6.13)$$

6.1.1 N Particle Wave Function

The N particle Hamiltonian reads

$$\hat{H} = \frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \underbrace{\sum_{i=1}^N u(\vec{r}_i)}_{\text{external potential}} + \underbrace{\sum_{i=1}^N v(\vec{r}_i - \vec{r}_j)}_{\text{interaction potential}} \quad (6.14)$$

The Schrödinger equation becomes

$$\hat{H} \Psi_n(\vec{r}_1, \dots, \vec{r}_N) = E_n \Psi_n(\vec{r}_1, \dots, \vec{r}_N) \quad (6.15)$$

Assuming Ψ_n is an eigenfunction of \hat{H}

Pauli 1940 in his famous paper (Physical Reviews 58, 716) introduced a permutation operator P_{ij} , exchanging the i th and the j th particle.

$$\hat{P}_{ij} \Psi_n(\vec{r}_1, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) = \Psi_n(\vec{r}_1, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N) \quad (6.16)$$

Clearly double application of P results in the original order.

$$\hat{P}_{ij}^2 \Psi_n(\vec{r}_1, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) = \Psi_n(\vec{r}_1, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) \quad (6.17)$$

But how is this interesting? The eigenvalue of P^2 is 1. In principle the sign in front of Ψ after application of P can be either one (+) or minus one.

$$\hat{P}_{ij} \Psi_n(\vec{r}_1, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) = \pm \Psi_n(\vec{r}_1, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N) \quad (6.18)$$

So it looks this sign does not matter at all, when applying P again, but as it turns out the sign tells what kind of particles one is dealing with.

Sign	Spin	Particles
+	integer	Bosons (Photons, Phonons, He ⁴ atoms, Li, Na, ...)
-	half integer	Fermions (electrons, He ³ atoms, ...)

Table 6.1: Particle overview, sorted by spin and sign of Ψ after application of the permutation operator

Consequences For Fermions

A product wave function can be expressed as

$$\Psi_{(\alpha_1, \alpha_2, \dots)}(\vec{r}_1, \dots, \vec{r}_N) = \phi_{(\alpha_1)}(\vec{r}_1) \phi_{(\alpha_2)}(\vec{r}_2) \dots \phi_{(\alpha_N)}(\vec{r}_N) \quad (6.19)$$

Where α are quantum numbers characterising the N particle state. Now \hat{P} can be applied. We assume Fermions

$$\hat{P}_{ij} \phi_{(\alpha_1)}(\vec{r}_1) \dots \phi_{(\alpha_i)}(\vec{r}_i) \dots \phi_{(\alpha_j)}(\vec{r}_j) \dots \phi_{(\alpha_N)}(\vec{r}_N) \quad (6.20)$$

$$= -\phi_{(\alpha_1)}(\vec{r}_1) \dots \phi_{(\alpha_j)}(\vec{r}_j) \dots \phi_{(\alpha_i)}(\vec{r}_i) \dots \phi_{(\alpha_N)}(\vec{r}_N) \quad (6.21)$$

If the particles i and j are in the same quantum state $\alpha_i = \alpha_j = \alpha$ then

$$\hat{P}_{ij} \phi_{\alpha}(\vec{r}_i) \phi_{\alpha}(\vec{r}_j) \stackrel{!}{=} -\phi_{\alpha}(\vec{r}_j) \phi_{\alpha}(\vec{r}_i) \quad (6.22)$$

$$= \phi_{\alpha}(\vec{r}_j) \phi_{\alpha}(\vec{r}_i) \quad (6.23)$$

Which would result in $1 = -1$ which means that the assumption was wrong. So what this shows is that all particles, that have a negative sign when the permutation operator is applied, can never have been in the same state. This is called Pauli's principle that states that all fermions must be in different states.

In the occupation number picture n_{α} is the occupation number of state α with the normalisation

$$N = \sum_{\alpha=1}^{\infty} n_{\alpha} \quad n_{\alpha} = 0 \text{ or } 1 \quad (6.24)$$

For Fermions there can be either one or no particles in any state, For bosons however there can be any number of particles (also none or all) in any state at the same time.

6.2 Boson and Fermion Statistics: General Results

A quantum system of N particles is characterised by the occupation numbers n_i of state i and single particle energy levels ϵ_i . The total number of particles N is

$$N = \sum_{i=1}^{\infty} n_i \quad (6.25)$$

And the Hamiltonian \mathbb{H} is

$$\mathbb{H}(\{n_i\}) = \sum_{i=1}^{\infty} n_i \epsilon_i \quad (6.26)$$

The partition function Z_N is the sum over all distributions n_i of $e^{-\beta \mathbb{H}(\{n_i\})}$

$$Z_N = \sum_{\{n_i\}} e^{-\beta \mathbb{H}(\{n_i\})} \quad (6.27)$$

6 Quantum Statistics

And the grand canonical partition function $\mathbb{Z}(z)$ becomes

$$\mathbb{Z}(z) = \sum_{N=0}^{\infty} z^N \sum_{\{n_i\}} e^{-\beta \sum_i \epsilon_i n_i} \quad (6.28)$$

$$= \sum_{\{n_i\}} z^{\sum_i n_i} e^{-\beta \sum_i \epsilon_i n_i} \quad (6.29)$$

$$= \sum_{n_1} \sum_{n_2} \dots z^{\sum_i n_i} e^{-\beta \sum_i \epsilon_i n_i} \quad (6.30)$$

$$= \sum_{n_1} z^{n_1} e^{-\beta \epsilon_1 n_1} \sum_{n_2} z^{n_2} e^{-\beta \epsilon_2 n_2} \dots \quad (6.31)$$

so this factorises completely. For fermions this becomes

$$= \sum_{n_1=0}^1 z^{n_1} e^{-\beta \epsilon_1 n_1} \sum_{n_2=0}^1 z^{n_2} e^{-\beta \epsilon_2 n_2} \dots \quad (6.32)$$

$$= (1 + ze^{-\beta \epsilon_1})(1 + ze^{-\beta \epsilon_2}) \dots \quad (6.33)$$

And the grand canonical partition function for Fermions becomes

$$\mathbb{Z}(z) = \prod_{i=1}^{\infty} (1 + ze^{-\beta \epsilon_i}) \quad (6.34)$$

For Bosons the grand canonical partition function is

$$\mathbb{Z}(z) = \sum_{n_1=0}^{\infty} z^{n_1} e^{-\beta \epsilon_1 n_1} \sum_{n_2=0}^{\infty} z^{n_2} e^{-\beta \epsilon_2 n_2} \dots \quad (6.35)$$

$$\sum_{n_1=0}^{\infty} z^{n_1} e^{-\beta \epsilon_1 n_1} = 1 + ze^{-\beta \epsilon_1} + (ze^{-\beta \epsilon_1})^2 + (ze^{-\beta \epsilon_1})^3 + \dots \quad (6.36)$$

$$= \frac{1}{1 - ze^{-\beta \epsilon_1}} \quad (6.37)$$

$$\mathbb{Z}(z) = \frac{1}{1 - ze^{-\beta \epsilon_1}} \cdot \frac{1}{1 - ze^{-\beta \epsilon_2}} \dots \quad (6.38)$$

And the grand canonical partition function for Bosons becomes

$$\mathbb{Z}(z) = \prod_{i=1}^{\infty} \frac{1}{1 - ze^{-\beta \epsilon_i}} \quad (6.39)$$

There is a problem, when $ze^{-\beta \epsilon_i} \rightarrow 1$ as \mathbb{Z} diverges. This results in a phase transition, the Bose-Einstein condensation. So the grand canonical partition functions $\mathbb{Z}(z, T, V)$ are calculated exactly for Bosons and Fermions. And from these all thermodynamic relations can be calculated. The mean occupation of energy level m is

$$\langle n_m \rangle = \frac{\sum_{\{n_j\}} n_m z^{\sum_k n_k} e^{-\beta \sum_j \epsilon_j n_j}}{\sum_{\{n_j\}} z^{\sum_k n_k} e^{-\beta \sum_j \epsilon_j n_j}} \quad (6.40)$$

$$= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_m} \ln \left(\sum_{\{n_j\}} z^{\sum_k n_k} e^{-\beta \sum_j \epsilon_j n_j} \right) \quad (6.41)$$

$$\langle n_m \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_m} \ln(\mathbb{Z}) = \pm \sum_{i=1}^{\infty} \ln(1 \pm ze^{-\beta \epsilon_j}) \quad (6.42)$$

$\ln \mathbb{Z} = \dots$

Here the equation with the plus sign is true for **F**ermions and the one with the minus sign corresponds to the **B**osons. sign

$$\langle n_m \rangle = \frac{ze^{-\beta\epsilon_m}}{1 \pm ze^{-\beta\epsilon_m}} \quad (6.43)$$

$$= \frac{1}{e^{\pm\beta\epsilon_m} z^{-1} \pm 1} \quad (6.44)$$

This now is the distribution function of the ratio between Fermions and Bosons. The total particle number is

$$\langle n_m \rangle = N \quad (6.45)$$

$$= \sum_m \langle n_m \rangle \quad (6.46)$$

$$= \sum_m \frac{1}{e^{\pm\beta\epsilon_m} z^{-1} \pm 1} \quad (6.47)$$

And the internal energy U is

$$U = \sum_m \langle n_m \rangle \epsilon_m \quad (6.48)$$

$$= \sum_m \frac{\epsilon_m}{e^{\pm\beta\epsilon_m} z^{-1} \pm 1} \quad (6.49)$$

$$(6.50)$$

6.3 Free Ideal Fermions

How to correctly count quantum states? A normalised plane wave can be written as

$$\phi_p(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{p}\vec{r}/\hbar} \quad (6.51)$$

with

$$\int_V d^3r |\phi_p(\vec{r})|^2 = 1. \quad (6.52)$$

$$(6.53)$$

So the kinetic energy operator operates on the plane wave such that

$$-\frac{\hbar^2}{2m} \nabla^2 \phi_p(\vec{r}) = \frac{\vec{p}^2}{2m} \phi_p(\vec{r}) \quad (6.54)$$

So $\phi_p(\vec{r})$ are eigenfunctions to the kinetic energy (and many more) operator(s). With periodic boundary conditions in a box of length L with Volume $V = L^3$ the wave function is invariant under translation.

$$\phi_p(\vec{r} + L\hat{e}_x) = \phi_p(\vec{r}) \quad (6.55)$$

6 Quantum Statistics

This means that

$$\bar{p} = \frac{2\pi\hbar}{L} \bar{n} \quad (6.56)$$

$$\bar{n} = \begin{pmatrix} 0, 1, 2, \dots \\ 0, 1, 2, \dots \\ 0, 1, 2, \dots \end{pmatrix} \quad (6.57)$$

So the momentum quantum numbers form a cubic lattice with lattice constant

$$\frac{2\pi\hbar}{L} = \frac{h}{L} \quad (6.58)$$

In the continuum limit $L \rightarrow \infty$ this becomes.

$$\int d^3p \rightarrow \left(\frac{h}{L}\right)^3 \sum_{\bar{p}} \quad (6.59)$$

$$\sum_{\bar{p}} = \frac{V}{h^3} \int d\bar{p}. \quad (6.60)$$

So for fermions such as electrons again $\langle n_m \rangle$ is

$$\langle n_m \rangle = \frac{1}{e^{\beta\epsilon_m} z^{-1} + 1} \quad (6.61)$$

with $z \equiv e^{\beta\epsilon_F} n(\epsilon)$ is

$$n(\epsilon) = \frac{1}{1 + e^{\beta(\epsilon - \epsilon_F)}} \quad (6.62)$$

So the Fermi energy is the chemical potential.

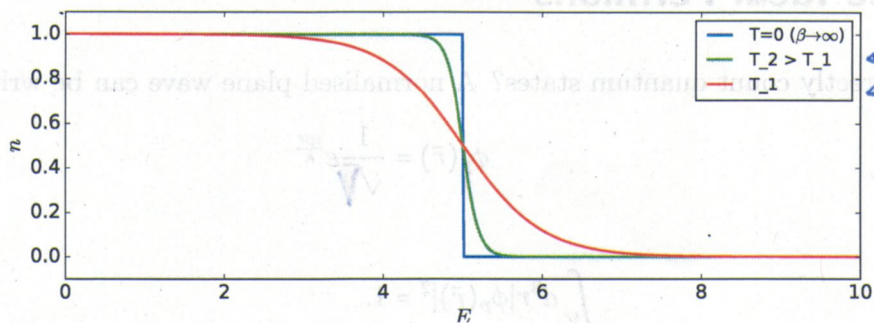


Figure 6.1: Fermi distribution for three different temperatures

The Fermi energy ϵ_F is determined by the total number of particles N . At $T = 0$ N is

$$N = g \sum_{p_i < p_F} 1 \quad (6.63)$$

$$= \frac{gV}{h^3} \int_{|p| < p_F} d^3p \quad (6.64)$$

$$= \frac{gV}{h^3} \frac{4\pi}{3} p_F^3 \quad (6.65)$$

where g is the multiplicity of a state

6.4 Free Ideal Bosons and Black Body Radiation

We use

So the $\epsilon_F = \frac{p_F^2}{2m}$ and the multiplicity which is $g = 2$ for spin $s = \frac{1}{2}$ particles. With that p_F^3 is

$$p_F^3 = \frac{N h^3}{V g 4\pi} \quad (6.66)$$

$$= (2m\epsilon_F)^{\frac{3}{2}}. \quad (6.67)$$

and the Fermi energy is

$$\epsilon_F = \frac{h^2}{2m} \left(\frac{N}{V} \frac{3}{4\pi g} \right)^{\frac{2}{3}}. \quad (6.68)$$

With

So the electron mass of $m_e = 9 \cdot 10^{-31} \text{ kg}$, Planck's constant $h = 7 \cdot 10^{-34} \text{ Js}$ and $n = \frac{N}{V} = \frac{1}{(0.3 \cdot 10^{-9} \text{ m})^3}$ the Fermi energy at room temperature becomes

$$\epsilon_F \approx 2 \cdot 10^{-19} \text{ J} \quad (6.69)$$

$$= 50 k_B T \quad (6.70)$$

So typical electrons in metals are in fact very "hot".

6.4 Free Ideal Bosons and Black Body Radiation

From $E = mc^2$ follows

$$E = mc^2 \quad (6.71)$$

$$= \frac{m_0 c^2}{(1 - \frac{v^2}{c^2})^{1/2}} \quad (6.72)$$

$$E^2 \left(1 - \frac{v^2}{c^2} \right) = m_0^2 c^4 \quad (6.73)$$

$$E^2 = m_0^2 c^4 + E^2 \frac{v^2}{c^2} \quad (6.74)$$

$$= m_0^2 c^4 + m^2 v^2 c^2 \quad (6.75)$$

$$E = \sqrt{m_0^2 c^4 + p^2 c^2} \quad (6.76)$$

So in the non-relativistic limit this becomes

$$E = m_0 c^2 \sqrt{1 + \frac{p^2}{m_0^2 c^2}} \quad (6.77)$$

$$\approx m_0 c^2 + \frac{p^2}{2m_0} \quad (6.78)$$

In the ultra-relativistic limit this becomes

$$E = pc \sqrt{1 + \frac{m_0^2 c^2}{p^2}} \quad (6.79)$$

$$\approx pc \quad (6.80)$$

which is the correct limit for photons

which do not have a resting mass.

where the first term is a constant and the second term is the normal energy-momentum relation

6 Quantum Statistics

the ultra-relativistic

From these dispersion relations the internal energy becomes

$$U = g \sum_p \epsilon_p \langle n_p \rangle \tag{6.81}$$

$$= g \sum_p \frac{pcze^{-\beta pc}}{1 - ze^{-\beta pc}} \tag{6.82}$$

Here g is the multiplicity which is $g = 2$ for photons and U becomes

$$U = 2 \frac{V}{h^3} \int_{-\infty}^{\infty} d^3p \frac{|p|ce^{-\beta|p|c}}{1 - ze^{-\beta|p|c}} \tag{6.83}$$

Here the fugacity $z = 1$ as $\mu = 0$ and the energy is

$$U = \frac{2V4\pi c}{h^3} \int_0^{\infty} dp p^3 \frac{e^{-\beta pc}}{1 - e^{-\beta pc}} \tag{6.84}$$

With $p = \frac{\hbar}{c}\omega$ this becomes

$$\frac{U}{V} = \frac{8\pi\hbar^4}{c^3h^3} \int d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \tag{6.85}$$

$$\equiv \int_0^{\infty} d\omega u(\omega) \tag{6.86}$$

density $u(\omega) = \frac{\hbar}{\pi^2c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \tag{6.87}$

Here $u(\omega)$ is the spectral energy. For small ω the denominator $e^{\beta\hbar\omega} - 1$ becomes $\beta\hbar\omega$ and from that the famous Rayleigh-Jeans law becomes *is obtained*

$$u(\omega) \approx \frac{k_B T \omega^2}{c^3 \pi^2} \tag{6.88}$$

and for large ω this becomes Wien's law

$$u(\omega) \approx \frac{\hbar}{\pi^2 c^3} \omega^3 e^{-\beta\hbar\omega} \tag{6.89}$$

Where the maximum of $u(\omega)$ is *at located at*

$$\omega_{\max} = 2.8 \frac{k_B T}{\hbar} \tag{6.90}$$

So for every temperature there is a different curve. This can be seen in figure 6.2.

and shifts to higher frequency with rising temperatures.

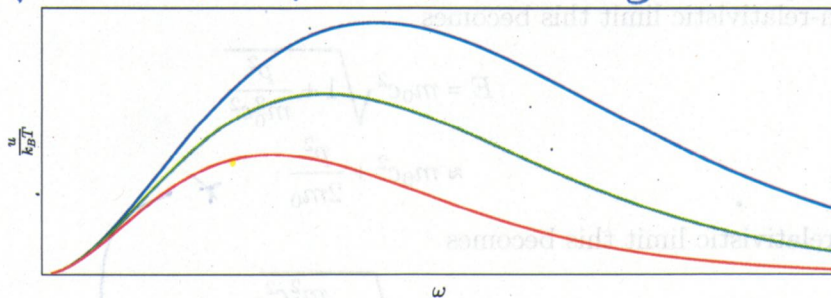


Figure 6.2: Wien's law for three different temperatures

plot the full Planck formula!

add Bose-Einstein condensation!

7 Appendix

7.1 About this Script

This lecture was given by Prof. Roland Netz in the summer of 2016. This document started as off as private notes that were turned into a full script.

Most of the script was proof read multiple times, but if you find any errors, please mark them on a printed or PDF version of the script (or in a plain list with page numbers) and send them to me. I will try to correct them directly. Most importantly we want to correct the contextual and mathematical errors, but if you find layout errors, wrong labels on figures, simple typos or wrong commata or anything else, please also send them to me. I hope this script helps you with your studies :)

Martin Borchert (martin.b@fu-berlin.de)

7.1.1 Distribution

For the rights about distribution to people outside the physics department or for other uses, please contact Professor Netz.

7.1.2 Graphs and Figures

All graphs and figures were done in latex via the Tikz package or in python with Matplotlib (of course via Jupyter Notebook!). Note: `svg2tikz` is an awesome extension for Inkscape (awesome vector graphics drawing tool) to create Tikz easily!

7.1.3 Version

The current version is 1.1 (18.4.2017)- Updates since the last version (1.0)(16.4.17) are for example (in addition to small typo corrections):

- Nothing yet

Code character count: 110862

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