

summary of statistical physics

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Contents

1	Probability moments – definitions	3
2	bases of thermodynamics	4
2.1	I. law of thermodynamics	4
2.2	entropy	4
2.2.1	partial differentials of $S(E, V, N)$	4
2.2.2	maximum of S	5
2.3	extensive, intensive variable	5
2.4	homogeneous systems	5
2.5	thermodynamic potentials	5
2.5.1	thermodynamic force	5
2.5.2	Definition	6
2.5.3	Differentials	6
2.5.4	partial differentials	6
3	statistic ensembles	7
3.1	definitions	7
3.2	partition functions	7
3.3	thermodynamic potentials	8
3.4	entropy	9
4	classical statistics	10
4.1	equipartition theorem	10
4.2	Maxwell-Boltzmann-distribution	10
5	one-atomic ideal gas	11
5.1	General properties	11
5.2	partition functions	11
5.3	phase volume	11
6	ideal quantum gases	12
6.1	Bose particles	12
6.2	Fermi particles	13
6.3	variables in terms of generalised zeta function	14
6.4	ideal Fermi gas ($g=2$)	15

6.5	ideal Bose gas (photon gas)	15
6.5.1	Planck's law	16
6.6	phonon gas	16
6.7	paramagnetism	17
7	Thermodynamics (Phenomenological)	19
7.1	I. law of thermodynamics	19
7.2	Equations of state	19
7.3	Thermodynamic coefficients	19
7.4	Thermodynamic relations	20
7.4.1	consequences of the I. law	20
7.4.2	consequences of the integrability conditions – Maxwell-relations	20
7.4.3	consequences of the homogeneity properties	21
7.4.4	change of thermodynamic variables	21
8	Thermodynamic processes	22
8.1	quasistatic processes	22

1 Probability moments – definitions

with the probability distribution $f(n)$ we find the *generating function*:

$$F(x) = \sum_{n=0}^N f(n)x^n$$

then the moments of statistics are

1. moment	$\langle n \rangle = \partial_x F(x) _{x=1}$	mean value
2. moment	$(\Delta n)^2 = \partial_x^2 F(x) _{x=1} = \partial_x \langle n \rangle$	variance
3. moment	$m_3 = \partial_x^3 F(x) _{x=1} = \partial_x (\Delta n)^2$	

1. moment of the square value:

$$\langle n^2 \rangle = \partial_x^2 F(x)|_{x=1} + \partial_x F(x)|_{x=1}$$

then we find for the variance (2. moment)

$$(\Delta n)^2 = \langle n^2 \rangle - \langle n \rangle^2$$

example: energy

$$F(\beta) = \sum \rho_c \beta^n = \sum \frac{e^{-\beta E}}{Z_c} \beta^n = \frac{1}{Z_c} \sum e^{-\beta E} \beta^n$$

mean value	$\langle E \rangle = -\partial_\beta \ln Z_c$	internal energy	(1)
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variance	$(\Delta n)^2 = -\partial_\beta^2 \ln Z_c$	(2)
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3. moment	$m_3 = -\partial_\beta^3 \ln Z_c$	(3)
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2 bases of thermodynamics

2.1 I. law of thermodynamics

$$\begin{aligned}dE &= T dS - p dV + \mu dN \\ &= \delta Q + \delta A + \delta_N E\end{aligned}\tag{4}$$

it follows

$$T = \left(\frac{\partial E}{\partial S} \right)_{V,N}\tag{5}$$

$$p = - \left(\frac{\partial E}{\partial V} \right)_{S,N}\tag{6}$$

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} = -T \left(\frac{\partial S}{\partial N} \right)_{E,V} \quad \text{chemical potential}\tag{7}$$

2.2 entropy

common definition

$$\begin{aligned}S &= -k_B \sum_n \rho_n \ln \rho_n \\ S &= -k_B \text{Tr}(\hat{\rho}_n \ln \hat{\rho}_n)\end{aligned}\tag{8}$$

with ρ_n : probability to find the system in state n

2.2.1 partial differentials of $S(E, V, N)$

By rearranging the I. law of thermodynamics we find the full differential

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN$$

it follows

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N}\tag{9}$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N}\tag{10}$$

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N} \right)_{V,E}\tag{11}$$

2.2.2 maximum of S

The entropy S is maximum if all ρ_n 's are equal. In a spin system for example, if all spins are aligned. Maximum Value:

$$S_{\max} = k_B \ln g \quad (12)$$

2.3 extensive, intensive variable

Quantities are called *extensive* if the enlargement of the system enlarges the quantity too (mass), and *intensive* if the quantity stays the same if the system is enlarged (temperature, pressure, densities). So for one state-variable applies, if the system is enlarged by a factor λ :

$$\begin{aligned} x \text{ is extensive, if } & x \mapsto \lambda x \quad \text{i.e.} \quad f(\lambda x) = \lambda f(x) \\ x \text{ is intensive, if } & x \mapsto x \end{aligned}$$

examples:

- extensive {energy, mass, number of particles, heat capacity, entropy, volume}
- intensive {energy-density, density of particles, specific heat capacity, temperature, pressure }

2.4 homogeneous systems

from the extensivity of the entropy $S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$ follows

$$S = \frac{1}{T}E + \frac{p}{T}V - \frac{\mu}{T}N$$

which is called the *Duham-Gibbs relation* in this way

$$E = TS - pV + \mu N \quad (13)$$

For the grand canonical ensemble $J = E - TS - \mu N$ we derive then

$$J(T, V, \mu) = -p(T, \mu)V \quad (14)$$

and for the Gibbs potential

$$G(T, p, \mu) = \mu(p, T)N \quad (15)$$

2.5 thermodynamic potentials

2.5.1 thermodynamic force

The temperature T is the driving force for the heat and entropy exchange and the pressure p is the driving force for the volume exchange. Thus T and p are thermodynamic forces which lead to a change in state $E(S, V, N)$.

2.5.2 Definition of thermodynamic potentials

$$\text{energy} \quad E \quad (16)$$

$$\text{free energy} \quad F = E - TS \quad (17)$$

$$\text{enthalpy} \quad H = E + pV \quad (18)$$

$$\text{free enthalpy} \quad G = E - TS + pV \quad (19)$$

$$\text{grand canonical potential} \quad J = E - TS - \mu N \quad (20)$$

2.5.3 Differentials of thermodynamic potentials

From

$$dE = T dS - p dV + \mu dN$$

$$d(TS) = T dS + S dT$$

$$d(pV) = p dV + V dp$$

we get

$$dE(S, V, N) = T dS - p dV + \mu dN \quad (21)$$

$$dF(T, V, N) = -S dT - p dV + \mu dN \quad (22)$$

$$dH(S, p, N) = T dS + V dp + \mu dN \quad (23)$$

$$dG(T, p, N) = -S dT + V dp + \mu dN \quad (24)$$

$$dJ(T, V, \mu) = -S dT - p dV - N d\mu \quad (25)$$

2.5.4 partial differentials of thermodynamic potentials

$$T = \left(\frac{\partial E}{\partial S} \right)_{V,N} \quad -p = \left(\frac{\partial E}{\partial V} \right)_{S,N} \quad \mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} \quad (26)$$

$$-S = \left(\frac{\partial F}{\partial T} \right)_{V,N} \quad -p = \left(\frac{\partial F}{\partial V} \right)_{T,N} \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} \quad (27)$$

$$T = \left(\frac{\partial H}{\partial S} \right)_{p,N} \quad V = \left(\frac{\partial H}{\partial p} \right)_{S,N} \quad \mu = \left(\frac{\partial H}{\partial N} \right)_{p,S} \quad (28)$$

$$-S = \left(\frac{\partial G}{\partial T} \right)_{p,N} \quad V = \left(\frac{\partial G}{\partial p} \right)_{T,N} \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{T,p} \quad (29)$$

$$-S = \left(\frac{\partial J}{\partial T} \right)_{V,\mu} \quad -p = \left(\frac{\partial J}{\partial V} \right)_{T,\mu} \quad -N = \left(\frac{\partial J}{\partial \mu} \right)_{T,V} \quad (30)$$

3 statistic ensembles

3.1 definitions

microcanonical ensemble

totally isolated system with fixed: E, V, N

canonical ensemble

isolated system in thermal contact (energy exchange) with fixed: T, V, N

grandcanonical ensemble

system with particle and energy exchange with fixed: T, V, μ

3.2 partition functions

The partition functions describe the System in equilibrium state:

$$\begin{array}{ll} \text{microcanonical} & \Omega(E, V, N) \\ \text{canonical} & Z_c(T, V, N) \\ \text{grand canonical} & Z_{gc}(T, V, \mu) \end{array}$$

The probability P for being in a micro state:

$$\rho(E, V, N) = \begin{cases} \frac{1}{\Omega(E, V, N)} & E - \delta E \leq E(V, N) \leq E \\ 0 & \text{otherwise} \end{cases} \quad (31)$$

$$\rho_c(T, V, N) = \frac{1}{Z_c} e^{-\beta E} \quad \text{Gibbs/Boltzmann distr.} \quad (32)$$

$$\rho_{gc}(T, V, \mu) = \frac{1}{Z_{gc}} e^{-\beta(E - \mu N)} \quad (33)$$

with $\Omega(E)$: Number of states with energy E – more precise: $\Omega(E) = \frac{d\phi(E)}{dE}$. $\phi(E)$ is the number of states between 0 and E – we call it the *phase volume*. Then $\Omega(E) = \phi(E + \delta E) - \phi(E)$.

The probabilities inhibit the normalisation conditions

$$\sum \rho_j = 1 \quad \text{microcanonical, canonical, grand canonical} \quad (34)$$

$$\sum \rho_j E_j = E \quad \text{canonical, grand canonical} \quad (35)$$

$$\sum \rho_j N_j = N \quad \text{grand canonical} \quad (36)$$

the equivalent statistical operator is

$$\hat{\rho} = \sum_j |j\rangle \frac{1}{\Omega(E)} \langle j| \quad (37)$$

$$\hat{\rho}_c = \frac{1}{Z_c} e^{-\beta \hat{H}} \quad (38)$$

$$\hat{\rho}_{gc} = \frac{1}{Z_{gc}} e^{-\beta(\hat{H} - \mu \hat{N})} \quad (39)$$

with the first normalisation condition follow the partition functions

$$\Omega(E, V, N) = \sum_{E - \delta E \leq E(V, N) \leq E} 1 \quad (40)$$

$$Z_c(T, V, N) = \sum_j g_j e^{-\beta E_j} \quad (41)$$

$$\begin{aligned} Z_{gc}(T, V, \mu) &= \sum_j g_j e^{-\beta(E_j - \mu N)} \quad (42) \\ &= \sum_j e^{\beta \mu N} Z_c(T, V, N) \quad \text{for classical gas } (N_i = N) \end{aligned}$$

3.3 thermodynamic potentials

All partition functions are determined by the eigenvalues E_j of an Hamiltonian. The relation to the macroscopic thermodynamics is as follows:

$$S = k_B \ln \Omega = k_B \ln \phi \quad (43)$$

$$F = -k_B T \ln Z_c \quad (44)$$

$$J = -k_B T \ln Z_{gc} \quad (45)$$

From the full differentials can by partial differentiation the variables E, p, μ, N be found:

$$dS = \frac{1}{T} dE - \frac{p}{T} dV - \frac{\mu}{T} dN \quad (46)$$

$$dF = -S dT - p dV + \mu dN \quad (47)$$

$$dJ = -S dT - p dV - N d\mu \quad (48)$$

So the derivation of the macroscopic structure from the microscopic structure, can be schematised as follows

$$H(V, N) \rightarrow E_j(V, N) \rightarrow \left\{ \begin{array}{l} \Omega(E, V, N) \rightarrow S(E, V, N) \\ Z_c(T, V, N) \rightarrow F(T, V, N) \\ Z_{gc}(T, V, \mu) \rightarrow J(T, V, \mu) \end{array} \right\} \rightarrow \begin{array}{l} \text{all thermo-} \\ \text{dynamic} \\ \text{relations} \end{array} \quad (49)$$

The variables E, p, β, μ, N in terms of the partition functions:

microcanonical

$$p = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial V} \quad (50)$$

$$\beta = \frac{\partial \ln \Omega}{\partial E} \quad (51)$$

canonical

$$p = \frac{1}{\beta} \frac{\partial \ln Z_c}{\partial V} \quad (52)$$

$$E = - \frac{\partial \ln Z_c}{\partial \beta} \quad (53)$$

grand canonical

$$N = \frac{1}{\beta} \frac{\partial \ln Z_{gc}}{\partial \mu} \quad (54)$$

$$p = \frac{1}{\beta} \frac{\partial \ln Z_{gc}}{\partial V} \quad (55)$$

$$E = - \frac{\partial \ln Z_{gc}}{\partial \beta} + \mu N \quad (56)$$

3.4 entropy

In general the entropy is $S = -k_B \sum_n \rho_n \ln \rho_n$ with these values for the probabilities ρ

$$\rho = 1/\Omega(E) = 1/g$$

$$\rho_c = e^{-\beta E} / Z_c$$

$$\rho_{gc} = e^{-\beta(E-\mu N)} / Z_{gc}$$

we get

$$S = k_B \ln \Omega = k_B \ln g \quad (57)$$

$$S_c = \frac{E}{T} + k_B \ln Z_c \quad (58)$$

$$S_{gc} = \frac{E}{T} - \frac{\mu N}{T} + k_B \ln Z_c \quad (59)$$

4 classical statistics

4.1 equipartition theorem

We find

$$\left\langle p_{i\alpha} \frac{\partial \mathcal{H}}{\partial p_{i\alpha}} \right\rangle_{cl} = k_B T \quad (60)$$

$$\left\langle x_{i\alpha} \frac{\partial \mathcal{H}}{\partial x_{i\alpha}} \right\rangle_{cl} = k_B T \quad (61)$$

from which follows

$$\left\langle \frac{p_{i\alpha}}{2m} \right\rangle = \frac{1}{2} k_B T \quad (62)$$

Theorem: *each degree of freedom, on which the Hamiltonian depends quadratically contributes the amount $\frac{1}{2}k_B T$ to the total internal energy E .*

4.2 Maxwell-Boltzmann-distribution

$$\rho_{\text{MB}} d^3\vec{p} = (2\pi m k_B T)^{-3/2} e^{-3/2} \exp\left(\frac{1}{k_B T} \frac{\vec{p}^2}{2m}\right) d^3\vec{p} \quad (63)$$

5 one-atomic ideal gas

5.1 General properties

$$pV = Nk_B T \quad (64)$$

$$E = \frac{3}{2} Nk_B T \quad (65)$$

$$\mu = -k_B T \ln \left(\frac{NV}{\lambda^3} \right)$$

5.2 partition functions

For an ideal gas there is no interaction between the particles, so that $Z_N = Z_1^N$. We find by inserting values for the energy in the general terms the following partition functions

$$\begin{aligned} \Omega(E, V, N) &= c^N \left(\frac{V}{N} \right)^N \left(\frac{E}{N} \right)^{3N/2} \\ Z_c(T, V, N) &= \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N \\ Z_{gc}(T, V, \mu) &= \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta\mu N} \left(\frac{V}{\lambda^3} \right)^N \end{aligned} \quad \lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \quad (66)$$

5.3 phase volume

$$\phi(E, V, N) = \frac{1}{N!} \left(\frac{V}{8\pi^3} \right)^N \frac{1}{\frac{3}{2}N!} \left(\frac{2m\pi E}{\hbar^2} \right)^{\frac{3N}{2}} \quad (67)$$

6 ideal quantum gases

6.1 Bose particles

We have noninteracting, indistinguishable particles. To proceed we define their variables:

number of particles	N
states	λ
set of occupation	$\{n_\lambda\}$
total energy of set $\{n_\lambda\}$	$E\{n_\lambda\}$
eigenvalues	ε_λ (energy of particle in state λ)
occupation number	$n_\lambda = 0, 1, 2, \dots$ (particles in state λ)

with

$$N = \sum_{\lambda} n_{\lambda} \quad (68)$$

$$E\{n_{\lambda}\} = \sum_{\lambda} \varepsilon_{\lambda} n_{\lambda} \quad (69)$$

Example:

$$\begin{aligned} \{n_{\lambda}\} &= \{1, 0, 3, 2, 4, 0, 1, 0, 0, 0, \dots\} \\ E\{n_{\lambda}\} &= 1\varepsilon_1 + 3\varepsilon_3 + 2\varepsilon_4 + 4\varepsilon_5 + 1\varepsilon_7 \end{aligned}$$

In order to determine the partition function we sum over all possible configurations of occupation numbers $\{n_\lambda\}$. According to the definition of the canonical ensemble the number of particles are fixed:

$$Z_c(N) = \sum_{\substack{\{n_\lambda\} \\ \sum_{\lambda} n_\lambda = N}} e^{-\beta E\{n_\lambda\}} \quad (70)$$

This is difficult to evaluate because N is not necessarily known and of a very high magnitude, which makes the constrain hard to satisfy.

To overcome this problem one usually employs the Grand Canonical partition function, where the particle number is not fixed. Thus we have to sum over the number of particles.

$$\begin{aligned} Z_{gc}^B &= \sum_N (Z_c(N) \cdot e^{\beta\mu N}) \\ &= \sum_N \left(\sum_{\substack{\{n_\lambda\} \\ \sum_{\lambda} n_\lambda = N}} e^{-\beta(E\{n_\lambda\} - \mu N)} \right) \end{aligned}$$

by replacing $E\{n_\lambda\}$ and N by their sums – where goes the first sum ??

$$\begin{aligned}
&= \sum_N \sum_{\{n_\lambda\}} e^{-\beta(\sum_\lambda \varepsilon_\lambda n_\lambda - \mu \sum_\lambda n_\lambda)} = \sum_{\{n_\lambda\}} e^{-\beta(\sum_\lambda (\varepsilon_\lambda - \mu) n_\lambda)} \\
&= \sum_{\{n_\lambda\}} \prod_\lambda e^{-\beta(\varepsilon_\lambda - \mu) n_\lambda}
\end{aligned}$$

This is the sum over all possible configurations of occupation numbers, summed over all states. This way each occupation number will change its number from zero to infinity. Thus we can rearrange the summation

$$= \prod_\lambda \sum_{n_\lambda=0}^{\infty} e^{-\beta(\varepsilon_\lambda - \mu) n_\lambda} = \prod_\lambda \sum_{n_\lambda=0}^{\infty} (e^{-\beta(\varepsilon_\lambda - \mu)})^{n_\lambda}$$

by using the rule of geometrical sum we get finally the grand canonical partition function

$$Z_{gc}^B = \prod_\lambda (1 - e^{-\beta(\varepsilon_\lambda - \mu)})^{-1} \quad (71)$$

potential

$$\begin{aligned}
J^B(T, V, \mu) &= -k_B T \ln Z_{gc}^B \\
&= k_B T \sum_n \ln (1 - e^{\beta(\varepsilon_n - \mu)})
\end{aligned} \quad (72)$$

mean occupation number

$$\langle n \rangle^B = -\partial_\mu J^B(T, V, \mu) = \frac{1}{e^{\beta(\varepsilon_n - \mu)} - 1} \quad (73)$$

6.2 Fermi particles

partition function

$$\begin{aligned}
Z_{gc}^F &= \prod_\lambda \sum_{n_\lambda=0,1} e^{-\beta(\varepsilon_\lambda - \mu) n_\lambda} \\
&= \prod_n (1 + e^{-\beta(\varepsilon_n - \mu)})
\end{aligned} \quad (74)$$

potential

$$\begin{aligned}
J^F(T, V, \mu) &= -k_B T \ln Z_{gc}^F \\
&= -k_B T \sum_n \ln (1 + e^{\beta(\varepsilon_n - \mu)})
\end{aligned} \quad (75)$$

mean occupation number

$$\langle n \rangle^F = -\partial_\mu J^F(T, V, \mu) = \frac{1}{e^{\beta(\varepsilon_n - \mu)} + 1} \quad (76)$$

density of states

$$\rho(\varepsilon) \equiv \sum_i \delta(\varepsilon - \varepsilon_i) \quad (77)$$

With dispersion relation $\varepsilon_k = \hbar k^2 / 2m$ we get exact numbers for density of states

$$3\text{D} : \quad \rho(\varepsilon) = gV \frac{m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \sqrt{\varepsilon} = \frac{gV}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} \quad (78)$$

$$2\text{D} : \quad \rho(\varepsilon) = \frac{Am}{2\pi \hbar^2} \quad (79)$$

$$1\text{D} : \quad \rho(\varepsilon) = \frac{Lm^{1/2}}{2^{3/2} \pi \hbar} \frac{1}{\sqrt{\varepsilon}} \quad (80)$$

6.3 variables in terms of generalised zeta function

Define:

$$\begin{aligned} n &= \frac{N}{V} && \text{particle density} \\ v &= \frac{V}{N} && \text{specific volume} \\ z &= e^{\beta\mu} && \text{fugacity} \end{aligned}$$

generalised zeta function

$$\left. \begin{aligned} f_\nu(z) \\ g_\nu(z) \end{aligned} \right\} = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1}}{\frac{e^x}{z} \pm 1} dx$$

mean occupation number / particle density

$$1\text{D} : \quad n = \frac{\pi}{2\lambda} \cdot \begin{cases} f_{\frac{1}{2}} & \text{Fermi} \\ g_{\frac{1}{2}} & \text{Bose} \end{cases} \quad (81)$$

$$2\text{D} : \quad n = \frac{1}{\lambda^2} \cdot \begin{cases} f_1 & \text{Fermi} \\ g_1 & \text{Bose} \end{cases} \quad (82)$$

$$3\text{D} : \quad n = \frac{g}{\lambda^3} \cdot \begin{cases} f_{\frac{3}{2}} & \text{Fermi} \\ g_{\frac{3}{2}} & \text{Bose} \end{cases} \quad (83)$$

grand canonical potential

$$J = -gV \frac{k_B T}{\lambda^3} \cdot \begin{cases} f_{\frac{3}{2}} & \text{Fermi} \\ g_{\frac{3}{2}} & \text{Bose} \end{cases} \quad (84)$$

$$J = -pV = -\frac{2}{3}E \quad (85)$$

6.4 ideal Fermi gas (g=2)

Mean number of particles

$$\langle N \rangle = 2 \int d\varepsilon \rho(\varepsilon) n(\varepsilon) \quad (86)$$

Internal energy

$$\langle E \rangle = 2 \int d\varepsilon \rho(\varepsilon) \varepsilon n(\varepsilon) \quad (87)$$

Fermi-momentum

$$p_F = \hbar k_F \quad (88)$$

Fermi-wave-vector

$$1\text{D} : k_F = 2\pi n \quad (89)$$

$$2\text{D} : k_F = (4\pi n)^{1/2} \quad (90)$$

$$3\text{D} : k_F = (3\pi^2 n)^{1/3} \quad (91)$$

Fermi-energy

$$\varepsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad (92)$$

6.5 ideal Bose gas (photon gas)

Total Energy (in quantisation)

$$E = \sum_K \hbar \omega_K N_K \quad (93)$$

mean occupation number ($\mu = 0$)

$$\langle N \rangle = \frac{1}{e^{\beta \omega_K} - 1} \quad (94)$$

partition function

$$Z^{\text{Phot}} = \prod_k (1 - e^{-\beta\hbar\omega_k})^{-1} \quad (95)$$

with *Stefan Boltzmann constant*

$$b = \frac{\pi^2}{45(\hbar c)^3}$$

we find

$$\text{Free energy} \quad F = k_B T \ln Z = -Vb(k_B T)^4 \quad (96)$$

$$\text{entropy} \quad S = -(\partial_T F)_V = 4k_B Vb(k_B T)^3 \quad (97)$$

$$\text{internal energy} \quad E = F + TS = 3bV(k_B T)^4 \quad (98)$$

$$\text{pressure} \quad p = -(\partial_V F)_T = b(k_B T)^4 = \frac{E}{3V} \quad (99)$$

mean number of photons

$$\langle N \rangle = 2 \sum_k \langle N_k \rangle \quad (100)$$

6.5.1 Planck's law

spektral density of the energy in black-body radiation

$$u(\omega) d\omega = D(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} d\omega \quad (101)$$

with mode density

$$D(\omega) = \frac{\omega^2}{\pi^2 c^3}$$

6.6 phonon gas

dispersion relation

$$\omega_k = 2\sqrt{\frac{f}{m}} \sin\left(\frac{1}{2}ka\right) \quad (102)$$

Free energy

$$F^{\text{Phon}}(T, V) = W_0 + \sum_k \frac{\hbar\omega_k}{2} + \sum_k k_B T \ln(1 - e^{-\beta\hbar\omega_k}) \quad (103)$$

density of states

$$g(\omega) = \frac{1}{3N} \sum_k \delta(\omega - \omega_k) = \frac{V}{N} \frac{\omega^2}{6\pi^2} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \quad (104)$$

internal energy

$$\begin{aligned} E^{\text{Phon}} &= W_0 + E_0 + 3N \int_0^\infty g(\omega) \hbar\omega \langle N \rangle^B \\ &= W_0 + E_0 + 3N \int_0^\infty g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \end{aligned} \quad (105)$$

$$\simeq W_0 + E_0 + \frac{V\pi^2 k_B^4}{30\hbar^2} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) T^4 \quad (106)$$

6.7 paramagnetism

energy states

$$E_{M_J} = -g_J \mu_B M_J B \quad (107)$$

partition function:

$$\begin{aligned} Z_N(T, B, N) &= Z^N \quad (\text{noninteracting, distinguishable}) \\ &= \prod_{n=1}^N \sum_{M_J=-J}^J e^{-\beta E_{M_J}} \end{aligned}$$

with

$$\begin{aligned} Z(T, B) &= \sum_{M_J=-J}^J e^{-\beta E_{M_J}} \\ &= \sum_{M_J=-J}^J e^{-\frac{x M_J}{J}} \quad \text{with } x = \beta g_J B J \end{aligned} \quad (108)$$

$$= \frac{\sinh\left(\frac{2J+1}{2J}x\right)}{\sinh\left(\frac{x}{2J}\right)} \quad (109)$$

define

$$f(T, B) = -k_B T \frac{1}{N} \ln Z_N \quad (110)$$

magnetisation

$$\langle m \rangle = -\partial_B f(T, B) = g_j \mu_B J B_J(x) \quad (111)$$

Brillouin function

$$B(J, x) = \left(1 + \frac{1}{2J}\right) \coth \left[\left(1 + \frac{1}{2J}\right) x \right] - \frac{1}{2J} \coth \left(\frac{x}{2J} \right) \quad (112)$$

7 Thermodynamics (Phenomenological)

7.1 I. law of thermodynamics

follows from full differential of entropy

$$dE = T dS - p dV + \mu dN \quad (113)$$

$$= \delta Q + \delta A + \delta_N E \quad (114)$$

with

$$\delta Q = T dS \quad \text{change in heat}$$

$$\delta A = -p dV \quad \text{work done on the system}$$

$$\delta_N E = \mu dN \quad \text{chemical energy}$$

7.2 Equations of state

$$E = k_B T^2 \partial_T \ln Z_c \quad \Rightarrow E \quad \text{caloric equation of state} \quad (115)$$

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} \quad \Rightarrow p \quad \text{thermal equation of state} \quad (116)$$

$$\mu = - \left(\frac{\partial F}{\partial N} \right)_{T,V} \quad \Rightarrow \mu \quad \text{chemical equation of state} \quad (117)$$

7.3 Thermodynamic coefficients

heat capacity

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{E,V} = \left(\frac{\partial E}{\partial T} \right)_{E,V} \quad (118)$$

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{E,p} = \left(\frac{\partial H}{\partial T} \right)_{E,p} \quad (119)$$

compressibility

$$\kappa_T = - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{E,T} \quad (120)$$

$$\kappa_S = - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{E,S} \quad (121)$$

expansion coefficient

$$\alpha_T = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{E,p} \quad (122)$$

stress coefficient

$$\beta = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_{E,V} \quad (123)$$

7.4 Thermodynamic relations

7.4.1 consequences of the I. law

$$p = -T \left(\frac{\partial S}{\partial V} \right)_{T,N} \quad (124)$$

7.4.2 consequences of the integrability conditions – Maxwell-relations

with the condition of twice continuously differentiable functions $f(x, y)$:

$$\frac{\partial^2 f(x, y)}{\partial x \partial y} = \frac{\partial^2 f(x, y)}{\partial y \partial x}$$

we obtain the Maxwell-relations by differentiating by the natural variables:

$$\left. \begin{aligned} - \left(\frac{\partial p}{\partial S} \right)_{V,N} &= \left(\frac{\partial T}{\partial V} \right)_{S,N} & (3.23) \\ \left(\frac{\partial T}{\partial N} \right)_{V,S} &= \left(\frac{\partial \mu}{\partial S} \right)_{V,N} \\ - \left(\frac{\partial p}{\partial N} \right)_{S,V} &= \left(\frac{\partial \mu}{\partial V} \right)_{S,N} \end{aligned} \right\} \text{energy E}$$

$$\left. \begin{aligned} - \left(\frac{\partial S}{\partial V} \right)_{E,T} &= - \left(\frac{\partial p}{\partial T} \right)_{V,N} & (3.24) \\ - \left(\frac{\partial S}{\partial N} \right)_{T,V} &= \left(\frac{\partial \mu}{\partial T} \right)_{V,N} \\ - \left(\frac{\partial p}{\partial N} \right)_{T,V} &= \left(\frac{\partial \mu}{\partial V} \right)_{E,T} & (3.24) \end{aligned} \right\} \text{free energy F}$$

$$\left. \begin{aligned} \left(\frac{\partial V}{\partial S} \right)_{p,N} &= \left(\frac{\partial T}{\partial p} \right)_{S,N} \\ \left(\frac{\partial V}{\partial N} \right)_{p,S} &= \left(\frac{\partial \mu}{\partial p} \right)_{E,S} \\ \left(\frac{\partial \mu}{\partial S} \right)_{E,p} &= \left(\frac{\partial T}{\partial N} \right)_{p,S} \end{aligned} \right\} \text{enthalpy H}$$

$$\left. \begin{aligned}
\left(\frac{\partial \mu}{\partial p}\right)_{E,T} &= \left(\frac{\partial V}{\partial N}\right)_{T,p} \\
\left(\frac{\partial \mu}{\partial T}\right)_{E,p} &= -\left(\frac{\partial S}{\partial N}\right)_{T,p} \\
\left(\frac{\partial V}{\partial T}\right)_{p,N} &= -\left(\frac{\partial S}{\partial p}\right)_{E,T}
\end{aligned} \right\} \text{ free enthalpy } G \quad (3.25)$$

Application of Maxwell relations

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V \quad (125)$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p \quad (126)$$

7.4.3 consequences of the homogeneity properties

p, μ intensive:

$$p(T, V, N) = p(T, \lambda V, \lambda N)$$

$$\mu(T, V, N) = \mu(T, \lambda V, \lambda N)$$

leads to

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,V} = -\frac{V^2}{N^2} \left(\frac{\partial p}{\partial V}\right)_{T,N} = \frac{N}{V^2} \frac{1}{\kappa_T} \quad (127)$$

7.4.4 change of thermodynamic variables

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T} \quad (128)$$

$$C_p - C_V = TV\alpha^2 \frac{1}{\kappa_T} \geq 0 \quad (129)$$

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}(\alpha T - 1) \quad (130)$$

$$\left(\frac{\partial T}{\partial p}\right)_S = TV \frac{\alpha}{C_p} \quad (131)$$

8 Thermodynamic processes

Definitions

isobaric	$p = \text{const}$
isochoric	$V = \text{const}$
isothermal	$T = \text{const}$
adiabatic	$\delta Q = 0$

8.1 quasistatic processes

we assume ideal gas: $pV = Nk_B T$, $C_p = \frac{5}{2}Nk_B$, $C_V = \frac{3}{2}Nk_B$

We use the total differential of S : $dS = \left(\frac{\partial S}{\partial p}\right)_{V,N} dp + \left(\frac{\partial S}{\partial V}\right)_{p,N} dV$ in the intergral of $Q = \int T dS$ in each process.

isobaric : $p = \text{const}$

$$\Delta Q = \int T \left(\frac{\partial S}{\partial V}\right)_{p,N} dV = \int C_p dT = C_p(T_f - T_i) = \frac{5}{2}Nk_B(T_f - T_i) \quad (132)$$

$$\Delta W = \int p dV = p \int dV = p(V_f - V_i) = Nk_B(T_f - T_i) \quad (133)$$

isochoric : $V = \text{const}$

$$\Delta Q = \int T \left(\frac{\partial S}{\partial p}\right)_{V,N} dp = \int C_V dT = C_V(T_f - T_i) = \frac{3}{2}Nk_B(T_f - T_i) \quad (134)$$

$$\Delta W = \int p dV = 0 \quad (135)$$

isothermal : $T = \text{const}$

$$\Delta Q = T \int dS = T(S_f - S_i) = Nk_B T \ln \left(\frac{V_f}{V_i}\right) \quad (136)$$

$$\Delta W = \int p dV = - \int pV \kappa_t dp = -Nk_B T \int \frac{1}{p} dp = Nk_B T \ln \left(\frac{V_f}{V_i}\right) \quad (137)$$

adiabatic : $\delta Q = 0$ or $S = \text{const}$

$$\Delta Q = \int \delta Q = 0 \quad (138)$$

$$\Delta W = \int p dV = -\Delta E = \frac{3}{2}Nk_B(T_i - T_f) = C_V(T_i - T_f) \quad (139)$$