Basic concepts and relations of statistical physics

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January 5, 2021

Lecture course 'Methods of statistical physics'

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topics:

- basic concepts and relations ($\sim$ 3 lectures, I.T.)
- mean-field approximation and classical Ising model ($\sim$ 3 lectures, I.T.)
- Kubo linear response and electron liquid ($\sim$ 3 lectures, I.T.)
- bosonic systems (Bose-Einstein condensation, magnons) ($\sim$ 3 lectures, B.V., R.K.)

excersize/classes:

- conducted by R.K.; the credit ('zápočet', issued by R.K.) is needed for admission to the (oral) examination

0 Statistical physics

- macroscopic systems with a large number of (interacting) particles
- both classical and quantum systems
- properties and quantities relevant for experiment
- systems under time-independent external conditions (equilibrium properties)
- systems under (well-defined) time-dependent perturbations (nonequilibrium properties)

• in this course:
focus on theoretical techniques and condensed systems

1 Thermodynamic equilibrium, classical phase space and distribution functions

1.1 Thermodynamic equilibrium and time averages

• the state of a classical N-particle system is represented by a point $(p, q) = (\{p_i\}_{i=1}^{3N}, \{q_i\}_{i=1}^{3N})$ in the $6N$-dimensional phase space

• dynamics of the system is given by the Hamiltonian $H(p, q)$ (time-independent) and the equations of motion

$$\frac{\mathrm{d}p_i(t)}{\mathrm{d}t} = -\frac{\partial H(p,q)}{\partial q_i}, \qquad \frac{\mathrm{d}q_i(t)}{\mathrm{d}t} = \frac{\partial H(p,q)}{\partial p_i} \tag{1}$$

• their solution for specified initial conditions yields the trajectory $(p(t), q(t))$ in the phase space

• for any observable quantity $A = A(p, q)$, one can then define its time average $\bar{A}$ as

$$\bar{A} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(p(t), q(t)) \, \mathrm{d}t \tag{2}$$

• for interacting many-particle systems:
the time averages do not depend on the initial conditions

• assessment of the dependence of these time averages on the parameters (ξ) of the Hamiltonian represents one of the central problems of equilibrium statistical physics

$$H = H(p, q; \xi) \quad \Longrightarrow \quad \bar{A} = \bar{A}(\xi)$$

1.2 Distribution functions and statistical averages

• the time averages can be replaced by statistical averages defined as

$$\langle A \rangle \equiv \bar{A} = \int A(p,q)\,\rho(p,q)\,\mathrm{d}\Gamma, \quad \mathrm{d}\Gamma = \prod_{i=1}^{3N} \mathrm{d}p_i\,\mathrm{d}q_i, \qquad (3)$$

where $\rho(p,q)$ is the distribution function

• according to a general theory, the distribution function should be a function of the Hamiltonian only,

$$\rho(p,q) = \varphi(H(p,q)), \qquad (4)$$

where the function φ has to be specified

1.3 Microcanonical distribution and ergodicity

• for an isolated system with a prescribed total energy E, the microcanonical distribution is defined as

$$\rho(p, q; E) \sim \delta(H(p, q) - E)\,, \tag{5}$$

which yields the statistical averages as functions of the total energy E (and of the other parameters ξ of the Hamiltonian):

$$\langle A \rangle(E) \equiv \bar{A}(E) = \frac{\int A(p, q)\, \delta(H(p, q) - E)\, \mathrm{d}\Gamma}{\int \delta(H(p, q) - E)\, \mathrm{d}\Gamma} \tag{6}$$

• the microcanonical distribution, Eq. (5), can be justified by the so-called ergodic hypothesis: each trajectory of the system scans the whole isoenergetic surface $H(p, q) = E$

2 Classical canonical distribution

2.1 Canonical distribution and partition function

• for a system with thermal contact with its surroundings at temperature T, the canonical distribution function (Boltzmann statistics) is appropriate, namely,

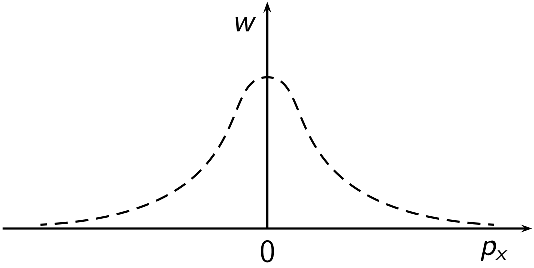
$$\rho(p, q; T) \sim \exp[-\beta H(p, q)] \,, \qquad \beta = \frac{1}{k_{\mathrm{B}} T} \,, \tag{7}$$

where k_{B} is the Boltzmann constant.
Here, we assume a fixed number of particles ($N = \mathrm{const}$).

• the value of k_{B}: 1 eV $\approx$ 11600 K

• the simplest consequence is the Maxwell-Boltzmann distribution of velocities (or momenta) of individual particles (of mass m) in a gas (or a liquid or a solid):

$$w(p_x) \sim \exp\left(-\frac{p_x^2}{2mk_\mathrm{B}T}\right)$$



• the normalized canonical distribution ($\int \rho \, \mathrm{d}\Gamma = 1$) requires knowledge of the partition function ('Zustandssumme')

$$Z(T) \;=\; \int \exp[-\beta H(p,q)] \, \mathrm{d}\Gamma \,, \tag{8}$$

which yields

$$\rho(p,q;T) \;=\; \frac{1}{Z(T)} \exp[-\beta H(p,q)] \tag{9}$$

and general temperature-dependent statistical averages

$$\bar{A}(T) \;=\; \frac{1}{Z(T)} \int A(p,q) \exp[-\beta H(p,q)] \, \mathrm{d}\Gamma \,, \tag{10}$$

including, e.g., the internal energy of the system (for $A = H$)

$$U(T) \;=\; \bar{H}(T) \;=\; -\frac{\partial}{\partial \beta} \ln[Z(T)] \tag{11}$$

2.2 Free energy and its derivatives

• the partition function can also be used to calculate the free energy $F(T)$:

$$Z(T) = \exp[-\beta F(T)], \quad F(T) = -k_{\mathrm{B}} T \ln[Z(T)], \qquad (12)$$

from which various expressions for the entropy follow, namely,

$$S(T) = -\frac{\partial F(T)}{\partial T}, \qquad (13)$$

$$S(T) = -k_{\mathrm{B}} \int \rho(p, q; T) \ln[\rho(p, q; T)] \, \mathrm{d}\Gamma \qquad (14)$$

[analogy to the mathematical entropy $\sigma = -\sum_n w_n \ln(w_n)$ related to probabilities $w_n \geq 0$ such that $\sum_n w_n = 1$]

- $U(T)$, $F(T)$, and $S(T)$ satisfy the Helmholtz relation

$$U(T) = F(T) + TS(T) \tag{15}$$

and their derivatives define the heat capacity (specific heat)

$$C(T) = \frac{\partial U(T)}{\partial T} = T\,\frac{\partial S(T)}{\partial T} = -T\,\frac{\partial^2 F(T)}{\partial T^2} \tag{16}$$

- classical equipartition theorem $\implies$ heat capacity for
  - ideal gases: $C(T) = (3/2)Nk_{\mathrm{B}}$
  - solids (in harmonic approximation): $C(T) = 3Nk_{\mathrm{B}}$ (the Dulong-Petit law)

• for an external parameter ξ entering the Hamiltonian, $H = H(p, q; \xi) \implies F = F(T; \xi)$, and one can prove

$$\left\langle \frac{\partial H(\xi)}{\partial \xi} \right\rangle (T) = \frac{\partial F(T; \xi)}{\partial \xi} \qquad (17)$$

• for a special (linear) ξ-dependence of H, i.e.,

$$H(p, q; \xi) = H_0(p, q) + \xi B(p, q), \qquad \xi \to 0, \qquad (18)$$

where the second term defines a small perturbation added to the unperturbed Hamiltonian H_0, we get

$$\langle B \rangle_0(T) = \partial F(T; \xi = 0)/\partial \xi, \qquad (19)$$

where $\langle \ldots \rangle_0$ – average with the unperturbed Hamiltonian H_0

• for a system in an applied magnetic field b:
the perturbed Hamiltonian is

$$H(b) = H_0 - bM\,,$$

where M is the total magnetic moment;
its value in zero field is $(B \equiv -M,\ \xi \equiv b \to 0)$:

$$M_0(T) = -\,\frac{\partial F(T;b=0)}{\partial b}$$

2.3 Linear response and fluctuations

• the standard measure of fluctuations of a random real quantity A around its average value $\bar{A} = \langle A \rangle$ is defined as

$$(\Delta A)^2 = \left\langle \left(A - \bar{A}\right)^2 \right\rangle = \overline{A^2} - (\bar{A})^2 , \qquad (20)$$

$$\begin{aligned} (\Delta A)^2 \ &- \ \text{scatter of the quantity } A, \\ \sqrt{(\Delta A)^2} \ &- \ \text{root-mean-square (r.m.s.) deviation} \end{aligned}$$

• for the canonical distribution and $A = H$, one can prove

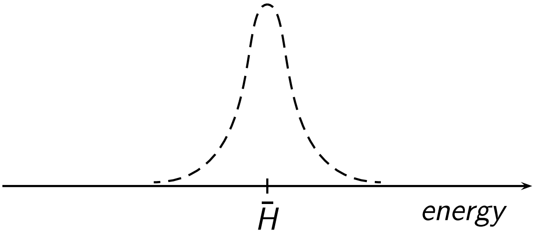
$$(\Delta H)^2(T) = k_{\mathrm{B}} T^2 \, C(T) , \qquad (21)$$

where $C(T)$ is the heat capacity; this is a direct relation between a macroscopic quantity C and a microscopic feature of the system $(\Delta H)^2$ (energy fluctuations around $U = \bar{H}$)

• if we consider dependence of the quantities on the system size (number of particles N), we find $U(T) = \bar{H}(T)$ and $C(T)$ proportional to N (extensive quantities), which yields

$$\frac{\sqrt{(\Delta H)^2}}{\bar{H}} \propto \frac{1}{\sqrt{N}},$$

i.e., the energy fluctuations in large systems ($N \to \infty$) are negligible as compared to the internal energy (canonical distribution $\sim$ microcanonical distribution)



• similarly, for correlation of fluctuations of two random quantities A and B (with respect to their average values $\bar{A}$ and $\bar{B}$), we introduce the quantity

$$\left\langle \left(A-\bar{A}\right)\left(B-\bar{B}\right)\right\rangle = \overline{AB} - \bar{A}\bar{B} \tag{22}$$

• let us consider a perturbation B added to the Hamiltonian H_0 according to Eq. (18) $[H(\xi) = H_0 + \xi B, \ \xi \to 0]$; this perturbation induces a change in the statistical average of an observable A and it leads to the following linear-response coefficient

$$\kappa_{AB}(T) = \frac{\partial \bar{A}(T;\xi=0)}{\partial \xi}\,, \tag{23}$$

the so-called isothermic susceptibility

• one can prove the relation

$$\kappa_{AB}(T) = -\beta \left\langle \left(A - \bar{A}\right) \left(B - \bar{B}\right) \right\rangle_0 (T)$$
$$= -\beta \left[\langle AB \rangle_0 - \langle A \rangle_0 \langle B \rangle_0 \right] (T) \,, \qquad (24)$$

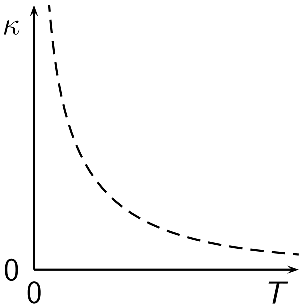
where all averages on the r.h.s. are taken in the unperturbed system

• this relation connects the linear-response coefficient $\kappa_{AB}(T)$ (a macroscopic property) with the correlation of fluctuations in the unperturbed system (a microscopic quantity)

• a special form of Eq. (24) for $B = -A$ yields

$$\kappa_{A,-A}(T) = \beta\,(\Delta A)_0^2(T) = \beta\left[\langle A^2\rangle_0 - \langle A\rangle_0^2\right](T)\,, \qquad (25)$$

which explains, e.g., the Curie law for magnetic susceptibilities at low temperatures: $\kappa(T) \sim T^{-1}$



3 Elementary quantum statistics

3.1 Quantum-mechanical and statistical averaging

- basic statements of the quantum theory:
  - the pure state of a quantum-mechanical system is defined by a state vector $|\Psi\rangle$ in the Hilbert space
  - a real physical observable is represented by a Hermitian operator A
  - the quantum-mechanical average of the quantity (operator) A in the state $|\Psi\rangle$ is given by

$$\bar{A}\{\Psi\} = \langle\Psi|A|\Psi\rangle \,, \tag{26}$$

where we assume the state vector normalized to unity, $\langle\Psi|\Psi\rangle = 1$

• if the system can be prepared in several states $|\Psi_i\rangle$ with probabilities p_i $(i = 1, 2, \ldots;\ p_i \geq 0,\ \sum_i p_i = 1)$, the quantum-mechanical and statistical average is given by

$$\langle A \rangle = \bar{A} = \sum_i p_i \langle \Psi_i | A | \Psi_i \rangle = \sum_i p_i \,\mathrm{Tr}\,\{A|\Psi_i\rangle\langle\Psi_i|\}$$
$$= \mathrm{Tr}\left\{ A \left[\sum_i p_i |\Psi_i\rangle\langle\Psi_i| \right] \right\} = \mathrm{Tr}(A\rho)\,, \qquad (27)$$

where Tr denotes the trace and where we introduced the density matrix (statistical operator) ρ given by

$$\rho = \sum_i |\Psi_i\rangle\, p_i\, \langle \Psi_i|\,, \qquad (28)$$

which is a positive-definite Hermitian operator

- (two technical notes)

  - within the Dirac formalism, a ket-vector $|\phi\rangle$ and a bra-vector $\langle\chi|$ define a linear operator $|\phi\rangle\langle\chi|$; its action is given by $|\psi\rangle \mapsto |\phi\rangle\langle\chi|\psi\rangle$; its trace equals the scalar product of both vectors:
  $$\mathrm{Tr}\left(|\phi\rangle\langle\chi|\right) = \langle\chi|\phi\rangle$$
  - for any operators X and Y: $\mathrm{Tr}(XY) = \mathrm{Tr}(YX)$

- the density matrix satisfies relations

$$\mathrm{Tr}(\rho) = 1\,, \qquad \mathrm{Tr}(\rho^2) \leq 1\,, \tag{29}$$

where the former one is a direct consequence of $\langle\Psi_i|\Psi_i\rangle = 1$ and $\sum_i p_i = 1$; the equality sign in the latter relation is encountered only for pure states

3.2 Canonical distribution and partition function

• the canonical distribution (Boltzmann statistics) for a system with Hamiltonian H and at temperature T is defined as

$$\rho(T) = \frac{1}{Z(T)} \exp(-\beta H), \tag{30}$$

where the partition function $Z(T)$ is given by

$$Z(T) = \mathrm{Tr}[\exp(-\beta H)] \tag{31}$$

• if the eigenvalues and normalized eigenvectors of H are denoted by E_n and $|n\rangle$ $(n = 1, 2, \ldots)$, we get for $Z(T)$

$$Z(T) = \sum_n \exp(-\beta E_n), \tag{32}$$

for the density matrix ρ and its matrix elements ρ_{mn}

$$\rho(T) = \sum_n |n\rangle\, w_n(T)\, \langle n|\,, \qquad w_n(T) = \frac{\exp(-\beta E_n)}{Z(T)}\,,$$
$$\rho_{mn}(T) = \langle m|\rho(T)|n\rangle = w_n(T)\, \delta_{mn}\,, \qquad (33)$$

and for the general quantum-mechanical and statistical average (with matrix elements $A_{mn} = \langle m|A|n\rangle$)

$$\langle A\rangle(T) = \bar{A}(T) = \mathrm{Tr}[A\rho(T)] = \sum_n w_n(T)\,\langle n|A|n\rangle$$
$$= \sum_n w_n(T)\, A_{nn} = \frac{1}{Z(T)} \sum_n \exp(-\beta E_n)\, A_{nn}\,, \qquad (34)$$

which has the form of Eq. (27) [$\bar{A} = \sum_i p_i \langle\Psi_i|A|\Psi_i\rangle$]

• (a technical note)
if we know all eigenvalues E_n $(n = 1, 2, \dots)$ and normalized eigenvectors $|n\rangle$ of the Hamiltonian H, we can write its spectral representation

$$H = \sum_n E_n \, |n\rangle\langle n| = \sum_n |n\rangle \, E_n \, \langle n| \, ;$$

this representation enables one to extend an arbitrary function $f(.)$ of a real variable to the same function of the operator H:

$$f(H) = \sum_n f(E_n) \, |n\rangle\langle n| = \sum_n |n\rangle \, f(E_n) \, \langle n| \, ;$$

this definition can be used, e.g., for $f(H) = \exp(-\beta H)$

3.3 Free energy and its derivatives

• from the partition function $Z(T)$, the internal energy $U(T)$, the free energy $F(T)$, the entropy $S(T)$, and the heat capacity $C(T)$ can be obtained in the same way as in the classical case; this leads, e.g., to expressions

$$\begin{aligned} S(T) &= -k_\mathrm{B}\,\mathrm{Tr}\{\rho(T)\ln[\rho(T)]\} \\ &= -k_\mathrm{B}\sum_n w_n(T)\ln[w_n(T)] \end{aligned} \qquad (35)$$

• the relations involving derivatives with respect to an external parameter ξ of the Hamiltonian $H(\xi)$ require more effort in the quantum case, since the operators $H(\xi)$ and $\partial H(\xi)/\partial\xi$ do not commute in general

• it can be proved that [the quantum version of Eq. (17)]

$$\left\langle \frac{\partial H(\xi)}{\partial \xi} \right\rangle (T) \,=\, \frac{\partial F(T;\xi)}{\partial \xi}\,,$$

while in the special case of a linear ξ-dependence

$$H(\xi) \,=\, H_0 + \xi B\,, \qquad \xi \to 0\,, \tag{36}$$

we get [the quantum version of Eq. (19)]

$$\langle B \rangle_0(T) \,=\, \frac{\partial F(T;\xi=0)}{\partial \xi}$$

• for the proof, we define $u(\beta, \xi) = \exp[-\beta H(\xi)]$, for which we get (the Bloch equation):

$$\frac{\partial u(\beta, \xi)}{\partial \beta} + H(\xi)\, u(\beta, \xi) = 0\,, \quad u(0, \xi) = 1\,, \qquad (37)$$

and for $v(\beta, \xi) = \partial u(\beta, \xi)/\partial \xi$, we get:

$$\frac{\partial v(\beta, \xi)}{\partial \beta} + H(\xi)\, v(\beta, \xi) = -\frac{\partial H(\xi)}{\partial \xi}\, u(\beta, \xi)\,, \quad v(0, \xi) = 0\,. \quad (38)$$

The last equation can be solved with an Ansatz

$$v(\beta, \xi) = u(\beta, \xi)\, c(\beta, \xi) = \exp[-\beta H(\xi)]\, c(\beta, \xi)$$

and with initial condition $c(\beta, \xi) = 0$:

$$\exp[-\beta H(\xi)]\, \frac{\partial c(\beta, \xi)}{\partial \beta} = -\frac{\partial H(\xi)}{\partial \xi} \exp[-\beta H(\xi)]\,,$$

$$
\begin{aligned}
c(\beta,\xi) &= -\int_0^\beta \exp[\alpha H(\xi)]\,\frac{\partial H(\xi)}{\partial \xi}\,\exp[-\alpha H(\xi)]\,\mathrm{d}\alpha\,, \\
v(\beta,\xi) &= -\exp[-\beta H(\xi)] \\
&\quad \times \int_0^\beta \exp[\alpha H(\xi)]\,\frac{\partial H(\xi)}{\partial \xi}\,\exp[-\alpha H(\xi)]\,\mathrm{d}\alpha\,. \qquad (39)
\end{aligned}
$$

From this result, we get:

$$
\begin{aligned}
-\frac{\partial Z(T,\xi)}{\partial \xi} &= -\frac{\partial}{\partial \xi}\,\mathrm{Tr}[u(\beta,\xi)] = -\,\mathrm{Tr}[v(\beta,\xi)] \\
&= \mathrm{Tr}\Big\{\exp[-\beta H(\xi)] \\
&\qquad \times \int_0^\beta \exp[\alpha H(\xi)]\,\frac{\partial H(\xi)}{\partial \xi}\,\exp[-\alpha H(\xi)]\,\mathrm{d}\alpha\Big\}
\end{aligned}
$$

$$
\begin{aligned}
&= \int_0^\beta \mathrm{Tr}\left\{\exp[(\alpha-\beta)H(\xi)]\,\frac{\partial H(\xi)}{\partial \xi}\,\exp[-\alpha H(\xi)]\right\}\mathrm{d}\alpha \\
&= \int_0^\beta \mathrm{Tr}\left\{\exp[-\beta H(\xi)]\,\frac{\partial H(\xi)}{\partial \xi}\right\}\mathrm{d}\alpha \\
&= \beta\,\mathrm{Tr}\left\{\exp[-\beta H(\xi)]\,\frac{\partial H(\xi)}{\partial \xi}\right\} \\
&= \beta\, Z(T,\xi)\left\langle \frac{\partial H(\xi)}{\partial \xi}\right\rangle (T)\,. \qquad (40)
\end{aligned}
$$

This means

$$
-\frac{\partial Z(T,\xi)}{\partial \xi} = \beta\, Z(T,\xi)\left\langle \frac{\partial H(\xi)}{\partial \xi}\right\rangle (T)\,,
$$

from which the quantum version of Eq. (17) follows immediately.

3.4 Linear response and fluctuations

• the quantum version of the relation between the energy fluctuation $(\Delta H)^2(T)$ and the heat capacity $C(T)$ is the same as in the classical case, Eq. (21):

$$(\Delta H)^2(T) \,=\, k_{\mathrm{B}}\, T^2\, C(T)$$

• for a perturbation B added to the Hamiltonian H_0 $[\ H(\xi) = H_0 + \xi B,\ \ \xi \to 0\ ]$, the linear response of an observable A leads to the susceptibility defined by Eq. (23):

$$\kappa_{AB}(T) \,=\, \frac{\partial \bar{A}(T; \xi = 0)}{\partial \xi}$$

• the result can be written using the eigenvectors $|n\rangle$ and eigenvalues E_n of the Hamiltonian H_0 and with $A_{mn} = \langle m|A|n\rangle$, $B_{nm} = \langle n|B|m\rangle$ as

$$\kappa_{AB}(T) = \sum_{mn} A_{mn} B_{nm} \frac{w_m(T) - w_n(T)}{E_m - E_n} + \beta \langle A\rangle_0(T) \langle B\rangle_0(T) , \quad (41)$$

where in the first term, one has to use (L'Hospital's rule)

$$\frac{w_m(T) - w_n(T)}{E_m - E_n} = -\beta w_m(T) \qquad \text{for } E_m = E_n . \quad (42)$$

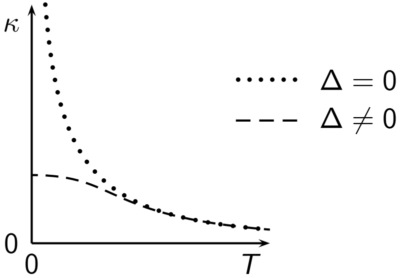
This proves the importance of the ground-state degeneracy for the Curie-like behavior of the low-temperature susceptibility [$\kappa(T) \sim T^{-1}$]

• (an example) for a 2-dimensional Hilbert space, we take $H_0 = \Delta\sigma_z$ with a real constant Δ, and $A = -B = \sigma_x$, where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix};$$

we get

$$\kappa(T) = \begin{cases} \tanh(\beta\Delta)/\Delta & \text{for } \Delta \neq 0 \\ \beta & \text{for } \Delta = 0 \end{cases}$$



• the proof of Eq. (41) starts from

$$\bar{A}(T;\xi) = Z^{-1}(T,\xi)\,\mathrm{Tr}\,\{A\exp[-\beta(H_0+\xi B)]\}\ ,$$
$$Z(T,\xi) = \mathrm{Tr}\,\{\exp[-\beta(H_0+\xi B)]\} \qquad (43)$$

and it employs

$$v(\beta) = \frac{\partial}{\partial\xi}\exp[-\beta(H_0+\xi B)]\bigg|_{\xi=0}$$
$$= -\exp(-\beta H_0)\int_0^\beta \exp(\alpha H_0)\,B\exp(-\alpha H_0)\,\mathrm{d}\alpha\,, \qquad (44)$$

which is a special case of Eq. (39). This yields:

$$-\frac{\partial Z(T,\xi=0)}{\partial\xi} = \beta\,\mathrm{Tr}[B\exp(-\beta H_0)] = \beta\,Z(T,0)\,\langle B\rangle_0(T), \qquad (45)$$

see also Eq. (40). The last two relations are used in calculation of the ξ-derivative of $\bar{A}(T;\xi)$, Eq. (43), which yields

$$\begin{aligned}\kappa_{AB}(T) \;=\; & -Z^{-1}(T,0) \\ & \times \ \mathrm{Tr}\left\{A\int_0^{\beta} \exp[(\alpha-\beta)H_0]\, B \exp(-\alpha H_0)\,\mathrm{d}\alpha\right\} \\ & + \ \beta\,\langle A\rangle_0(T)\,\langle B\rangle_0(T)\,. \end{aligned} \qquad (46)$$

The first term is evaluated in the orthonormal basis of eigenvectors of H_0 which leads to the final result, Eq. (41).

- in special cases, when A or B commutes with H_0, Eq. (46) yields

$$\kappa_{AB}(T) \;=\; -\beta\,[\langle AB\rangle_0 \,-\, \langle A\rangle_0\,\langle B\rangle_0]\,(T)\,,$$

which is the quantum version of the classical relation, Eq. (24)

• a direct relation between the linear-response coefficient $\kappa_{AB}(T)$ and the correlation of fluctuations cannot be given. In the special case of $B = -A$, one obtains

$$\kappa_{A,-A}(T) \;=\; -\sum_{mn} |A_{mn}|^2 \,\frac{w_m(T) - w_n(T)}{E_m - E_n} \;-\; \beta \,\langle A \rangle_0^2(T)\,. \tag{47}$$

For the fraction in the first term, one can use inequality [a consequence of $\tanh(x)/x \leq 1$ valid for arbitrary real x]

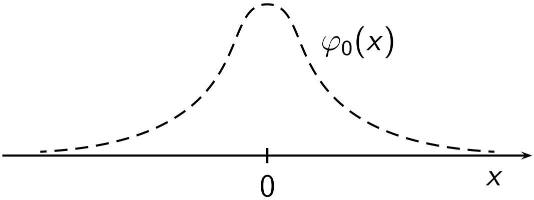
$$-\frac{w_m(T) - w_n(T)}{E_m - E_n} \;\leq\; \frac{\beta}{2}\,[w_m(T) + w_n(T)]\,, \tag{48}$$

which yields

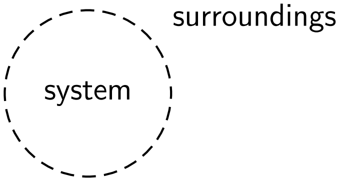
$$\kappa_{A,-A}(T) \leq \beta\,(\Delta A)_0^2(T) = \beta\left[\langle A^2\rangle_0 - \langle A\rangle_0^2\right](T) \qquad (49)$$

instead of the classical equality relation, Eq. (25).
The difference is due to quantum-mechanical fluctuations.

linear harmonic oscillator:
ground-state wavefunction



4 Systems with varying particle number



• exchange of particles between the studied system and its surroundings can be treated both within classical and quantum statistics by using the concept of chemical potential μ (in analogy to exchange of energy treated by means of temperature T); here we focus on the quantum case

4.1 Quantum grandcanonical distribution

• we consider systems with identical particles of one kind;
basis vectors in the N-particle ($N \geq 1$) Hilbert space $\mathcal{H}^{(N)}$:

$$\mathcal{S}\left\{|\lambda_1\rangle \otimes |\lambda_2\rangle \otimes \ \ldots \ \otimes |\lambda_N\rangle\right\} , \tag{50}$$

where $\lambda_1, \ldots, \lambda_N$ run over values of an index λ labelling the orthogonal basis vectors $|\lambda\rangle$ in the one-particle Hilbert space $\mathcal{H}^{(1)}$ and where $\mathcal{S}$ denotes a symmetrization (for bosons) or antisymmetrization (for fermions – 'Slater determinant');
the complete Hilbert space (Fock space) is

$$\mathcal{H} = \mathcal{H}^{(0)} \oplus \mathcal{H}^{(1)} \oplus \mathcal{H}^{(2)} \oplus \ldots \equiv \sum_{N=0}^{\infty} \oplus \, \mathcal{H}^{(N)} , \tag{51}$$

where $\mathcal{H}^{(0)}$ – the one-dimensional subspace of vacuum

• the identity operator I and the operator of the total number of particles N are given by

$$\begin{aligned} I &= I^{(0)} \oplus I^{(1)} \oplus I^{(2)} \oplus I^{(3)} \oplus \ldots \equiv \sum_{N=0}^{\infty} \oplus I^{(N)} , \\ N &= I^{(1)} \oplus 2I^{(2)} \oplus 3I^{(3)} \oplus \ldots \equiv \sum_{N=0}^{\infty} \oplus N\, I^{(N)} , \end{aligned} \qquad (52)$$

where $I^{(N)}$ – the identity operator in the Hilbert space $\mathcal{H}^{(N)}$

• operators that do not change the number of particles have a similar structure. Here we confine ourselves only to such operators, i.e., the Hamiltonian is

$$H = H^{(0)} \oplus H^{(1)} \oplus H^{(2)} \oplus \ldots \equiv \sum_{N=0}^{\infty} \oplus H^{(N)} , \qquad (53)$$

and observables can be reduced to

$$A = A^{(0)} \oplus A^{(1)} \oplus A^{(2)} \oplus \ldots \equiv \sum_{N=0}^{\infty} \oplus A^{(N)} \qquad (54)$$

• (a comment)
by using the creation and annihilation operators $(a_\lambda^+,\, a_\lambda)$, further operators conserving the number of particles are

$$M = \sum_{\lambda'\lambda} V_{\lambda'\lambda}\, a_{\lambda'}^+ a_\lambda + \sum_{\lambda'\nu'\lambda\nu} W_{\lambda'\nu'\lambda\nu}\, a_{\lambda'}^+ a_{\nu'}^+ a_\lambda a_\nu + \ldots$$

where $V_{\lambda'\lambda}$, $W_{\lambda'\nu'\lambda\nu}$, $\ldots$ are some constants, i.e., no terms with different number of creation and annihilation operators are present (such as, e.g., a_λ^+, $a_\lambda a_\nu$, $a_\kappa^+ a_\lambda^+ a_\nu$, $\ldots$)

• the density matrix of the grandcanonical distribution for the Hamiltonian H, Eq. (53), is defined by

$$\rho(T,\mu) \;=\; \frac{1}{\mathcal{Z}(T,\mu)}\,\exp[\beta(\mu N - H)]\,, \tag{55}$$

where μ denotes the chemical potential and where the grandcanonical partition function is equal to

$$\mathcal{Z}(T,\mu) \;=\; \mathrm{Tr}\,\{\exp[\beta(\mu N - H)]\} \tag{56}$$

• the average value of the observable A, Eq. (54), is

$$\langle A\rangle(T,\mu) \;=\; \bar{A}(T,\mu) \;=\; \mathrm{Tr}\,[A\rho(T,\mu)] \tag{57}$$

• in more details:

$$\rho(T,\mu) = \frac{1}{\mathcal{Z}(T,\mu)} \exp[\beta(\mu N - H)] = \sum_{N=0}^{\infty} \oplus \rho^{(N)}(T,\mu)$$

$$= \frac{1}{\mathcal{Z}(T,\mu)} \sum_{N=0}^{\infty} \oplus \exp(\beta\mu N) \exp\left[-\beta H^{(N)}\right] ,$$

$$\mathcal{Z}(T,\mu) = \mathrm{Tr}\left\{\exp[\beta(\mu N - H)]\right\} =$$

$$= \sum_{N=0}^{\infty} \exp(\beta\mu N)\, \mathrm{Tr}^{(N)} \left\{\exp\left[-\beta H^{(N)}\right]\right\}$$

$$= \sum_{N=0}^{\infty} \exp(\beta\mu N) \sum_{n} \exp\left[-\beta E_n^{(N)}\right] ,$$

where the trace $\mathrm{Tr}^{(N)}$ refers to the subspace $\mathcal{H}^{(N)}$ and where $E_n^{(N)}$ denote eigenvalues of the Hamiltonian $H^{(N)}$, and for the average of the observable A:

$$\bar{A}(T,\mu) = \mathrm{Tr}\left[A\rho(T,\mu)\right] = \sum_{N=0}^{\infty} \mathrm{Tr}^{(N)}\left[A^{(N)}\rho^{(N)}(T,\mu)\right]$$
$$= \frac{1}{\mathcal{Z}(T,\mu)} \sum_{N=0}^{\infty} \exp(\beta\mu N)\,\mathrm{Tr}^{(N)}\left\{A^{(N)}\exp\left[-\beta H^{(N)}\right]\right\}$$
$$= \frac{1}{\mathcal{Z}(T,\mu)} \sum_{N=0}^{\infty} \exp(\beta\mu N) \sum_{n} \exp\left[-\beta E_n^{(N)}\right] A_{nn}^{(N)}\,,$$

where $A_{nn}^{(N)}$ are diagonal matrix elements of $A^{(N)}$ between the normalized eigenvectors $|N,n\rangle$ of the eigenvalue $E_n^{(N)}$:

$$A_{nn}^{(N)} = \langle N,n|\,A^{(N)}\,|N,n\rangle$$

• in analogy to the canonical distribution, following relations are valid in the grandcanonical case $[U(T,\mu) = \bar{H}(T,\mu)]$:

$$U(T,\mu) - \mu\bar{N}(T,\mu) \; = \; -\frac{\partial}{\partial\beta}\ln[\mathcal{Z}(T,\mu)]\,, \qquad (58)$$

where $\bar{N}(T,\mu)$ denotes the average number of particles,

$$\begin{aligned} \mathcal{Z}(T,\mu) &= \exp[-\beta\Omega(T,\mu)]\,, \\ \Omega(T,\mu) &= -k_{\mathrm{B}}T\ln[\mathcal{Z}(T,\mu)]\,, \end{aligned} \qquad (59)$$

where $\Omega(T,\mu)$ denotes the grandcanonical potential,

$$S(T,\mu) \;=\; -\,\frac{\partial\Omega(T,\mu)}{\partial T}\,, \tag{60}$$

and

$$\bar{N}(T,\mu) \;=\; -\,\frac{\partial\Omega(T,\mu)}{\partial\mu}\,, \tag{61}$$

and a generalization of the Helmholtz relation, namely,

$$U(T,\mu) \;=\; \Omega(T,\mu) + TS(T,\mu) + \mu\bar{N}(T,\mu) \tag{62}$$

• for the Hamiltonian depending on an external parameter ξ, we get

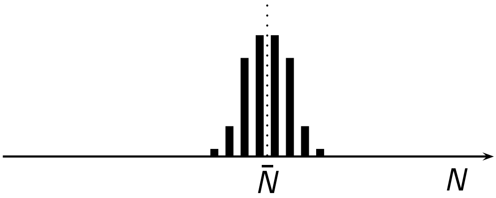
$$\left\langle\frac{\partial H(\xi)}{\partial\xi}\right\rangle(T,\mu) \;=\; \frac{\partial\Omega(T,\mu;\xi)}{\partial\xi} \tag{63}$$

as a counterpart of Eq. (17)

- for the fluctuation of the number of particles N, we get

$$(\Delta N)^2(T, \mu) \;=\; k_{\mathrm{B}} T \, \frac{\partial \bar{N}(T, \mu)}{\partial \mu} \tag{64}$$

as a counterpart of Eq. (21)



for large systems:
grandcanonical distribution $\sim$ canonical distribution

4.2 Systems of identical non-interacting particles

- systems of non-interacting particles: ideal gases
- in the quantum case:
  identical particles are indistinguishable
- two different classes (according to symmetry of wave-function Ψ with respect to permutation of two particles)
- bosons: Ψ symmetric,
  integer spin (photons, phonons, magnons, . . .)
- fermions: Ψ antisymmetric (Pauli exclusion principle),
  half-integer spin (electrons, protons, neutrons, . . .)

4.2.1 One-particle Hamiltonians and occupation numbers

• let us consider all orthonormalized eigenvectors $|\lambda\rangle$ and eigenvalues E_λ, where $\lambda = 1, 2, \ldots, \mathcal{M}$, of a one-particle Hamiltonian $H^{(1)}$, i.e.,

$$H^{(1)} = \sum_{\lambda=1}^{\mathcal{M}} |\lambda\rangle \, E_\lambda \, \langle\lambda| \equiv H \,. \tag{65}$$

The individual contributions to the full Hamiltonian [$\sum_N \oplus H^{(N)}$, Eq. (53)] for a *non-interacting system* are

$$\begin{aligned} H^{(0)} &= 0 \,, \quad H^{(1)} = H \,, \quad H^{(2)} = H \otimes I + I \otimes H \,, \\ H^{(3)} &= H \otimes I \otimes I + I \otimes H \otimes I + I \otimes I \otimes H \,, \ \ldots \end{aligned} \tag{66}$$

where I denotes the one-particle identity operator.

• the eigenstates of the full Hamiltonian are then given by Eq. (50); we rewrite them in terms of the so-called occupation numbers n_λ, so that

$$\mathcal{S}\left\{|\lambda_1\rangle \otimes |\lambda_2\rangle \otimes \ldots \otimes |\lambda_N\rangle\right\} = \left|\{n_\lambda\}_{\lambda=1}^{\mathcal{M}}\right\rangle , \tag{67}$$

where the (anti)symmetrization $\mathcal{S}$ includes normalization to unity and where

$$\begin{aligned} \text{for bosons}: \quad & n_\lambda \in \{0, 1, 2, \ldots\} \\ \text{for fermions}: \quad & n_\lambda \in \{0, 1\} \end{aligned} \tag{68}$$

• the total number of particles in a particular eigenstate, Eq. (67), can be expressed as

$$N = \sum_{\lambda=1}^{\mathcal{M}} n_\lambda , \tag{69}$$

and the corresponding eigenvalue of the full Hamiltonian is

$$E_{\{n_\lambda\}}^{(N)} = \sum_{\lambda=1}^{\mathcal{M}} n_\lambda E_\lambda \tag{70}$$

• the occupation numbers n_λ can also be considered as operators; the full non-interacting Hamiltonian, Eq. (66), can be then written as

$$\sum_{N=0}^{\infty} \oplus H^{(N)} = \sum_{\lambda=1}^{\mathcal{M}} E_\lambda n_\lambda \,, \tag{71}$$

and the operator of the total number of particles, Eq. (52), is given by Eq. (69) [$N = \sum_{\lambda=1}^{\mathcal{M}} n_\lambda$]

• (a comment on second quantization)
in terms of the creation (a_λ^+) and annihilation (a_λ) operators, the occupation numbers (as operators) are

$$n_\lambda = a_\lambda^+ a_\lambda \,,$$

the operator of the total number of particles is

$$N \;=\; \sum_{\lambda=1}^{\mathcal{M}} n_\lambda \;=\; \sum_{\lambda=1}^{\mathcal{M}} a_\lambda^+ a_\lambda \,,$$

and the full non-interacting Hamiltonian can be expressed as

$$\sum_{N=0}^{\infty} \oplus H^{(N)} \;=\; \sum_{\lambda=1}^{\mathcal{M}} E_\lambda n_\lambda \;=\; \sum_{\lambda=1}^{\mathcal{M}} E_\lambda a_\lambda^+ a_\lambda$$

4.2.2 One-particle distribution functions

• the $\mathcal{Z}(T,\mu)$, Eq. (56), can be evaluated exactly due to the linear dependence of N, Eq. (69), and of energy eigenvalues, Eq. (70), on the occupation numbers n_λ; this yields

$$\begin{aligned} \mathcal{Z}(T,\mu) &= \sum_{\{n_\lambda\}} \exp\left[\beta \sum_{\lambda=1}^{\mathcal{M}} n_\lambda(\mu - E_\lambda)\right] \\ &= \prod_{\lambda=1}^{\mathcal{M}} \sum_{n_\lambda} \exp[\beta(\mu - E_\lambda)n_\lambda] \\ &= \prod_{\lambda=1}^{\mathcal{M}} \{1 \mp \exp[\beta(\mu - E_\lambda)]\}^{\mp 1} , \end{aligned} \qquad (72)$$

where the upper (lower) sign refers to bosons (fermions). Note that the bosonic case requires $\mu < E_\lambda$ for all λ.

• the grandcanonical potential is then

$$\Omega(T,\mu) \;=\; \pm\, k_{\mathrm{B}} T \sum_{\lambda=1}^{\mathcal{M}} \ln\{1 \mp \exp[\beta(\mu - E_\lambda)]\}\,, \qquad (73)$$

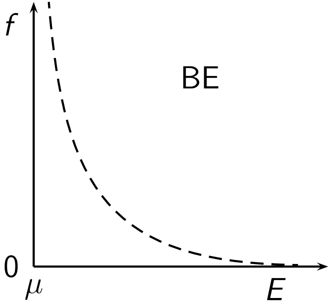
from which the *average values of the occupation numbers* can be obtained with use of Eq. (63) (ξ-derivative, $\xi = E_\lambda$):

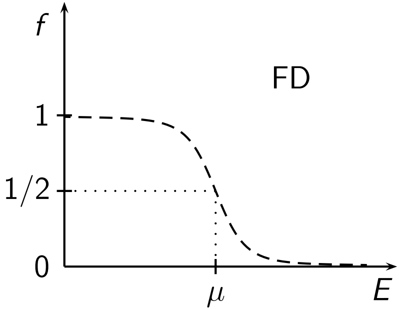
$$\begin{aligned} \langle n_\lambda\rangle(T,\mu) \;&=\; \frac{\partial\Omega(T,\mu;\{E_\nu\})}{\partial E_\lambda} \\ &=\; \frac{1}{\exp[\beta(E_\lambda - \mu)] \mp 1} \;\equiv\; f_\lambda(T,\mu)\,. \qquad (74) \end{aligned}$$

This is the well-known Bose-Einstein or Fermi-Dirac distribution function.

- Bose-Einstein / Fermi-Dirac distribution functions

$$f(E; T, \mu) = \frac{1}{\exp[\beta(E-\mu)] \mp 1} \quad (75)$$





4.2.3 One-particle density matrix

- consider a one-particle operator A as an observable, so that

$$A^{(1)} \; = \; \sum_{\lambda,\nu=1}^{\mathcal{M}} |\lambda\rangle \, A_{\lambda\nu} \, \langle\nu| \; \equiv \; A \, , \quad A_{\lambda\nu} \; = \; \langle\lambda|A|\nu\rangle \, , \qquad (76)$$

while the other terms $A^{(N)}$ in the full observable [$\sum_N \oplus A^{(N)}$, Eq. (54)] are constructed according to Eq. (66) for the Hamiltonian [$\sum_N \oplus A^{(N)} = \sum_{\lambda\nu} A_{\lambda\nu} a_\lambda^+ a_\nu$]

- the quantum-mechanical average of the full observable $\sum_N \oplus A^{(N)}$ in a particular eigenvector, Eq. (67), is equal to

$$\left\langle \{n_\lambda\}_{\lambda=1}^{\mathcal{M}} \right| \sum_{N=0}^{\infty} \oplus \, A^{(N)} \left| \{n_\lambda\}_{\lambda=1}^{\mathcal{M}} \right\rangle \; = \; \sum_{\lambda=1}^{\mathcal{M}} n_\lambda A_{\lambda\lambda} \, , \qquad (77)$$

and its quantum-mechanical and statistical average is

$$\bar{A}(T,\mu) = \sum_{\lambda=1}^{\mathcal{M}} A_{\lambda\lambda}\,\langle n_\lambda\rangle(T,\mu) = \sum_{\lambda=1}^{\mathcal{M}} A_{\lambda\lambda}\, f_\lambda(T,\mu)\,, \qquad (78)$$

with an obvious physical meaning

- the last result can be given another form, namely,

$$\bar{A}(T,\mu) = \sum_{\lambda=1}^{\mathcal{M}} \langle\lambda|A|\lambda\rangle\, f_\lambda(T,\mu) = \mathrm{Tr}[Af(T,\mu)]\,, \qquad (79)$$

where the trace refers to the *one-particle Hilbert space* and where we introduced a one-particle density matrix

$$f(T,\mu) = \sum_{\lambda=1}^{\mathcal{M}} |\lambda\rangle\, f_\lambda(T,\mu)\,\langle\lambda| \qquad (80)$$

4.2.4 One-particle linear response

• for a one-particle Hamiltonian H_0, its perturbation B $[H(\xi) = H_0 + \xi B]$, and an observable A, the linear response yields the susceptibility, defined with constant T and μ as

$$\kappa_{AB}(T,\mu) \;=\; \frac{\partial \bar{A}(T,\mu;\xi=0)}{\partial \xi} \qquad (81)$$

• its value, expressed in the basis defined by the eigenvectors and eigenvalues (E_λ) of the unperturbed Hamiltonian H_0, is

$$\kappa_{AB}(T,\mu) \;=\; \sum_{\lambda,\nu=1}^{\mathcal{M}} A_{\lambda\nu} B_{\nu\lambda} \, \frac{f_\lambda(T,\mu) - f_\nu(T,\mu)}{E_\lambda - E_\nu}\,, \qquad (82)$$

where for $E_\lambda = E_\nu$, one has to use (L'Hospital's rule)

$$\frac{f_\lambda(T,\mu) - f_\nu(T,\mu)}{E_\lambda - E_\nu} \;=\; \left.\frac{\partial f(E;T,\mu)}{\partial E}\right|_{E=E_\lambda} \qquad (83)$$

• the proof of Eq. (82) is based on relation (T and μ omitted)

$$\bar{A} = \mathrm{Tr}[Af(H)] = \int_{-\infty}^{\infty} \mathrm{Tr}[A\delta(E-H)]\, f(E)\, \mathrm{d}E\,, \tag{84}$$

on the well-known limit

$$\delta(x) = \lim_{\varepsilon \to 0^+} \frac{\mathrm{i}}{2\pi} \left(\frac{1}{x + \mathrm{i}\varepsilon} - \frac{1}{x - \mathrm{i}\varepsilon} \right)\,, \tag{85}$$

and on the resolvent $G(z)$ of a Hamiltonian H, defined for a complex energy variable z by

$$G(z) = (z - H)^{-1}\,. \tag{86}$$

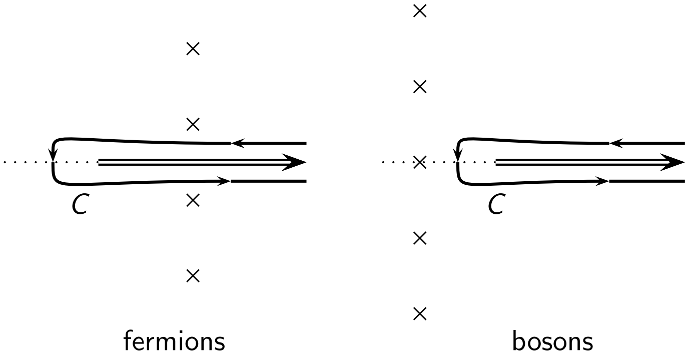
This yields

$$\delta(E - H) = \lim_{\varepsilon \to 0^+} \frac{\mathrm{i}}{2\pi} \left[G(E + \mathrm{i}\varepsilon) - G(E - \mathrm{i}\varepsilon) \right]\,, \tag{87}$$

and [due to the analyticity of $G(z)$] $\bar{A}$ as a complex integral

$$\bar{A} = \frac{1}{2\pi\mathrm{i}} \int_C \mathrm{Tr}[AG(z)]\, f(z)\, \mathrm{d}z\,, \tag{88}$$

where the complex integration path C is shown below
[double line – one-particle spectrum, crosses – poles of $f(z)$]



• the resolvents $G(z)$ (of H) and $G_0(z)$ (of H_0) are related by the Dyson equation

$$G(z) = G_0(z) + G_0(z)\xi B G(z)\,, \tag{89}$$

from which we get

$$\left.\frac{\partial G(z)}{\partial \xi}\right|_{\xi=0} = G_0(z) B G_0(z)\,, \tag{90}$$

as well as a compact expression for the susceptibility

$$\kappa_{AB} = \frac{1}{2\pi\mathrm{i}} \int_C \mathrm{Tr}[A G_0(z) B G_0(z)]\, f(z)\, \mathrm{d}z \tag{91}$$

• the eigenvalues E_λ and eigenvectors $|\lambda\rangle$ of H_0 lead to

$$G_0(z) = \sum_{\lambda=1}^{\mathcal{M}} |\lambda\rangle \frac{1}{z - E_\lambda} \langle\lambda| \tag{92}$$

and

$$\kappa_{AB} = \sum_{\lambda,\nu=1}^{\mathcal{M}} A_{\lambda\nu} B_{\nu\lambda} \, \frac{1}{2\pi\mathrm{i}} \int_C \frac{f(z)}{(z-E_\lambda)(z-E_\nu)} \, \mathrm{d}z \,. \tag{93}$$

The last complex integral can easily be evaluated:

$$\frac{1}{2\pi\mathrm{i}} \int_C \frac{f(z)}{(z-E_\lambda)(z-E_\nu)} \, \mathrm{d}z = \begin{cases} [f(E_\lambda) - f(E_\nu)]/(E_\lambda - E_\nu) & \text{for } E_\lambda \neq E_\nu \,, \\ \partial f(E)/\partial E|_{E=E_\lambda} & \text{for } E_\lambda = E_\nu \,, \end{cases} \tag{94}$$

which completes the proof.

4.2.5 Ideal quantum gases – a summary

- the full Hamiltonian (the dynamics) of an ideal gas is specified by the one-particle Hamiltonian
- the basic statistical properties (thermodynamic potentials) within Boltzmann statistics (grandcanonical distribution) are given by the spectrum of the one-particle Hamiltonian
- the average occupation numbers of individual one-particle eigenstates are given by the corresponding one-particle eigenvalues and by the BE/FD distribution function
- the average value of a one-particle observable and its linear response to a one-particle perturbation of the Hamiltonian can be evaluated within the one-particle Hilbert space