Grandcanonical Ensemble [tsc13]

In an open thermodynamic system, not only the energy content fluctuates, but also the number of particles. This complicates the search for the equilibrium condition, but the benefit is immense as we shall see.

Consider a classical system with an average internal energy U and an average number $\mathcal{N}$ of particles in a region of volume V.

A set of phase spaces Γ_N, $N = 0, 1, 2, \ldots$ with probability densities $\rho_N(\mathbf{X})$ and interaction Hamiltonians $H_N(\mathbf{X})$ is required for the specification.

Extremum principle:

Determine the $\rho_N(\mathbf{X})$ that maximize the Gibbs entropy subject to three auxiliary conditions: normalization and averages of energy and number of particles:

- Gibbs entropy:[1] $S = -k_B \sum_{N=0}^{\infty} \int_{\Gamma} d^{6N}X \, \rho_N(\mathbf{X}) \ln[C_N \rho_N(\mathbf{X})]$,

- normalization: $\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) = 1$,

- internal energy: $\langle H \rangle \doteq \sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) H_N(\mathbf{X}) = U$,

- number of particles: $\langle N \rangle \doteq \sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X}) N = \mathcal{N}$.

Application of calculus of variation with Lagrange multipliers $\alpha_0, \alpha_U, \alpha_N$:

$$\delta \left[\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \left\{ -k_B \rho_N \ln[C_N \rho_N] + \alpha_0 \rho_N + \alpha_U H_N \rho_N + \alpha_N N \rho_N \right\} \right] = 0$$

$$\Rightarrow \sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \delta\rho_N \left\{ -k_B \ln[C_N \rho_N] - k_B + \alpha_0 + \alpha_U H_N + \alpha_N N \right\} = 0$$

These integrals must vanish for arbitrary variations $\delta\rho_N$. In consequence, the contents of each $\{\cdots\}$ must vanish.

$$\Rightarrow \rho_N(\mathbf{X}) = \frac{1}{C_N} \exp\left(\frac{\alpha_0}{k_B} - 1 + \frac{\alpha_U}{k_B} H_N(\mathbf{X}) + \frac{\alpha_N}{k_B} N \right).$$

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[1] Adding a (constant) term for $N = 0$ in each sum is a mere convenience and makes no difference. The values $C_N = h^{3N}$ ($C_N = h^{3N} N!$) are for distinguishable (indistinguishable) particles as explained in [tsc10].

We determine the three Lagrange multipliers by substitution of $\rho_N(\mathbf{X})$ into the auxiliary conditions. We begin with the normalization and name the resulting integral expression:

$$\exp\left(1 - \frac{\alpha_0}{k_B}\right) = \sum_{N=0}^{\infty} \frac{1}{C_N} \int_{\Gamma_N} d^{6N}X \exp\left(\frac{\alpha_U}{k_B} H_N(\mathbf{X}) + \frac{\alpha_N}{k_B} N\right) \doteq Z.$$

We implement the other two conditions with $\{\cdots\}$ from above as follows:

$$\sum_{N=0}^{\infty} \int_{\Gamma_N} d^{6N}X \, \rho_N(\mathbf{X})\{-k_B \ln[C_N\rho_N(\mathbf{X})] - (k_B - \alpha_0) + \alpha_U H_N(\mathbf{X}) + \alpha_N N\} = 0.$$

The four terms of this sum of integrals are readily related to the entropy S, the quantity named Z, internal energy U, and the average number $\mathcal{N}$ of particles, respectively:

$$\Rightarrow \; S - k_B \ln Z + \alpha_U U + \alpha_N \mathcal{N} = 0.$$

With $\alpha_U = -1/T$ and $\alpha_N = \mu/T$, this is a familiar thermodynamic relation:

$$\Rightarrow \; U + \frac{1}{\alpha_U} S + \frac{\alpha_N}{\alpha_U} \mathcal{N} = \frac{k_B}{\alpha_U} \ln Z \quad \Leftrightarrow \quad U - TS - \mu\mathcal{N} = \Omega.$$

Grand potential: $\Omega(T, V, \mu) = -k_B T \ln Z = -pV.$

Grandcanonical partition function:

$$Z = \sum_{N=0}^{\infty} \frac{1}{C_N} \int_{\Gamma_N} d^{6N}X \, e^{-\beta(H_N(\mathbf{X}) - \mu N)}.$$

Equilibrium probability densities: $\rho_N(\mathbf{X}) = \frac{1}{ZC_N} e^{-\beta(H_N(\mathbf{X}) - \mu N)}.$

Thermodynamic functions from grand potential:

- entropy: $S = -\left(\dfrac{\partial \Omega}{\partial T}\right)_{V,\mu}$,

- pressure: $p = -\left(\dfrac{\partial \Omega}{\partial V}\right)_{T,\mu}$,

- average number of particles: $\mathcal{N} = -\left(\dfrac{\partial \Omega}{\partial \mu}\right)_{T,V}$.

Fugacity: $z \doteq e^{\mu/k_B T}$ (often used as independent variable instead of μ).

The grand partition function is rendered as $Z(\beta, V, \mu)$ or $Z(\beta, V, z)$.

Relation between canonical and grandcanonical partition functions:

$$Z = \sum_{N=0}^{\infty} e^{\mu N/k_B T} Z_N = \sum_{N=0}^{\infty} z^N Z_N.$$

Open system of indistinguishable noninteracting particles:

$$Z_N = \frac{1}{N!} \tilde{Z}^N, \quad Z = \sum_{N=0}^{\infty} \frac{1}{N!} z^N \tilde{Z}^N = e^{z\tilde{Z}}$$

$$\Rightarrow \ \Omega = -k_B T \ln Z = -k_B T z \tilde{Z}.$$

Density fluctuations and compressibility:

Average number of particles (in some volume V):

$$\mathcal{N} = \langle N \rangle = \sum_{N=0}^{\infty} \frac{1}{ZC_N} \int_{\Gamma_N} d^{6N}X \, N e^{-\beta(H_N(\mathbf{X}) - \mu N)} = \frac{1}{Z\beta} \frac{\partial Z}{\partial \mu} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z.$$

Alternatively: $\mathcal{N} = -\left(\dfrac{\partial \Omega}{\partial \mu}\right)_{T,V} = \dfrac{\partial}{\partial \mu}\left(\beta^{-1} \ln Z\right) = \dfrac{1}{\beta} \dfrac{\partial}{\partial \mu} \ln Z.$

Fluctuations in particle number (in volume V):

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{Z\beta^2} \frac{\partial^2 Z}{\partial \mu^2} - \left[\frac{1}{Z\beta} \frac{\partial Z}{\partial \mu}\right]^2 \overset{\text{(i)}}{=} \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial \mu^2}.$$

(i): $\dfrac{1}{\beta^2} \dfrac{\partial^2 \ln Z}{\partial \mu^2} = \dfrac{1}{\beta^2} \dfrac{\partial}{\partial \mu} \dfrac{1}{Z} \dfrac{\partial Z}{\partial \mu} = \dfrac{1}{Z\beta^2} \dfrac{\partial^2 Z}{\partial \mu^2} + \dfrac{1}{\beta^2}\left(-\dfrac{1}{Z^2}\right)\left(\dfrac{\partial Z}{\partial \mu}\right)^2 = \dots$

Use $\dfrac{\partial}{\partial \mu} \ln Z = \beta \mathcal{N}.$

$$\Rightarrow \ \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \frac{\partial(\beta\langle N \rangle)}{\partial \mu} = k_B T \left(\frac{\partial \mathcal{N}}{\partial \mu}\right)_{TV}.$$

Use the Gibbs-Duhem relation, $V dp - \mathcal{N} d\mu - S dT = 0.$

$$\Rightarrow \ d\mu = \frac{V}{\mathcal{N}} dp - \frac{S}{\mathcal{N}} dT \quad \Rightarrow \quad \left(\frac{\partial \mu}{\partial(V/\mathcal{N})}\right)_T = \frac{V}{\mathcal{N}}\left(\frac{\partial p}{\partial(V/\mathcal{N})}\right)_T.$$

Use $\left(\dfrac{\partial}{\partial(V/\mathcal{N})}\right)_V = \left(\dfrac{\partial(V/\mathcal{N})}{\partial\mathcal{N}}\right)_V^{-1}\dfrac{\partial}{\partial\mathcal{N}} = -\dfrac{\mathcal{N}^2}{V}\dfrac{\partial}{\partial\mathcal{N}}.$

Use $\left(\dfrac{\partial}{\partial(V/\mathcal{N})}\right)_{\mathcal{N}} = \left(\dfrac{\partial(V/\mathcal{N})}{\partial V}\right)_{\mathcal{N}}^{-1}\dfrac{\partial}{\partial V} = \mathcal{N}\dfrac{\partial}{\partial V}.$

$$\Rightarrow \quad -\dfrac{\mathcal{N}^2}{V}\left(\dfrac{\partial\mu}{\partial\mathcal{N}}\right)_{TV} = V\left(\dfrac{\partial p}{\partial V}\right)_{TN}.$$

Isothermal compressibility: $\kappa_T \doteq -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_{TN}.$

$$\Rightarrow \quad \left(\dfrac{\partial\mu}{\partial\mathcal{N}}\right)_{TV} = \dfrac{V}{\mathcal{N}^2}\kappa_T^{-1} \quad\Rightarrow\quad \langle N^2\rangle - \langle N\rangle^2 = \dfrac{\mathcal{N}^2}{V}k_B T\kappa_T.$$

An alternative expression for $\langle N^2\rangle - \langle N\rangle^2$ is calculated in [tex95]. The density fluctuations for a classical ideal gas are calculated in [tex96].

At the critical point of a liquid-gas transition, the isotherm has an inflection point with zero slope, $\partial p/\partial V = 0$, implying $\kappa_T \to \infty$. The strongly enhanced density fluctuations are responsible for critical opalescence.

Gentle introduction to quantum statistics:

Quantum mechanics demands that the many-body eigenvectors have a definite symmetry under permutation of identical particles. This requirement is often easiest to implement in the grandcanonical ensemble.

Consider an ideal quantum gas. Bosons have spin $s = 0, 1, 2, \ldots$ and symmetric eigenvectors. Fermions have spin $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ and antisymmetric eigenvectors. It is safe to ignore the spin for what follows immediately.

Hamiltonian: $\hat{H}_N = \displaystyle\sum_{\ell=1}^{N}\hat{h}_\ell.$

1-particle eigenvalue equation: $\hat{h}_\ell|\mathbf{k}_\ell\rangle = \epsilon_\ell|\mathbf{k}_\ell\rangle.$

N-particle eigenvalue equation: $\hat{H}_N|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle = E_N|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle.$

Total energy: $E_N = \displaystyle\sum_{\ell=1}^{N}\epsilon_\ell, \quad \epsilon_\ell = \dfrac{\hbar^2\mathbf{k}_\ell^2}{2m}.$

N-particle product eigenstates: $|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle = |\mathbf{k}_1\rangle\ldots|\mathbf{k}_N\rangle.$

Each particle is identified by its wave vector $\mathbf{k}_i$.

Permutation symmetry:

Exchanging the wave numbers of otherwise identical particles does not produce a distinct quantum state. This is important in sums over states.

Product wave functions are readily symmetrized or antisymmetrized by taking specific linear combinations.[2]

    ▷ Bosons: symmetrized states $|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle^{(S)}$.

$$N = 2: \ |\mathbf{k}_1, \mathbf{k}_2\rangle^{(S)} = \frac{1}{\sqrt{2}} \left(|\mathbf{k}_1\rangle|\mathbf{k}_2\rangle + |\mathbf{k}_2\rangle|\mathbf{k}_1\rangle\right).$$

    ▷ Fermions: antisymmetrized states $|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle^{(A)}$.

$$N = 2: \ |\mathbf{k}_1, \mathbf{k}_2\rangle^{(A)} = \frac{1}{\sqrt{2}} \left(|\mathbf{k}_1\rangle|\mathbf{k}_2\rangle - |\mathbf{k}_2\rangle|\mathbf{k}_1\rangle\right).$$

Occupation number representation:

    ▷ Bosons: $|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle^{(S)} \doteq |n_1, n_2, \ldots\rangle, \quad n_k = 0, 1, 2, \ldots$
    ▷ Fermions: $|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle^{(A)} \doteq |n_1, n_2, \ldots\rangle, \quad n_k = 0, 1.$

Antisymmetric wave functions vanish identically if two particles have identical wave numbers. Hence the single-occupancy restriction for fermionic 1-particle states.

Here $\mathbf{k}_\ell$ represents the wave vector of ℓth particle, whereas n_k refers to the number of particles in the kth 1-particle state.

The label k of a 1-particle state corresponds (in the current context) to the wave number $\mathbf{k}$ of a particle if it occupies that state. The energy ϵ_k of a 1-particle state is the energy ϵ_ℓ of particle ℓ if it occupies that state.

    – Energy: $\hat{H}|n_1, n_2, \ldots\rangle = E|n_1, n_2, \ldots\rangle, \quad E = \sum_{k=1}^{\infty} n_k \epsilon_k.$

    – Number of particles: $\hat{N}|n_1, n_2, \ldots\rangle = N|n_1, n_2, \ldots\rangle, \quad N = \sum_{k=1}^{\infty} n_k.$

In the microcanonical ensemble, E and N are fixed. In the canonical ensemble, $\langle E \rangle$ is controlled by the temperature T. In the grandcanonical ensemble, $\langle N \rangle$ is controlled by the chemical potential μ.

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[2]The (readily available) expressions for general N are of no concern here.

Canonical partition function:

$$Z_N = \sideset{}{'}\sum_{\{n_k\}} \sigma(n_1, n_2, \ldots) \exp\left(-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right).$$

The sum $\sideset{}{'}\sum_{\{n_k\}}$ is subject to the constraint $\sum_{k=1}^{\infty} n_k = N$.

The statistical-weight $\sigma(n_1, n_2, \ldots)$ depends on the symmetry requirement:

  ▷ Bose-Einstein statistics: $\sigma_{BE}(n_1, n_2, \ldots) = 1$ for $n_k = 0, 1, 2, \ldots$

  ▷ Fermi-Dirac statistics: $\sigma_{FD}(n_1, n_2, \ldots) = \begin{cases} 1 & : \text{ if } n_k = 0, 1, \\ 0 & : \text{ otherwise.} \end{cases}$

What is the statistical weight factor for the Maxwell-Boltzmann gas?

We recall the partition function for the classical ideal gas from [tsc11] and adapt it to fit the notation used here:

$$Z_N = \frac{1}{N!} \tilde{Z}^N = \frac{1}{N!} \left(\sum_{k=1}^{\infty} e^{-\beta \epsilon_k}\right)^N.$$

Next we use a multinomial generalization of the binomial expansion for the contents of parenthesis:

$$(a + b)^N = \sum_{n=1}^{N} \frac{N!}{n!(N-n)!} a^n b^{N-n}.$$

$$\Rightarrow \ Z_N = \frac{1}{N!} \sideset{}{'}\sum_{\{n_k\}} \frac{N!}{n_1! n_2! \ldots} \left(e^{-\beta \epsilon_1}\right)^{n_1} \left(e^{-\beta \epsilon_2}\right)^{n_2} \cdots$$

Then we make contact with the general expression above, which determines the statistical weight:

$$Z_N = \sideset{}{'}\sum_{\{n_k\}} \frac{1}{n_1! n_2! \ldots} \exp\left(-\beta \sum_{k=1}^{\infty} n_k \epsilon_k\right).$$

  ▷ Maxwell-Boltzmann statistics: $\sigma_{MB}(n_1, n_2, \ldots) = \dfrac{1}{n_1! n_2! \ldots}$.

All three statistical weights are the same if multiple occupancy of 1-particle states is very unlikely. This is the case in dilute gases at high temperatures.

Grandcanonical partition function:

The constrained sum in the canonical partition function, which makes its evaluation difficult, is turned into an unconstrained sum when we switch to the grandcanonical ensemble.

$$\Rightarrow \ Z = \sum_{N=0}^{\infty} z^N Z_N = \sum_{\{n_k\}} \sigma(n_1, n_2, \ldots) \exp\left(-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right),$$

where we have used $\ z^N = e^{\beta \mu N} = \exp\left(\beta \mu \sum_{k=1}^{\infty} n_k\right).$

In all three cases, FD, BE, and MB, the exponential function can be factorized. Sums over n_k can then be evaluated independently.

▷ FD statistics: each sum has just terms:

$$Z_{FD} = \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots \exp\left(-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right) = \prod_{k=1}^{\infty} \sum_{n_k=0}^{1} z e^{-\beta \epsilon_k n_k}.$$

$$\Rightarrow \ Z_{FD} = \prod_{k=1}^{\infty} \left(1 + z e^{-\beta \epsilon_k}\right).$$

▷ BE statistics: each sum is a geometric series:

$$Z_{BE} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \exp\left(-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right) = \prod_{k=1}^{\infty} \sum_{n_k=0}^{\infty} \left[z e^{-\beta \epsilon_k}\right]^{n_k}.$$

$$\Rightarrow \ Z_{BE} = \prod_{k=1}^{\infty} \frac{1}{1 - z e^{-\beta \epsilon_k}}.$$

▷ MB statistics: each sum is the series expansion of an exponential fct.:

$$Z_{MB} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \frac{1}{n_1! n_2! \ldots} \exp\left(-\beta \sum_{k=1}^{\infty} n_k(\epsilon_k - \mu)\right).$$

$$\Rightarrow \ Z_{MB} = \prod_{k=1}^{\infty} \sum_{n_k=0}^{\infty} \frac{1}{n_k!} \left[z e^{-\beta \epsilon_k}\right]^{n_k} = \prod_{k=1}^{\infty} \exp\left(z e^{-\beta \epsilon_k}\right).$$

The grandcanonical partition function for each statistics is a product of terms pertaining to 1-particle states.

Grand potential:

$$\Omega(T, V, \mu) = -k_B T \ln Z = U - TS - \mu \mathcal{N} = -pV.$$

The natural independent variables are as stated. Sometimes the fugacity z is substituted for the chemical potential μ. Care must be exercised with partial derivatives.

$$\triangleright \; \Omega_{FD} = -k_B T \sum_{k=1}^{\infty} \ln \left(1 + ze^{-\beta \epsilon_k}\right) = -k_B T \sum_{k=1}^{\infty} \ln \left(1 + e^{-\beta(\epsilon_k - \mu)}\right),$$

$$\triangleright \; \Omega_{BE} = k_B T \sum_{k=1}^{\infty} \ln \left(1 - ze^{-\beta \epsilon_k}\right) = k_B T \sum_{k=1}^{\infty} \ln \left(1 - e^{-\beta(\epsilon_k - \mu)}\right),$$

$$\triangleright \; \Omega_{MB} = -k_B T \sum_{k=1}^{\infty} ze^{-\beta \epsilon_k} = -k_B T \sum_{k=1}^{\infty} e^{-\beta(\epsilon_k - \mu)}.$$

The dependence of Ω on T and μ is explicit. Its dependence on V is concealed in the 1-particle energies ϵ_k and made explicit later.

Average number of particles and state occupancies:

$$\mathcal{N} = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T} = \sum_{k=1}^{\infty} \langle n_k \rangle = \begin{cases} \displaystyle\sum_{k=1}^{\infty} \frac{1}{z^{-1}e^{\beta \epsilon_k} + 1} & : \; \text{FD}, \\[2em] \displaystyle\sum_{k=1}^{\infty} \frac{1}{z^{-1}e^{\beta \epsilon_k} - 1} & : \; \text{BE}, \\[2em] \displaystyle\sum_{k=1}^{\infty} ze^{-\beta \epsilon_k} & : \; \text{MB}. \end{cases}$$

Entropy and state occupancies: [tex178]

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = \begin{cases} -k_B \displaystyle\sum_{k=1}^{\infty} \left[\langle n_k \rangle \ln \langle n_k \rangle + (1 - \langle n_k \rangle) \ln(1 - \langle n_k \rangle)\right] & : \; \text{(FD)} \\[2em] -k_B \displaystyle\sum_{k=1}^{\infty} \left[\langle n_k \rangle \ln \langle n_k \rangle - (1 + \langle n_k \rangle) \ln(1 + \langle n_k \rangle)\right] & : \; \text{(BE)} \\[2em] -k_B \displaystyle\sum_{k=1}^{\infty} \left[\langle n_k \rangle \ln \langle n_k \rangle - \langle n_k \rangle\right] & : \; \text{(MB)} \end{cases}$$

Internal energy and state occupancies: [tex178]

$$U = \Omega + TS + \mu \mathcal{N} = \sum_{k=1}^{\infty} \epsilon_k \langle n_k \rangle.$$

Fluctuations of state occupancies: [tex110]

$$\langle n_k \rangle = -\beta^{-1} \frac{\partial \ln Z}{\partial \epsilon_k}, \quad \langle n_k^2 \rangle - \langle n_k \rangle^2 = \beta^{-2} \frac{\partial^2 \ln Z}{\partial \epsilon_k^2} = -\beta^{-1} \frac{\partial \langle n_k \rangle}{\partial \epsilon_k}.$$

Density of states:

Thus far we derived all expressions for thermodynamic quantities of quantum gases as sums over 1-particle states. For their further evaluation, we must know the distribution of 1-particle energies ϵ_k.

Particles (fermions or bosons) of rest mass m have relativistic energy-momentum relation,

$$\epsilon(p) = \sqrt{m^2 c^4 + p^2 c^2} - mc^2 \quad \rightsquigarrow \quad \begin{cases} \dfrac{p^2}{2m} & : \ \epsilon \ll mc^2, \\[2mm] pc & : \ \epsilon \gg mc^2, \end{cases}$$

with the nonrelativistic and ultrarelativistic limits indicated.

Consider a hypercubic box of volume $V = L^{\mathcal{D}}$, small enough that the density of particles in real space can be assumed uniform.[3] The density of 1-particle states is uniform in **k**-space: $(L/2\pi)^{\mathcal{D}}$.

Invoking isotropy we can write for the density of energy levels:

$$D(\epsilon)d\epsilon = \left(\frac{L}{2\pi}\right)^{\mathcal{D}} d^{\mathcal{D}}k = \frac{V}{(2\pi)^{\mathcal{D}}} \mathcal{A}_{\mathcal{D}} \, k^{\mathcal{D}-1} dk, \quad \mathcal{A}_{\mathcal{D}} = \frac{2\pi^{\mathcal{D}/2}}{\Gamma(\mathcal{D}/2)}.$$

Using $\epsilon(p)$ with $p = \hbar k$ we obtain the result [tex111],

$$D(\epsilon) = \frac{V \mathcal{A}_{\mathcal{D}}}{(hc)^{\mathcal{D}}} \epsilon^{\mathcal{D}/2-1} \big(\epsilon + 2mc^2\big)^{\mathcal{D}/2-1} \big(\epsilon + mc^2\big).$$

In the nonrelativistic and ultrarelativistic limits this relation turns into,

$$D(\epsilon) \quad \rightsquigarrow \quad \begin{cases} \dfrac{V}{\Gamma(\mathcal{D}/2)} \left(\dfrac{2\pi m}{h^2}\right)^{\mathcal{D}/2} \epsilon^{\mathcal{D}/2-1} & : \ \epsilon \ll mc^2 \\[4mm] \dfrac{2V\pi^{\mathcal{D}/2}}{\Gamma(\mathcal{D}/2)(ch)^{\mathcal{D}}} \epsilon^{\mathcal{D}-1} & : \ \epsilon \gg mc^2. \end{cases}$$

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[3]This condition matters when, in some applications, the factor V in the local density of state is replaced by an integral over density in real space.

With these expressions for $D(\epsilon)$ we can convert the sums over 1-particle states into integrals weighted by the density of 1-particle states.

Example: average number of nonrelativistic MB particles [tex112]:

$$\mathcal{N} = \sum_{k=1}^{\infty} z e^{-\beta \epsilon_k} = \int_0^{\infty} d\epsilon\, D(\epsilon) z e^{-\beta\epsilon} = \frac{Vz}{\lambda_T^{\mathcal{D}}}, \quad \lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}.$$
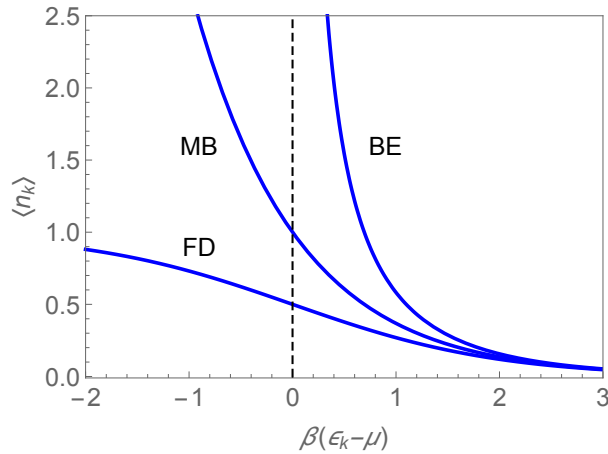
Occupancy of 1-particle states:

The average occupation number of energy level ϵ_k depends on the two control variables T and μ via the compound variable $\beta(\epsilon_k - \mu)$:

$$\langle n_k \rangle = \begin{cases} \dfrac{1}{e^{\beta(\epsilon_k - \mu)} + 1} & : \text{ FD}, \\[3mm] \dfrac{1}{e^{\beta(\epsilon_k - \mu)} - 1} & : \text{ BE}, \\[3mm] e^{-\beta(\epsilon_k - \mu)} & : \text{ MB}. \end{cases}$$

Range of 1-particle energies: $\epsilon_k \geq 0$.

BE gas restriction: $\mu \leq 0 \quad \Rightarrow \quad \beta(\epsilon_k - \mu) \geq 0$.

The BE and FD gases are well approximated by the MB gas if the thermal wavelength λ_T is small compared to the average interparticle distance d.

Average distance between particles: $d = \left(\dfrac{V}{\mathcal{N}}\right)^{1/\mathcal{D}}$ (rough measure).

Condition from graph: $\beta(\epsilon_k - \mu) \gg 1$,

$$\Rightarrow \quad -\beta\mu \gg 1 \quad \Rightarrow \quad e^{\beta\mu} = z \ll 1.$$

Result from above: $\mathcal{N} = \dfrac{V z}{\lambda_T^{\mathcal{D}}} \quad \Rightarrow \quad z = \dfrac{\mathcal{N}}{V} \lambda_T^{\mathcal{D}}.$

Conclusion: $z \ll 1 \quad \Rightarrow \quad \dfrac{V}{\mathcal{N}} \ll \lambda_T^{\mathcal{D}}.$

Exercises:

    ▷ Classical ideal gas [tex94]
    ▷ Ultrarelativistic ideal gas [tex169]
    ▷ Density fluctuations [tex95]
    ▷ Density fluctuations and compressibility [tex96]
    ▷ Energy fluctuations and thermal response functions [tex103]
    ▷ Occupation number fluctuations [tex110]
    ▷ Density of 1-particle states [tex111]
    ▷ Maxwell-Boltzmann gas in D dimensions [tex112]
    ▷ Some fantasy gas [tex171]
    ▷ Ideal lattice gase [tex172]
    ▷ Entropy and internal energy from state occupancies [tex178]