2015

12. Grandcanonical Ensemble

Gerhard Müller
University of Rhode Island, gmuller@uri.edu

Abstract
Part twelve of course materials for Statistical Physics I: PHY525, taught by Gerhard Müller at the University of Rhode Island. Documents will be updated periodically as more entries become presentable.
12. Grandcanonical Ensemble

- Grandcanonical ensemble. [tn60]
- Classical ideal gas (grandcanonical ensemble). [tex94]
- Density fluctuations and compressibility. [tn61]
- Density fluctuations in the grand canonical ensemble. [tex95]
- Density fluctuations and compressibility in the classical ideal gas. [tex96]
- Energy fluctuations and thermal response functions. [tex103]
- Microscopic states of quantum ideal gases. [tn62]
- Partition function of quantum ideal gases. [tn63]
- Ideal quantum gases: grand potential and thermal averages. [tn64]
- Ideal quantum gases: average level occupancies. [tsl35]
- Occupation number fluctuations. [tex110]
- Density of energy levels for ideal quantum gas. [tex111]
- Maxwell-Boltzmann gas in $D$ dimensions. [tex112]
Grandcanonical ensemble

Consider an open classical system (volume $V$, temperature $T$, chemical potential $\mu$). The goal is to determine the thermodynamic potential $\Omega(T, V, \mu)$ pertaining to that situation, from which all other thermodynamic properties can be derived.

A quantitative description of the grandcanonical ensemble requires a set of phase spaces $\Gamma_N$, $N = 0, 1, 2, \ldots$ with probability densities $\rho_N(X)$. The interaction Hamiltonian for a system of $N$ particles is $H_N(X)$.

Maximize Gibbs entropy $S = -k_B \sum_{N=0}^{\infty} \int_{\Gamma_N} d^6X \rho_N(X) \ln[C_N \rho_N(X)]$

subject to the three constraints

- $\sum_{N=0}^{\infty} \int_{\Gamma_N} d^6X \rho_N(X) = 1$ (normalization),
- $\sum_{N=0}^{\infty} \int_{\Gamma_N} d^6X \rho_N(X) H_N(X) = \langle H \rangle = U$ (average energy),
- $\sum_{N=0}^{\infty} \int_{\Gamma_N} d^6X \rho_N(X) N = \langle N \rangle = N$ (average number of particles).

Apply calculus of variation with three Lagrange multipliers:

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

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

$\Rightarrow \{ \cdots \} = 0 \Rightarrow \rho_N(X) = \frac{1}{C_N} \exp \left( \frac{\alpha_0}{k_B} - 1 + \frac{\alpha_U}{k_B} H_N(X) + \frac{\alpha_N}{k_B} N \right)$.

Determine the Lagrange multipliers $\alpha_0, \alpha_U, \alpha_N$:

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

$\sum_{N=0}^{\infty} \int_{\Gamma_N} d^6X \rho_N(X) \{ \cdots \} = 0 \Rightarrow S - k_B + \alpha_0 + \alpha_U U + \alpha_N N = 0$

$\Rightarrow U + \frac{1}{\alpha_U} S + \frac{\alpha_N}{\alpha_U} N = \frac{k_B}{\alpha_U} \ln Z.$

1
Compare with $U - TS - \mu N = -pV = \Omega \Rightarrow \alpha_U = -\frac{1}{T}, \alpha_N = \frac{\mu}{T}$.

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

Grand partition function: $Z = \sum_{N=0}^{\infty} \frac{1}{C_N} \int_{\Gamma_N} d^6 x \, e^{-\beta H_N(x) + \beta \mu N}$, $\beta = \frac{1}{k_B T}$.

Probability densities: $\rho_N(x) = \frac{1}{Z C_N} e^{-\beta H_N(x) + \beta \mu N}$.

Grandcanonical ensemble in quantum mechanics:

$$Z = \text{Tr} e^{-\beta (H - \mu N)}, \quad \rho = \frac{1}{Z} e^{-\beta (H - \mu N)}, \quad \Omega = -k_B T \ln Z.$$  

Derivation of thermodynamic properties from grand potential:

$$S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu}, \quad p = - \left( \frac{\partial \Omega}{\partial V} \right)_{T, \mu}, \quad \mathcal{N} = \langle N \rangle = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T, V}.$$  

Relation between canonical and grandcanonical partition functions:

$$Z = \sum_{N=0}^{\infty} e^{\mu N / k_B T} Z_N = \sum_{N=0}^{\infty} z^N Z_N, \quad z \equiv e^{\mu / k_B T} \text{ (fugacity)}.$$  

Open system of indistinguishable noninteracting particles:

$$Z_N = \frac{1}{N!} \tilde{Z}^N, \quad Z = \sum_{N=0}^{\infty} \frac{1}{N!} z^N \tilde{Z}^N = e^{z \tilde{Z}} \Rightarrow \Omega = -k_B T \ln Z = -k_B T z \tilde{Z}.$$  

Thermodynamic properties of the classical ideal gas in the grandcanonical ensemble are calculated in exercise [tex94].
Consider a classical ideal gas in a box of volume $V$ in equilibrium with heat and particle reservoirs at temperature $T$ and chemical potential $\mu$, respectively.

(a) Show that the grand partition function is $Z = \exp(zV/\lambda_T^3)$, where $z = \exp(\mu/k_B T)$ is the fugacity, and $\lambda_T = \sqrt{\hbar^2/2\pi mk_B T}$ is the thermal wavelength.

(b) Derive from $Z$ the grand potential $\Omega(T, V, \mu)$, the entropy $S(T, V, \mu)$, the pressure $p(T, V, \mu)$, and the average particle number $\langle N \rangle = \mathcal{N}(T, V, \mu)$.

(c) Derive from these expressions the familiar results for the internal energy $U = \frac{3}{2} N k_B T$, and the ideal gas equation of state $pV = N k_B T$.

Solution:
Density fluctuations and compressibility

Average number of particles in volume $V$:

$$\mathcal{N} = \langle N \rangle = \sum_{N=0}^{\infty} \frac{1}{Z_C N} \int_{\tau_N} d^6 x \, N e^{-\beta H_N(x) + \beta \mu N} = \frac{1}{Z} \frac{\partial Z}{\partial \mu} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z.$$  

Fluctuations in particle number (in volume $V$):

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

Here we use $Z = Z(\beta, V, \mu)$.

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

For $V =$ const:

$$\frac{\partial}{\partial (V/N)} = \frac{\partial \mathcal{N}}{\partial (V/N)} \frac{\partial}{\partial \mathcal{N}} = - \frac{N^2}{V} \frac{\partial}{\partial \mathcal{N}}.$$  

For $\mathcal{N} =$ const:

$$\frac{\partial}{\partial (V/N)} = \frac{\partial V}{\partial (V/N)} \frac{\partial}{\partial V} = \mathcal{N} \frac{\partial}{\partial V}.$$  

$$\Rightarrow - \frac{N^2}{V} \left( \frac{\partial \mu}{\partial \mathcal{N}} \right)_{TV} = V \left( \frac{\partial p}{\partial V} \right)_{TN} \Rightarrow \left( \frac{\partial \mu}{\partial \mathcal{N}} \right)_{TV} = \frac{V}{N^2} \kappa_T^{-1}.$$  

Compressibility: $\kappa_T \equiv - \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{TN}.$

Fluctuations in particle number: $\langle N^2 \rangle - \langle N \rangle^2 = \frac{N^2}{V} k_B T \kappa_T.$

An alternative expression for $\langle N^2 \rangle - \langle N \rangle^2$ is calculated in exercise [tex95].

The density fluctuations for a classical ideal gas are calculated in exercise [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.
Density fluctuations in the grandcanonical ensemble

Consider a system of indistinguishable particles in the grandcanonical ensemble. Derive the following two expressions for the fluctuations in the number of particles $N$ for an open system of volume $V$ in equilibrium with heat and particle reservoirs at temperature $T$ and chemical potential $\mu$, respectively:

$$\langle N^2 \rangle - \langle N \rangle^2 = z \frac{\partial}{\partial z} z \frac{\partial}{\partial z} \ln Z = k_B T V \frac{\partial^2 p}{\partial \mu^2},$$

where $z = \exp(\mu/k_B T)$ is the fugacity, $p(T, V, \mu) = -(\partial \Omega/\partial V)_{T \mu} = -\Omega/V$ is the pressure, and $\Omega(T, V, \mu) = -k_B T \ln Z$ is the grand potential.

Solution:
Density fluctuations and compressibility of the classical ideal gas

(a) Use the results of [tex94] and [tex95] to show that the variance of the number of particles in a classical ideal gas (open system) is equal to the average number of particles:

\[ \langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle = N. \]

(b) Use this result to show that the isothermal compressibility of the classical ideal gas is \( \kappa_T = 1/p. \)

Solution:
Energy fluctuations and thermal response functions

(a) Show that the following relation holds between the energy fluctuations in the microscopic ensemble and the heat capacity of a system described by a microscopic Hamiltonian $H$:

$$\langle (H - \langle H \rangle)^2 \rangle = k_B T^2 C_V.$$

(b) Prove the following relation in a similar manner:

$$\langle (H - \langle H \rangle)^3 \rangle = k_B^2 \left[ T^4 \left( \frac{\partial C_V}{\partial T} \right)_V + 2T^3 C_V \right].$$

(c) Determine the relative fluctuations as measured by the quantities $\langle (H - \langle H \rangle)^2 \rangle / \langle H \rangle^2$ and $\langle (H - \langle H \rangle)^3 \rangle / \langle H \rangle^3$ for the classical ideal gas with $N$ atoms.

Solution:
Microscopic states of ideal quantum gases

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

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

$N$-particle eigenvalue equation: $\hat{H}_N |k_1, \ldots, k_N\rangle = E_N |k_1, \ldots, k_N\rangle$.  

Energy: $E_N = \sum_{\ell=1}^N \epsilon_\ell$, $\epsilon_\ell = \frac{\hbar^2 k_\ell^2}{2m}$.  

$N$-particle product eigenstates: $|k_1, \ldots, k_N\rangle = |k_1\rangle \cdots |k_N\rangle$.  

Symmetrized states for bosons: $|k_1, \ldots, k_N\rangle^{(S)}$.  

- $N = 2$: $|k_1, k_2\rangle^{(S)} = \frac{1}{\sqrt{2}} (|k_1\rangle |k_2\rangle + |k_2\rangle |k_1\rangle)$.  

Antisymmetrized states for fermions: $|k_1, \ldots, k_N\rangle^{(A)}$.  

- $N = 2$: $|k_1, k_2\rangle^{(A)} = \frac{1}{\sqrt{2}} (|k_1\rangle |k_2\rangle - |k_2\rangle |k_1\rangle)$.  

Occupation number representation: $|k_1, \ldots, k_N\rangle \equiv |n_1, n_2, \ldots\rangle$.  

Here $k_1$ represents the wave vector of the first particle, whereas $n_1$ refers to the number of particles in the first 1-particle state.  

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

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

$\epsilon_\ell$: energy of particle $\ell$.  

$\epsilon_k$: energy of 1-particle state $k$.  

Allowed occupation numbers:  

- bosons: $n_k = 0, 1, 2, \ldots$  

- fermions: $n_k = 0, 1$.  

$\epsilon_\ell$: energy of particle $\ell$.  

$\epsilon_k$: energy of 1-particle state $k$.  

Allowed occupation numbers:  

- bosons: $n_k = 0, 1, 2, \ldots$  

- fermions: $n_k = 0, 1$.  

$\epsilon_\ell$: energy of particle $\ell$.  

$\epsilon_k$: energy of 1-particle state $k$.
Partition function of ideal quantum gases

Canonical partition function: \( Z_N = \sum_{\{n_k\}} \sigma(n_1, n_2, \ldots) \exp \left( -\beta \sum_{k=1}^{\infty} n_k \epsilon_k \right) \).

\( \sum_{\{n_k\}} \) : sum over all occupation numbers compatible with \( \sum_{k=1}^{\infty} n_k = N \).

The statistical weight factor \( \sigma(n_1, n_2, \ldots) \) is different for fermions and bosons:

- Bose-Einstein statistics: \( \sigma_{BE}(n_1, n_2, \ldots) = 1 \) for arbitrary values of \( n_k \).
- Fermi-Dirac statistics: \( \sigma_{FD}(n_1, n_2, \ldots) = \begin{cases} 1 & \text{if all } n_k = 0, 1 \\ 0 & \text{otherwise} \end{cases} \).

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

\[
Z_N = \frac{1}{N!} \tilde{Z}^N = \frac{1}{N!} \left( \sum_{k=1}^{\infty} e^{-\beta \epsilon_k} \right)^N = \frac{1}{N!} \sum_{\{n_k\}} \frac{N!}{n_1!n_2! \ldots} \exp \left( -\beta \sum_{k=1}^{\infty} n_k \epsilon_k \right) = \sum_{\{n_k\}} \frac{1}{n_1!n_2! \ldots} \exp \left( -\beta \sum_{k=1}^{\infty} n_k \epsilon_k \right). \]

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

Grandcanonical partition function:

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

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

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

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

- \( Z_{MB} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \frac{1}{n_1!n_2! \ldots} \exp \left( -\beta \sum_{k=1}^{\infty} n_k (\epsilon_k - \mu) \right) = \prod_{k=1}^{\infty} \exp (ze^{-\beta \epsilon_k}). \)
Ideal quantum gases: grand potential and thermal averages

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

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

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

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

Parametric representation \([a = 1 \text{ (FD)}, \ a = 0 \text{ (MB)}, \ a = -1 \text{ (BE)}]\):

\[
\ln Z = \frac{pV}{k_B T} = \frac{1}{a} \sum_{k=1}^{\infty} \ln \left(1 + az e^{-\beta \epsilon_k}\right). 
\]

Average number of particles:

\[
N = -\left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} = \frac{1}{\beta} \left( \frac{\partial \ln Z}{\partial \mu} \right)_{T,V} = \sum_{k=1}^{\infty} \frac{1}{z^{-1} e^{\beta \epsilon_k} + a} = \sum_{k=1}^{\infty} \langle n_k \rangle.
\]

Average energy (internal energy):

\[
U = -\left( \frac{\partial \ln Z}{\partial \beta} \right)_{z,V} = \sum_{k=1}^{\infty} \frac{\epsilon_k}{z^{-1} e^{\beta \epsilon_k} + a} = \sum_{k=1}^{\infty} \epsilon_k \langle n_k \rangle.
\]

Average occupation number of energy level \( \epsilon_k \):

\[
\langle n_k \rangle = -\beta^{-1} \frac{\partial \ln Z}{\partial \epsilon_k} = \frac{1}{e^{\beta(\epsilon_k - \mu)} + a}.
\]

Fluctuations in occupation number \([\text{tex110}]\):

\[
\langle n_k^2 \rangle - \langle n_k \rangle^2 = \beta^{-2} \frac{\partial^2 \ln Z}{\partial \epsilon_k^2}.
\]
Average occupation numbers for MB, FD, and BE gases

Average occupation number of energy level $\epsilon_k$:

$$\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} + a}$$

- $a = 1$: Fermi-Dirac gas,
- $a = 0$: Maxwell-Boltzmann gas,
- $a = -1$: Bose-Einstein gas.

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

BE gas restriction: $\mu \leq 0 \Rightarrow 0 \leq z \leq 1$.

The BE and FD gases are well approximated by the MB gas provided the thermal wavelength $\lambda_T = \sqrt{\hbar^2/2\pi mk_BT}$ is small compared to the average interparticle distance:

$$\beta(\epsilon_k - \mu) \gg 1 \Rightarrow -\beta\mu \gg 1 \Rightarrow z \ll 1.$$  

[tex94] for $D = 3$ : $\Rightarrow \lambda_T \ll (V/N)^{1/3}$. 
Occupation number fluctuations

Consider an ideal quantum gas specified by the grand partition function $Z$. Start from the expressions

$$\langle n^2_k \rangle - \langle n_k \rangle^2 = \frac{1}{Z} \beta^{-2} \frac{\partial^2 Z}{\partial \epsilon_k^2} - \left[ \frac{1}{Z} \beta^{-1} \frac{\partial Z}{\partial \epsilon_k} \right]^2, \quad \ln Z = \frac{1}{a} \sum_{k=1}^{\infty} \ln(1 + a z e^{-\beta \epsilon_k}),$$

where $a = +1, 0, -1$ represent the FD, MB, and BE cases, respectively, to derive the following result for the relative fluctuations in the occupation numbers:

$$\frac{\langle n^2_k \rangle - \langle n_k \rangle^2}{\langle n_k \rangle^2} = \frac{1}{\langle n_k \rangle} - a.$$

Note that in the BE (FD) statistics, these fluctuations are enhanced (suppressed) relative to those in the MB statistics.

Solution:
Density of energy levels for ideal quantum gas

Consider a nonrelativistic ideal quantum gas in $D$ dimensions and confined to a box of volume $V = L^D$ with rigid walls. Show that the density of energy levels is

$$D(\epsilon) = \frac{L^D}{\Gamma(D/2)} \left( \frac{m}{2\pi\hbar^2} \right)^{D/2} \epsilon^{D/2-1}.$$ 

Solution:
Maxwell-Boltzmann gas in $D$ dimensions

From the expressions for the grand potential and the density of energy levels of an ideal Maxwell-Boltzmann gas in $D$ dimensions and confined to a box of volume $V = L^D$ with rigid walls,

$$\Omega(T, V, \mu) = -k_B T \sum_k e^{-\beta (\epsilon_k - \mu)}, \quad D(\epsilon) = \frac{L^D}{\Gamma(D/2)} \left( \frac{m}{2\pi \hbar^2} \right)^{D/2} \epsilon^{D/2-1},$$

derive the familiar results $pV = Nk_B T$ for the equation of state, $C_{V,N} = (D/2) Nk_B$ for the heat capacity, and $pV^{(D+2)/D} = \text{const}$ for the adiabate at fixed $N$.

Solution: