

Canonical Ensemble I [tsc11]

In a closed thermodynamic system, the energy content fluctuates due to thermal contact: $H \neq \text{const.}$ The stationarity condition, $\rho = \rho(H)$, by itself is not enough. We must find a way to determine the function $\rho(H)$.

Consider a classical system of N interacting particles confined to a volume V at (average) internal energy U .

Extremum principle:

Determine the phase-space density $\rho(\mathbf{X})$ that maximizes the Gibbs entropy subject to auxiliary conditions related to normalization and average energy:

$$\text{– Gibbs entropy:}^1 \quad S = -k_B \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) \ln[C_N \rho(\mathbf{X})],$$

$$\text{– normalization:} \quad \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) = 1,$$

$$\text{– internal energy:} \quad \int_{\Gamma} d^{6N} X H(\mathbf{X}) \rho(\mathbf{X}) = U.$$

Application of calculus of variation with Lagrange multipliers α_0 and α_U :

$$\begin{aligned} \delta \int_{\Gamma} d^{6N} X \{ -k_B \rho \ln[C_N \rho] + \alpha_0 \rho + \alpha_U H \rho \} &= 0 \\ \Rightarrow \int_{\Gamma} d^{6N} X \{ -k_B \ln[C_N \rho] - k_B + \alpha_0 + \alpha_U H \} \delta \rho &= 0. \end{aligned}$$

This integral must vanish for arbitrary variations $\delta \rho$. In consequence, the contents of $\{\dots\}$ must vanish.

$$\Rightarrow \rho(\mathbf{X}) = \frac{1}{C_N} \exp \left(\frac{\alpha_0}{k_B} - 1 + \frac{\alpha_U}{k_B} H(\mathbf{X}) \right).$$

A quick look to the microcanonical ensemble: The first auxiliary condition is an integral over a thin energy shell. The second auxiliary condition and all terms with α_U are absent. The result is $\rho(\mathbf{X}) = \text{const}$ on the shell.

Returning to the canonical ensemble, we determine the Lagrange multipliers α_0 and α_U by substitution of $\rho(\mathbf{X})$ into the auxiliary conditions.

¹The values $C_N = h^{3N}$ for distinguishable particles and $C_N = h^{3N} N!$ for indistinguishable particles were explained in [tsc10].

We begin with the first condition and name the resulting integral expression:

$$\int_{\Gamma} d^{6N} X \rho(\mathbf{X}) = 1 \Rightarrow \exp\left(1 - \frac{\alpha_0}{k_B}\right) = \frac{1}{C_N} \int_{\Gamma} d^{6N} X \exp\left(\frac{\alpha_U}{k_B} H(\mathbf{X})\right) \doteq Z_N.$$

The second condition is implemented with $\{\dots\}$ from above as follows:

$$\int_{\Gamma} d^{6N} X \rho(\mathbf{X}) \{ -k_B \ln[C_N \rho(\mathbf{X})] - (k_B - \alpha_0) + \alpha_U H(\mathbf{X}) \} = 0.$$

The three terms of this integral are readily related to the entropy S , the quantity named Z_N , and internal energy U , respectively:

$$\Rightarrow S - k_B \ln Z_N + \alpha_U U = 0.$$

This is a familiar thermodynamic relation in disguise:

$$\Rightarrow U + \frac{1}{\alpha_U} S = \frac{k_B}{\alpha_U} \ln Z_N \quad \Leftrightarrow \quad U - TS = A, \quad \alpha_U = -\frac{1}{T}.$$

Helmholtz free energy: $A(T, V, N) = -k_B T \ln Z_N$.

Canonical partition function:

$$Z_N = \frac{1}{C_N} \int_{\Gamma} d^{6N} X \exp(-\beta H(\mathbf{X})), \quad \beta = \frac{1}{k_B T}.$$

Equilibrium probability density: $\rho(\mathbf{X}) = \frac{1}{Z_N C_N} \exp(-\beta H(\mathbf{X}))$.

Canonical ensemble in quantum mechanics:

– partition function: $Z_N = \text{Tr}[e^{-\beta H}] = \sum_{\lambda} e^{-\beta E_{\lambda}},$

– density operator: $\rho = \frac{1}{Z_N} e^{-\beta H},$

– Helmholtz free energy: $A = -k_B T \ln Z_N.$

If the Hamiltonian contains terms that represent a coupling to an external agent of work (e.g. an external field), then the canonical partition function is related to Gibbs free energy instead: $G = -k_B T \ln Z_N$.

Systems of noninteracting particles:

Consider a classical systems of N noninteracting particles.

$$\text{Hamiltonian: } H = \sum_{l=1}^N h_l(\mathbf{q}_l, \mathbf{p}_l).$$

Canonical partition function of distinguishable particles:

$$Z_N = \frac{1}{h^{3N}} \int_{\Gamma} d^{6N} X e^{-\beta H(\mathbf{X})} = \prod_{l=1}^N \tilde{Z}_l, \quad \tilde{Z}_l = \frac{1}{h^3} \int d^3 q_l d^3 p_l e^{-\beta h_l(\mathbf{q}_l, \mathbf{p}_l)}.$$

Factorizing phase-space probability density:

$$\rho(\mathbf{X}) = \frac{1}{Z_N h^{3N}} e^{-\beta H(\mathbf{X})} = \prod_{l=1}^N \rho_l(\mathbf{q}_l, \mathbf{p}_l) = \prod_{l=1}^N \left[\frac{1}{h^3 \tilde{Z}_l} e^{-\beta h_l(\mathbf{q}_l, \mathbf{p}_l)} \right].$$

Special case: identical one-particle Hamiltonians (distinguishable particles):

$$h_1 = \dots = h_N \doteq h(\mathbf{q}, \mathbf{p}) \quad \Rightarrow \quad \tilde{Z}_1 = \dots = \tilde{Z}_N = \tilde{Z} \doteq \frac{1}{h^3} \int d^3 q d^3 p e^{-\beta h(\mathbf{q}, \mathbf{p})}.$$

$$\Rightarrow Z_N = \tilde{Z}^N, \quad \rho(\mathbf{X}) = \prod_{l=1}^N \rho_l(\mathbf{q}_l, \mathbf{p}_l), \quad \rho_l(\mathbf{q}, \mathbf{p}) = \frac{1}{h^3 \tilde{Z}} e^{-\beta h(\mathbf{q}, \mathbf{p})}.$$

Special case: indistinguishable particles: $Z_N = \frac{1}{N!} \tilde{Z}^N$.

We must discriminate between noninteracting subsystems of two kinds:

- The subsystems are identical in their function, but distinguishable in their position (e.g. atoms vibrating at different sites of a lattice).
- The subsystems are identical in their function and free to exchange their position (e.g. atoms of a gas).

From phase-space density to Maxwell velocity distribution:

Classical ideal gas: N particles of mass m confined to a box of volume V .

- One-particle Hamiltonian: $h(\mathbf{q}, \mathbf{p}) = \frac{p^2}{2m}$.
- One particle partition function: $\tilde{Z} = \frac{V}{\lambda_T^3}$.

- Thermal wavelength: $\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$.
- One-particle phase-space density: $\rho_l(\mathbf{q}, \mathbf{p}) = \frac{e^{-p^2/2mk_B T}}{V(2\pi m k_B T)^{3/2}}$.
- Position distribution: $\rho_l(\mathbf{q}) \doteq \int d^3p \rho_l(\mathbf{q}, \mathbf{p}) = \frac{1}{V}$.
- Momentum distribution: $\Rightarrow \rho_l(\mathbf{p}) = \int d^3q \rho_l(\mathbf{q}, \mathbf{p}) = \frac{e^{-p^2/2mk_B T}}{(2\pi m k_B T)^{3/2}}$.
- Conversion to velocity distribution: $\rho_l(\mathbf{p}) d^3p = f(\mathbf{v}) d^3v$.
- Maxwell distribution: $f(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{-3/2} e^{-mv^2/2k_B T}$.

Ensemble averages:

All thermodynamic functions and response functions of a closed system can be inferred via derivatives from the Helmholtz or Gibbs potential. One or the other is directly related to the canonical partition function.

Further quantities of interest can be obtained from the probability density $\rho(\mathbf{X})$ via expectation values of dynamical variables $f(\mathbf{X})$:

$$\langle f \rangle = \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) f(\mathbf{X}), \quad \rho(\mathbf{X}) = \frac{1}{Z_N C_N} e^{-\beta H(\mathbf{X})}.$$

Some expectation values reproduce quantities derivable directly from Z_N :

- Internal energy:²

$$\begin{aligned} \langle H \rangle &= \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) H(\mathbf{X}) = \frac{1}{Z_N C_N} \int_{\Gamma} d^{6N} X H(\mathbf{X}) e^{-\beta H(\mathbf{X})} \\ \Rightarrow \langle H \rangle &= -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z_N = \frac{\partial}{\partial \beta} (\beta A) = A + TS = U. \end{aligned}$$

- Entropy: $S = -k_B \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) \underbrace{\ln(C_N \rho(\mathbf{X}))}_{-\ln Z_N - \beta H(\mathbf{X})}$.

$$\Rightarrow TS = k_B T \ln Z_N + \int_{\Gamma} d^{6N} X \rho(\mathbf{X}) H(\mathbf{X}) = -A + U.$$

²In cases where the canonical partition function is most directly associated with the Gibbs potential, $G = -k_B T \ln Z_N$, the expectation value of the Hamiltonian is the enthalpy: $\langle H \rangle = E$.

Energy fluctuations and heat capacity:

Thermal contact makes the internal energy (or the enthalpy) a fluctuating quantity. A quantitative measure of fluctuations is the variance:

$$\begin{aligned}\langle H^2 \rangle - \langle H \rangle^2 &= \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} - \left[\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \right]^2 = \frac{\partial}{\partial \beta} \left[\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \right] \\ \Rightarrow \langle H^2 \rangle - \langle H \rangle^2 &= \frac{\partial^2}{\partial \beta^2} \ln Z_N = -\frac{\partial U}{\partial \beta} = k_B T^2 \frac{\partial U}{\partial T} = k_B T^2 C_V.\end{aligned}$$

Whereas variances are measures of fluctuations, response functions often include measures of dissipation. The heat capacity describes heat transfer, which is dissipative in nature.

Fluctuation-dissipation relations such as this one, exist in many different forms. They are all realizations of a very general fluctuation-dissipation theorem – a topic in a different course: PHY626.

Classical ideal gas:

A dilute gas of N particles of mass m is confined to a box of volume V and in contact with a heat reservoir at temperature T .

We can employ classical statistical mechanics if the average inter-particle distance is large compared to the thermal wavelength $\lambda_T \doteq \sqrt{h^2/2\pi m k_B T}$.

We consider particles with relativistic kinetic energy [tex91], [tex92], [tex93],

$$H = \sum_{l=1}^N \left[\sqrt{m^2 c^4 + p_l^2 c^2} - mc^2 \right] \rightsquigarrow \begin{cases} \sum_{l=1}^N \frac{p_l^2}{2m} & : p_l c \ll mc^2, \\ \sum_{l=1}^N p_l c & : p_l c \gg mc^2. \end{cases}$$

If the gas is cold enough but still dilute, we can use the nonrelativistic energy-momentum relation [tex76]. For very hot gases, the ultrarelativistic energy-momentum relation is more adequate [tex77].

The canonical ensemble works well for the statistical mechanical analysis of the classical ideal gas. Comparison of [tex76] (canonical ensemble) with [tex73] (microcanonical ensemble) shows the advantage.

For quantum ideal gases (bosons and fermions) it is the grandcanonical ensemble that has the advantage – a huge advantage as we shall see.

In an earlier module [tsc4] we reconstructed thermodynamic potentials from the empirical information contained in equations of state.

Here we evaluate the canonical partition function from microscopic system specifications, infer the Helmholtz free energy from it, and calculate the equations of state from that thermodynamic potential via derivatives.

Only the caloric equation of state is modified by relativistic effects:

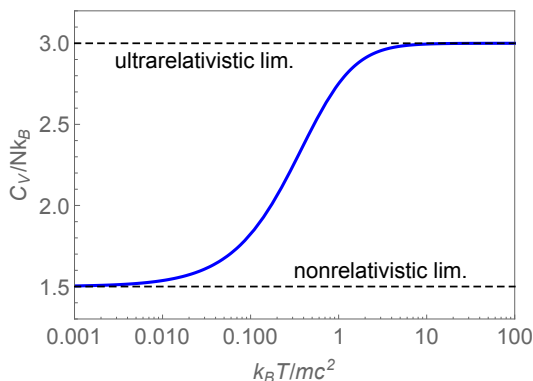
- Thermodynamic equation of state: $pV = Nk_B T$.
- Heat capacity (caloric equation of state):

$$C_V = Nk_B u \left[u + \frac{3}{u} - \frac{K_1(u)}{K_2(u)} \left(3 + u \frac{K_1(u)}{K_2(u)} \right) \right],$$

$K_n(u)$: modified Bessel function; $u \doteq \frac{mc^2}{k_B T}$,

nonrelativistic limit ($u \gg 1$): $\frac{K_1(u)}{K_2(u)} = 1 - \frac{3}{2u} + \frac{15}{8u^2} + \dots$

ultrarelativistic limit ($u \ll 1$): $\frac{K_1(u)}{K_2(u)} = \frac{u}{2} + \dots$



Inhomogeneous systems:

Systems of noninteracting particles are not necessarily homogeneous. Inhomogeneities can be caused, for example, by an external gravitational field [tex79] or by a centrifugal force [tex135].

Extra terms in the Hamiltonian modify the canonical partition function. The inhomogeneities are manifest in position distributions inferred from the phase space-density via integration over all non-relevant coordinates.

Partition function and density of states:

The equivalence of ensembles for macroscopic systems under specific conditions can be proven. Here we pursue a more modest goal.

Primary objects in the analysis of a classical statistical mechanical system:

- phase-space volume in the microcanonical ensemble:

$$\Omega(U, V, N) \doteq \int_{H(\mathbf{x}) < U} d^{6N} X,$$

- partition function in the canonical ensemble:

$$Z(T, V, N) \doteq \frac{1}{C_N} \int_{\Gamma} d^{6N} X e^{-\beta H(\mathbf{x})}.$$

(a) Derivation of $Z(T, V, N)$ from $\Omega(U, V, N)$.

Number of microstates up to energy U : $\Sigma(U, V, N) \doteq \frac{\Omega(U, V, N)}{C_N}$.

Density of microstates at energy U : $g(U, V, N) = \left(\frac{\partial \Sigma}{\partial U} \right)_{V, N}$.

Laplace transform of $g(U, V, N)$:

$$\int_0^\infty dU g(U) e^{-\beta U} = \frac{1}{C_N} \int_{\Gamma} d^{6N} X e^{-\beta H(\mathbf{x})} = Z(T, V, N).$$

The energy scale has been shifted such that $U_0 = 0$ for the ground state.

(b) Derivation of $\Omega(U, V, N)$ from $Z(T, V, N)$.

Complex continuation of the canonical partition function:

$$Z(T, V, N) \doteq \hat{Z}(\beta) \text{ for } \beta = \beta' + i\beta'' \text{ with } \beta' > 0.$$

Inverse Laplace transform:

$$g(U) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} d\beta e^{\beta U} Z(\beta), \quad \Omega(U, V, N) = C_N \int_0^U dU' g(U').$$

Both calculations are carried out [tex81] for the classical ideal gas.

Exercises:

- ▷ Nonrelativistic ideal gas [tex76]
- ▷ Ultrarelativistic ideal gas [tex77]
- ▷ Ultrarelativistic ideal gas in two dimensions [tex154]
- ▷ Relativistic ideal gas I: canonical partition function [tex91]
- ▷ Relativistic ideal gas II: entropy and internal energy [tex92]
- ▷ Relativistic ideal gas III: heat capacity [tex93]
- ▷ Classical ideal gas in uniform gravitational field [tex79]
- ▷ Gas pressure and density inside centrifuge [tex135]
- ▷ Irreversible decompression [tex136]
- ▷ Irreversible heat exchange [tex137]
- ▷ Reversible decompression [tex139]
- ▷ Reversible heat exchange [tex140]
- ▷ Heavy piston I [tex141]
- ▷ Ideal gas partition function and density of states [tex81]
- ▷ Relative momentum of two ideal-gas particles [tex80]