Chapter 6

General Formulation of Statistical Mechanics

6.1 The density matrix

6.1.1 Definition

Up to now we have assumed that

- the energy eigenvalues E_n and eigenstates $|n\rangle$ of the many-particle system are known, i.e. the many-particle problem has been solved;
- the system is in thermodynamic equilibrium , where the distribution probability $W(n)$ for an eigenstate $|n\rangle$ to be realized depends on its energy E_n only and is, in particular, time dependent.

In realistic situations neither the energy eigenvalues E_n are known in general nor is the system in equilibrium, i.e. in general the thermodynamic (mixed) state cannot simply be represented in terms of energy eigenstates. In such situations it is useful to have a basis independent formulation of the statistical formalism. We consider a general mixed state M of a system, represented by a statistical ensemble in which the many-particle states $|\psi_i\rangle$ of the system (not necessarily energy eigenstates!) occur with the relative frequencies h_i, $i = 1, 2, 3, \ldots$.

The thermodynamic average of an observable quantity A in this mixed state is

$$\langle A\rangle = \sum_i h_i \langle\psi_i|\widehat{A}|\psi_i\rangle \ , \tag{6.1}$$

where $\widehat{A}$ is the quantum mechanic operator representing A. Using an *arbitrary*, complete many-body basis set $\{|n\rangle\}$ of the system one can write

$$\begin{aligned}
\langle A\rangle &= \sum_i h_i \sum_{n,m} \langle\psi_i|n\rangle\langle n|\widehat{A}|m\rangle\langle m|\psi_i\rangle && (6.2)\\
&= \sum_i h_i \sum_{n,m} \langle n|\widehat{A}|m\rangle\langle m|\psi_i\rangle\langle\psi_i|m\rangle && (6.3)\\
&= \sum_i h_i \sum_{n} \langle n|\widehat{A}\widehat{P}_i|n\rangle && (6.4)\\
&= \sum_n \left\langle n \left| \widehat{A}\left(\sum_i h_i\widehat{P}_i\right)\right| n\right\rangle && (6.5)
\end{aligned}$$

where we have defined the operator $\widehat{P}_i = |\psi_i\rangle\langle\psi_i|$. $\widehat{P}_i$ is the projector in Hilbert space onto the (arbitrary, normalized) state $|\psi_i\rangle$:

1. $$\widehat{P}_i|\phi\rangle = |\psi_i\rangle\langle\psi_i|\phi\rangle \qquad \text{for arbitrary } |\phi\rangle\text{, and} \tag{6.6}$$

2. $$\widehat{P}_i^2 = |\psi_i\rangle \underbrace{\langle\psi_i|\psi_i\rangle}_{=1\text{ (normalization)}} \langle\psi_i| = |\psi_i\rangle\langle\psi_i| = \widehat{P}_i \tag{6.7}$$

We define the operator

$$\boxed{\widehat{W} = \sum_i h_i|\psi_i\rangle\langle\psi_i|} \tag{6.8}$$

as the *density matrix* or density operator of the mixed state M and one has from equation (*) above

$$\boxed{\langle A\rangle = \sum_n \langle n|\widehat{A}\widehat{W}|n\rangle = tr(\widehat{A}\widehat{W})} \tag{6.9}$$

Remarks:

1. The density operator is the sum of the projectors $\widehat{P}_i$ onto the states $|\psi_i\rangle$ in the mixed state M, weighted with the relative frequencies (probabilities) h, with which these states occur in M.
2. The above expression for $\langle A\rangle$ is independent of the chosen basis set $\{|n\rangle\}$ because of the basis independent of the trace tr.
3. If $\{|\psi_i\rangle\}$ is chosen to be an (orthonormal) energy eigenbasis of the system and $|\psi_i\rangle \equiv |i\rangle$ and the mixed state M is an equilibrium state, then the formalism reduces to the one used previously, with

   $$h_i = \frac{e^{-\frac{E_i}{k_B T}}}{Z_c}, \quad Z_c = \sum_i e^{-\frac{E_i}{k_B T}} \tag{6.10}$$

   in the canonical ensemble, and

   $$\begin{aligned} \langle A\rangle &= \sum_{n,i} \frac{e^{-\frac{E_i}{k_B T}}}{Z_c} \langle n|\widehat{A}|\psi_i\rangle \underbrace{\langle\psi_i|n\rangle}_{\delta_{in}} && (6.11)\\ &= \sum_i \frac{e^{-\frac{E_i}{k_B T}}}{Z_c} \langle i|\widehat{A}|i\rangle\ . && (6.12) \end{aligned}$$

6.1.2 The time dependence of the density matrix

The time dependence of $\widehat{W}$ is derived from the Schrödinger equation for the states $|\psi_i\rangle$:

$$\begin{aligned} i\hbar\frac{d}{dt}|\psi_i\rangle &= \widehat{H}|\psi_i\rangle && (6.13)\\ -i\hbar\frac{d}{dt}\langle\psi_i| &= \langle\psi_i|\widehat{H} && (6.14)\\ i\hbar\frac{d}{dt}|\psi_i\rangle\langle\psi_i| &= \widehat{H}|\psi_i\rangle\langle\psi_i| - |\psi_i\rangle\langle\psi_i|\widehat{H} && (6.15)\\ &= [\widehat{H}, \widehat{P}_i]\ . && (6.16) \end{aligned}$$

It follows

$$\begin{aligned} i\hbar\frac{d}{dt}\widehat{W}(t) &= i\hbar\frac{d}{dt}\sum_i h_i|\psi_i\rangle\langle\psi_i| && (6.17)\\ &= \sum_i h_i[\widehat{H},\widehat{P}_i] && (6.18)\\ &= [\widehat{H},\widehat{W}(t)] && (6.19)\end{aligned}$$

Note:
The values h_i are chosen as initial conditions at $t = 0$, i.e. they are time independent.

$$\boxed{i\hbar\frac{\partial}{\partial t}\widehat{W}(t) = [\widehat{H},\widehat{W}(t)]} \quad \text{von Neumann equation} \tag{6.20}$$

The von Neumann equation is analogous to the Heisenberg equation of motion of an operator in the Heisenberg picture, however with a relative ”-” sign.
Using the formal solution of the time dependent Schrödinger equation

$$|\psi_i(t)\rangle = e^{-\frac{i}{\hbar}\widehat{H}t}|\psi_i(0)\rangle \tag{6.21}$$

we obtain

$$\widehat{W}(t) = e^{-\frac{i}{\hbar}\widehat{H}t}\widehat{W}(0)e^{+\frac{i}{\hbar}\widehat{H}t}\ . \tag{6.22}$$

By preparing a system in a given (non-equilibrium) mixed state, $\widehat{W}(0)$ (i.e. h_i) is given, and

6.2 The reduced density matrix

In many situations one is only interested in the properties of a subsystem of the complete system S_{tot} or a physical quantity A depends only on the states of a subsystem.

Examples are

1. system S and reservoir R forming together the total system S_{tot}. A complete basis of S_{tot} can be chosen as the set of direct product states ("product of WF")

   $$|n_S\rangle \otimes |n_R\rangle = |n_S, n_R\rangle \equiv |n\rangle \tag{6.23}$$

   where $\{|n_S\rangle\}$ and $\{|n_R\rangle\}$ are complete basis sets of S and of R, respectively (without coupling between the two).

2. a single particle as a subsystem in a many-particle system S_{tot}.

The observable operators $\widehat{A}$ we are interested in act only on the states $|n_S\rangle$ of the system and not on the states of the reservoir $|n_R\rangle$. Therefore, it is useful in a thermodynamic average to perform the averaging over the reservoir states first:

$$\begin{aligned}
\langle n|\widehat{A}|m\rangle &= \langle n_S, n_R|\widehat{A}|m_S, m_R\rangle && (6.24)\\
&= \langle n_S|\widehat{A}|m_S\rangle \cdot \langle n_R|m_R\rangle && (6.25)\\
&= \langle n_S|\widehat{A}|n_S\rangle \delta_{n_R m_S} && (6.26)
\end{aligned}$$

$$\begin{aligned}
\langle A\rangle &= tr(\widehat{A}\widehat{W}) && (6.27)\\
&= \sum_n \langle n|\widehat{A}\widehat{W}|n\rangle && (6.28)\\
&= \sum_{nm} \langle n|\widehat{A}|m\rangle\langle m|\widehat{W}|n\rangle && (6.29)\\
&= \sum_{n_S,n_R,m_S,m_R} \langle n_S|\widehat{A}|m_S\rangle \delta_{n_R m_R} \langle m_S m_R|\widehat{W}|n_S n_R\rangle && (6.30)\\
&= \sum_{n_S m_S} \langle n_S|\widehat{A}|m_S\rangle \sum_{n_R} \langle m_S n_R|\widehat{W}|n_S n_R\rangle && (6.31)
\end{aligned}$$

$$\boxed{\langle A\rangle = \sum_{n_S} \langle n_S|\widehat{A}\widehat{W}_S|n_S\rangle = tr_S(\widehat{A}\widehat{W}_S)} \tag{6.32}$$

with

$$\boxed{\widehat{W}_S := \sum_{n_R} \langle n_R | \widehat{W} | n_R \rangle = tr_R(\widehat{W}_R)} \tag{6.33}$$

the reduced density matrix in the system S.

Note:
Let the system have a d_S dimensional Hilbert space, and the reservoir a d_R dimensional Hilbert space. Then the total Hilbert space is $d_S \cdot d_R = d$ dimensional.
$\widehat{W}$ corresponds to a $d_R \cdot d_S$ dimensional matrix.
$\widehat{W}_S$ corresponds to a d_S dimensional matrix and acts only in the Hilbert space of S, since the reservoir states have been "traced out".

6.3 Thermodynamic perturbation theory for the canonical ensemble

In general, the trace $Z_c = \text{tr } \widehat{W}_c = \text{tr } e^{-\frac{\widehat{H}}{k_B T}}$ cannot be evaluated in a straightforward way, because the eigenvalues of $\widehat{H}$ are not known. To develop a perturbation theory, we separate the total Hamiltonian $\widehat{H}$ as

$$\widehat{H} = \widehat{H}_0 + \widehat{V}, \tag{6.34}$$

where

- the eigenstate problem of $\widehat{H}_0$ is assumed to be solved exactly, and
- $\widehat{V}$ is a perturbation assumed to be small.

The expansion of $e^{-\frac{\widehat{H}}{k_B T}} = \widehat{W}_c$ in powers of g is still nontrivial, because $\left[\widehat{H}_0, \widehat{V}\right] \neq 0$ in general. A perturbation theory can be developed, however, by observing the formal analogy of the canonical density matrix $\widehat{W}_c(T)$ with the time evolution operator $U(t)$ of quantum mechanics:

$$Z_c W_c(T) = e^{-\frac{\widehat{H}}{k_B T}} \tag{6.35}$$

$$U(t) = e^{-\frac{i}{\hbar}\widehat{H}t} \tag{6.36}$$

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle \tag{6.37}$$

with the identification

$$\boxed{\frac{1}{k_B T} \quad \longrightarrow \quad i\frac{t}{\hbar}} \tag{6.38}$$

i.e. the inverse temperature plays the role of an *imaginary time !* (in appropriate units, $\hbar = 1, \;\; k_B = 1$).

Thus, we will first recall the quantum mechanical time dependent perturbation theory and then set $i\frac{t}{\hbar} = \frac{1}{k_B T}$ at the end.

Time-dependent perturbation theory

1. The *interaction picture* is chosen such that the arbitrary operator $\widehat{A}$ obeys the time evolution according to $\widehat{H}_0$, i.e. it is known:

$$\langle\psi(t)|\widehat{A}|\psi(t)\rangle = \langle\psi(0)|e^{\frac{i}{\hbar}\widehat{H}t}\widehat{A}\,\underbrace{e^{-\frac{i}{\hbar}\widehat{H}t}|\psi(0)\rangle}_{|\psi(t)\rangle} \tag{6.39}$$

$$= \langle\psi(0)|e^{\frac{i}{\hbar}\widehat{H}t}e^{-\frac{i}{\hbar}\widehat{H}_0 t}\,\underbrace{e^{+\frac{i}{\hbar}\widehat{H}_0 t}\widehat{A}e^{-\frac{i}{\hbar}\widehat{H}_0 t}}_{\widehat{A}_{\mathrm{I}}(t)} \tag{6.40}$$

$$\underbrace{e^{+\frac{i}{\hbar}\widehat{H}_0 t}e^{-\frac{i}{\hbar}\widehat{H}t}}_{|\psi_{\mathrm{I}}(t)\rangle}|\psi(0)\rangle$$

$$= \langle\psi_{\mathrm{I}}(t)|\widehat{A}_{\mathrm{I}}(t)|\psi_{\mathrm{I}}(t)\rangle \tag{6.41}$$

with

$$\begin{aligned}
\widehat{A}_{\mathrm{I}}(t) &= e^{\frac{i}{\hbar}\widehat{H}_0 t}\widehat{A}e^{-\frac{i}{\hbar}\widehat{H}_0 t} && (6.42)\\
|\psi_{\mathrm{I}}(t)\rangle &= e^{\frac{i}{\hbar}\widehat{H}_0 t}e^{-\frac{i}{\hbar}\widehat{H}t}|\psi(0)\rangle \equiv \widehat{S}(t)|\psi(0)\rangle && (6.43)
\end{aligned}$$

In the interaction picture, the operators and the states obey the equations of motion (assuming no explicit t-dependence of the Schrödinger operators $\widehat{A},\ \widehat{H},\ \widehat{H}_0$):

- $$\begin{aligned}
i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\widehat{A}_{\mathrm{I}}(t) &= \left[\widehat{A}_{\mathrm{I}}(t),\widehat{H}_0\right] && (6.44)\\
\text{and} & && (6.45)\\
i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi_{\mathrm{I}}(t)\rangle &= \Big(-e^{\frac{i}{\hbar}\widehat{H}_0 t}\cancel{\widehat{H}_0}\ e^{-\frac{i}{\hbar}\widehat{H}t} + e^{\frac{i}{\hbar}\widehat{H}_0 t}(\cancel{\widehat{H}_0}+\widehat{V}) && (6.46)\\
& \quad e^{-\frac{i}{\hbar}\widehat{H}t}\Big)|\psi(o)\rangle && \\
&= \underbrace{e^{\frac{i}{\hbar}\widehat{H}_0 t}\widehat{V}e^{-\frac{i}{\hbar}\widehat{H}_0 t}}_{\widehat{V}_{\mathrm{I}}(t)}\underbrace{e^{\frac{i}{\hbar}\widehat{H}_0 t}e^{-\frac{i}{\hbar}\widehat{H}t}|\psi(0)\rangle}_{|\psi_{\mathrm{I}}(t)\rangle} && (6.47)
\end{aligned}$$

- $$\begin{aligned}
i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi_{\mathrm{I}}(t)\rangle &= \widehat{V}_{\mathrm{I}}(t)|\psi_{\mathrm{I}}(t)\rangle && (6.48)\\
\text{or} & && (6.49)\\
i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\widehat{S}(t) &= \widehat{V}_{\mathrm{I}}(t)\widehat{S}(t), \qquad\qquad \widehat{S}(t=0)=1. && (6.50)
\end{aligned}$$

Knowing that $\widehat{S}(t)$, the total time evolution operator is given by

$$U(t) = e^{-\frac{i}{\hbar}\widehat{H}t} = e^{-\frac{i}{\hbar}\widehat{H}_0 t}\widehat{S}(t) \qquad (6.51)$$

2. *Formal integration* and *iterative solution* of $(*)$:

$$\begin{aligned}
\widehat{S}(t) &= 1-\frac{i}{\hbar}\int_0^t \mathrm{d}t'\widehat{V}_{\mathrm{I}}(t')\widehat{S}(t') && (6.52)\\
&= 1-\frac{i}{\hbar}\int_0^t \mathrm{d}t'\widehat{V}_{\mathrm{I}}(t') + \left(-\frac{i}{\hbar}\right)^2\int_0^t \mathrm{d}t'\int_0^{t'} \mathrm{d}t''\widehat{V}_{\mathrm{I}}(t')\widehat{V}_{\mathrm{I}}(t'') && (6.53)\\
&\quad +\ldots && \\
&= \widehat{T}e^{-\frac{i}{\hbar}\int_0^t \mathrm{d}t'\widehat{V}_{\mathrm{I}}(t')} && (6.54)
\end{aligned}$$

(power series of $\widehat{S}$ in terms of $\widehat{V}$)

with the t-ordering operator $\widehat{T}$.

3. Replacing $\frac{i}{\hbar}t$ by the "inverse temperature" $\beta = \frac{1}{k_B T}$, we obtain a power series for $W_c(T)$:

$$\begin{aligned}
\widehat{S}(\beta) &= \widehat{\widehat{T}} e^{-\int_0^\beta \mathrm{d}\beta' \widehat{V}_{\mathrm{I}}(\beta')} && (6.55)\\
&= 1 - \int_0^\beta \mathrm{d}\beta' \widehat{V}_{\mathrm{I}}(\beta') + (-1)^2 \int_0^\beta \mathrm{d}\beta' \int_0^{\beta'} \mathrm{d}\beta'' \widehat{V}_{\mathrm{I}}(\beta') \widehat{V}_{\mathrm{I}}(\beta'') && (6.56)\\
&\quad + \ldots
\end{aligned}$$

where

$$\widehat{V}_{\mathrm{I}}(\beta) = e^{\beta \widehat{H}_0} \widehat{V} e^{-\beta \widehat{H}_0}, \qquad \beta = \frac{1}{k_B T} \tag{6.57}$$

and

$$\boxed{\begin{aligned}
Z_c W_c(T) &= e^{-\beta \widehat{H}_0} \widehat{S}(\beta)\\
&= e^{-\beta \widehat{H}_0} - e^{-\beta \widehat{H}_0} \int\limits_0^\beta \mathrm{d}\beta' \widehat{V}_{\mathrm{I}}(\beta') + \ldots\\
&\qquad + (-1)^n \int\limits_0^\beta \mathrm{d}\beta^{(1)} \int\limits_0^{\beta^{(1)}} \mathrm{d}\beta^{(2)} \cdots \int\limits_0^{\beta(n)} \mathrm{d}\beta^{(n)} \widehat{V}_{\mathrm{I}}(\beta^{(1)}) \cdots \widehat{V}_{\mathrm{I}}(\beta^{(n)})\\
&\qquad + \ldots
\end{aligned}}$$

We obtain explicitly in first order in the perturbation:

- *Partition sum*:

$$\begin{aligned}
Z_c^{(0)} &= \mathrm{tr}\ e^{-\beta \widehat{H}_0} && (6.58)\\
Z_c &= Z_c^{(0)} - \mathrm{tr} \left\{ e^{-\beta \widehat{H}_0} \int\limits_0^\beta \mathrm{d}\beta' \widehat{V}_{\mathrm{I}}(\beta') \right\} && (6.59)\\
&= Z_c^{(0)} - \mathrm{tr} \int\limits_0^\beta \mathrm{d}\beta' \left\{ e^{-\beta \widehat{H}_0} e^{\beta' \widehat{H}_0} \widehat{V} e^{-\beta' \widehat{H}_0} \right\} && (6.60)\\
&\overset{\substack{\text{cyclic}\\ \text{invariance of tr}}}{\downarrow} && (6.61)\\
&= Z_c^{(0)} - \mathrm{tr} \int\limits_0^\beta \mathrm{d}\beta' e^{-\beta \widehat{H}_0} \widehat{V} + \mathcal{O}(\widehat{V}^2) && (6.62)
\end{aligned}$$

$$\boxed{\begin{aligned} Z_c &= Z_c^{(0)} - \tfrac{1}{k_BT}\ \mathrm{tr}\left\{ e^{-\frac{\widehat{H}_0}{k_BT}} \widehat{V} \right\} \\ &= Z_c^{(0)} \left(1 - \tfrac{\langle \widehat{V} \rangle_0}{k_BT} + \mathcal{O}\left(\widehat{V}^2 \right) \right) \\ &= Z_c^{(0)} \left(1 + \tfrac{Z_c^{(1)}}{Z_c^{(0)}} + \mathcal{O}\left(\widehat{V}^2 \right) \right) \end{aligned}} \tag{6.63}$$

with $\langle \widehat{V} \rangle_0 = \frac{\mathrm{tr}\left\{ e^{-\frac{\widehat{H}_0}{k_BT}} \widehat{V} \right\}}{Z_c^{(0)}} = \ \mathrm{tr}\left\{ \widehat{W}_c^{(0)} \widehat{V} \right\}$ the canonical thermal average of $\widehat{V}$ with respect to $\widehat{H}_0$.

$$Z_c = Z_c^{(0)} \left(1 + \frac{Z_c^{(1)}}{Z_c^{(0)}} \right) \tag{6.64}$$

$$Z_c^{(1)} = -Z_c^{(0)} \frac{\langle \widehat{V} \rangle_0}{k_BT} + \mathcal{O}\left(\widehat{V}^2 \right) \tag{6.65}$$

- *Density operator*

$$\widehat{W}_c = \frac{1}{Z_c} e^{-\beta \widehat{H}_0} \left(1 - \int_0^\beta \mathrm{d}\beta' \, \widehat{V}_\mathrm{I}(\beta') \right) + \mathcal{O}\left(\widehat{V}^2 \right) \tag{6.66}$$

$$= e^{-\beta \widehat{H}_0} \left(\frac{1}{Z_c^{(0)}} - \frac{Z_c^{(1)}}{{Z_c^{(0)}}^2} - \frac{1}{Z_c^{(0)}} \int_0^\beta \mathrm{d}\beta' \, \widehat{V}_\mathrm{I}(\beta') \right) \tag{6.67}$$

$$\boxed{\widehat{W}_c = \underbrace{\frac{1}{Z_c^{(0)}} e^{-\beta \widehat{H}_0}}_{\widehat{W}_c^{(0)}} \left(1 - \int_0^\beta \mathrm{d}\beta' \left[\widehat{V}_\mathrm{I}(\beta) - \langle \widehat{V} \rangle_0 \right] + \mathcal{O}\left(\widehat{V}^2 \right) \right)} \tag{6.68}$$

- *Free energy*:

$$F = -k_BT \ln Z_c = -k_BT \ln Z_c^{(0)} - k_BT \cdot \frac{Z_c^{(1)}}{Z_c^{(0)}} \tag{6.69}$$

$$\boxed{F = -k_BT \ln Z_c^{(0)} + \langle \widehat{V} \rangle_0} \tag{6.70}$$

Expressions of higher order in $\widehat{V}$ can be obtained successively.

From F all other thermodynamic quantities can be obtained.

Remark:
Based on the analogy $\frac{i}{\hbar}t \quad \leftrightarrow \quad \frac{1}{k_B T}$ and using the time dependent perturbation theory for Green's functions (QMII), a field theory for finite T can be developed.

6.4 The classical limit: equipartition theorem and virial theorem

For the classical limit it is crucial that the kinetic energy and the potential energy effectively commute in the high-temperature limit.

The thermal average of the commutator is in a momentum eigenbasis:

$$\bar{C} = \frac{1}{Z_c} \sum_{\vec{p}} \left\langle \vec{p} \middle| e^{-\frac{\widehat{H}}{k_B T}} \left[\frac{\widehat{\vec{p}}^2}{2m}, V(\vec{x}) \right] \middle| \vec{p} \right\rangle \tag{6.71}$$

with

$$\begin{aligned} \left[\frac{\widehat{\vec{p}}^2}{2m}, V(\vec{x}) \right] &= \frac{\hbar}{2mi} \left(\widehat{\vec{p}} \cdot \vec{\nabla} V(\vec{x}) + \widehat{\vec{p}} V(\vec{x}) \cdot \vec{\nabla} - V(\vec{x}) \widehat{\vec{p}} \cdot \vec{\nabla} \right) && (6.72) \\ &= \frac{\hbar}{2mi} \left(\widehat{\vec{p}} \cdot \vec{\nabla} V + \vec{\nabla} V(\vec{x}) \cdot \widehat{\vec{p}} \right) && (6.73) \end{aligned}$$

Using a typical thermal momentum

$$\begin{aligned}
\langle p\rangle_T \approx p_T &= \frac{2\pi\hbar}{\lambda_T} = \sqrt{2mk_BT} && (6.74)\\
\bar{C} &\approx \left\langle \vec{p}_T \middle| \left[\frac{\widehat{\vec{p}}^{\,2}}{2m}, V(\vec{x})\right] \middle| \vec{p}_T \right\rangle && (6.75)\\
&= \frac{\hbar}{2mi} 2p_T \left\langle \vec{p}_T \middle| \vec{\nabla} V \middle| \vec{p}_T \right\rangle && (6.76)
\end{aligned}$$

with $\vec{\nabla} V \approx \frac{V(\vec{x})}{a_0}$ and a_0: typical length scale on which V varies:

$$\begin{aligned}
\bar{C} &\approx \frac{\hbar}{2mi} 2\frac{p_T}{a_0}\langle V\rangle_T && (6.77)\\
&\overset{p_T^2\approx\langle p^2\rangle}{\approx} -i\left\langle\frac{p_T^2}{2m}\right\rangle \langle V\rangle \cdot \frac{1}{2\pi}\left(\frac{\lambda_T}{a_0}\right) && (6.78)
\end{aligned}$$

This estimate can be extended to many-particle systems and to interacting particles. Then

$$a_0 = \min\{\text{range of interaction potential, average particle spacing}\} \quad (6.79)$$

Conclusion:
In the $T \to \infty$ limit, $\frac{\lambda_T}{a_0} \ll 1$, the commutator $\left[\widehat{H}_{\text{kin}}, \widehat{V}\right]$ approaches ∞ more slowly than the product of the thermal averages and can, therefore, be neglected in $\left\langle e^{-\frac{H_{\text{kin}}-V}{k_BT}}\right\rangle$. Note that the criterion $\frac{\lambda_T}{a_0} \ll 1$ for this classical limit coincides with the heuristic argument given in the section about Bose systems.

In the $T \to \infty$ limit, the canonical partition sum for a single particle reads:

$$Z_c = \ \operatorname{tr}\left\{e^{-\frac{\widehat{\vec{p}}^{\,2}}{2mk_BT}} e^{-\frac{V(\vec{x})}{k_BT}}\right\}. \quad (6.80)$$

It can be evaluated using complete basis sets of momentum and position eigenstates:

$$\widehat{\vec{p}}|\vec{p}\rangle = \vec{p}|\vec{p}\rangle \qquad \langle\vec{p}|\vec{p}^{\,\prime}\rangle = \delta^3(\vec{p}-\vec{p}^{\,\prime}) \tag{6.81}$$

$$\widehat{\vec{x}}|\vec{x}\rangle = \vec{x}|\vec{x}\rangle \qquad \langle\vec{x}|\vec{x}^{\,\prime}\rangle = \delta^3(\vec{x}-\vec{x}^{\,\prime}) \tag{6.82}$$

$$\int \mathrm{d}^3x|\vec{x}\rangle\langle\vec{x}| = 1 \tag{6.83}$$

$$\int \frac{\mathrm{d}^3p}{(2\pi\hbar)^3}|\vec{p}\rangle\langle\vec{p}| = 1 \tag{6.84}$$

$$\tag{6.85}$$

$$Z_c = \int \frac{\mathrm{d}^3p}{(2\pi\hbar)^3}\left\langle \vec{p}\left| e^{-\frac{\widehat{\vec{p}}^2}{2mk_BT}} e^{-\frac{V(\vec{x})}{k_BT}}\right|\vec{p}\right\rangle \tag{6.86}$$

$$= \int \frac{\mathrm{d}^3p}{(2\pi\hbar)^3}\int \mathrm{d}^3x \left\langle \vec{p}\left| e^{-\frac{\widehat{\vec{p}}^2}{2mk_BT}}\right|\vec{x}\right\rangle \left\langle \vec{x}\left| e^{-\frac{V(\vec{x})}{k_BT}}\right|\vec{p}\right\rangle \tag{6.87}$$

$$= \int \frac{\mathrm{d}^3p}{(2\pi\hbar)^3}\int \mathrm{d}^3x e^{-\frac{\widehat{\vec{p}}^2/2m+V(\vec{x})}{k_BT}} \underbrace{\langle\vec{p}|\vec{x}\rangle\langle\vec{x}|\vec{p}\rangle}_{\substack{|\psi_p(x)|^2=\frac{1}{v}\\ \text{(density)}}} \tag{6.88}$$

$$\boxed{\begin{aligned} Z_c &= \int \frac{\mathrm{d}^3p}{(2\pi\hbar)^3}\int \frac{\mathrm{d}^3x}{v} e^{-\frac{H(\vec{p},\vec{x})}{k_BT}} \\ H(\vec{p},\vec{x}) &= \frac{\vec{p}^2}{2m} + V(\vec{x}) \qquad \text{classical Hamiltonian function} \end{aligned}} \tag{6.89}$$

In the classical limit, the canonical partition function Z_c is the classical Boltzmann factor integrated over the complete phase space of $(\vec{x}, \vec{p})$.

Liouville theorem:

The "volume of a classical system in phase space" Γ, is conserved in time:

$$\begin{aligned}
\Gamma &= \int \frac{\mathrm{d}^3 p}{2\pi\hbar} \int \mathrm{d}^3 x \rho(\vec{x},\vec{p}) && (6.90)\\
\frac{\mathrm{d}\Gamma}{\mathrm{d}t} &= 0 && (6.91)\\
\rho(\vec{x},\vec{p}) &= \sum_i \delta^3(\vec{x}-\vec{x}_i)\delta^3(\vec{p}-\vec{p}_i) && (6.92)
\end{aligned}$$

Can be proved using the classical Hamiltonian equations of motion.

6.4.1 Equipartition and virial theorems

In the canonical ensemble for one particle in 1 dimension one has *in the classical limit*:

$$\begin{aligned}
\left\langle p \frac{\partial H(\vec{p},\vec{x})}{\partial p} \right\rangle &= \frac{1}{Z_c} \int \frac{\mathrm{d}p\mathrm{d}x}{2\pi\hbar \cdot v} p \frac{\partial H}{\partial p} e^{-\frac{H}{k_B T}} && (6.93)\\
&= \frac{1}{Z_c} \int \frac{\mathrm{d}p\mathrm{d}x}{2\pi\hbar \cdot v} (-k_B T) p \frac{\partial}{\partial p} e^{-\frac{H}{k_B T}} && (6.94)\\
&\overset{\text{p.i.}}{=} k_B T \frac{1}{Z_c} \int \frac{\mathrm{d}p\mathrm{d}x}{2\pi\hbar \cdot v} e^{-\frac{H}{k_B T}} && (6.95)\\
&= k_B T && (6.96)
\end{aligned}$$

For the quadratic momentum dependence of the classical H function, $H = \frac{p^2}{2m} + V(x)$, this implies

$$\boxed{\langle H_{\text{kin}} \rangle = \left\langle \frac{\vec{p}^2}{2m} \right\rangle = \frac{1}{2} \left\langle p \frac{\partial H}{\partial p} \right\rangle = \frac{1}{2} k_B T.} \qquad (6.97)$$

Similarly, one can show the *Virial theorem*:

$$\boxed{\begin{aligned}
\left\langle x \frac{\partial H}{\partial x} \right\rangle &= k_B T\\
\left\langle x \frac{\partial V}{\partial x} \right\rangle &= k_B T
\end{aligned}} \qquad (6.98)$$

For a harmonic potential $V_h(x) \sim x^2$, it follows:

$$\boxed{\langle V_h(x)\rangle = \frac{1}{2}\left\langle x\frac{\partial V}{\partial x}\right\rangle = \frac{1}{2}k_B T} \tag{6.99}$$

Generalizing this to many-particle systems, this proves the

Equipartition theorem (classical thermodynamics):

Each degree of freedom (momentum, position, or other) which appears quadratically in the Hamilton function, gives a contribution $\frac{1}{2}k_B T$ to the internal energy.

This result has already been obtained for several explicit systems in the high-T-limit of the specific heat (e.g. Fermi gas, classical gas).