## Unit 3: Quantum Ensembles

In this unit we continue our discussion of statistical mechanics, but now applied to systems that obey quantum mechanics. We will discuss formally what we mean by a quantum ensemble, and the quantum density matrix. We will discuss how the symmetry of the wavefunction leads to two different types of particles, bosons and fermions. Most of our discussions will be based on systems of non-interacting particles (because that is the only case that is easy to solve analytically!). Yet we will see that, even for non-interacting particles, quantum statistics leads to non-classical correlations between particles. We will see that, for non-interacting particles, it is the grand canonical ensemble that is easiest to work with. We will discuss the leading quantum corrections to the classical limit, and then discuss situations where quantum effects are dominant. We will return to the problem of the specific heat of solids and see why the Law of Dulong and Petit fails. We will discuss blackbody radiation, the Sommerfeld model for conduction electrons in a metal, Pauli paramagnetism, and Bose-Einstein condensation.

## Unit 3-1: Quantum Ensembles and the Density Matrix

The classical ensemble is given by a probability density in phase space $\rho\left(q_{i}, p_{i}\right)$, such that the thermodynamic average of an observable $X$ is given by,

$$
\begin{equation*}
\langle X\rangle=\prod_{i} \int d q_{i} \int d p_{i} \rho\left(q_{i}, p_{i}\right) X\left(q_{i}, p_{i}\right) \tag{3.1.1}
\end{equation*}
$$

The ensemble interpretation of thermodynamics imagines that we make many (ideally infinitely many) copies of our system, each prepared identically as far as macroscopic parameters are concerned. The density $\rho\left(q_{i}, p_{i}\right)$ is then the probability density that a given copy will be found at coordinates $\left\{q_{i}, p_{i}\right\}$ in phase space. The average $\langle X\rangle$ above is the average over all copies of the system. The ergodic hypothesis states that this ensemble average over many copies will give the same result as averaging $X$ over the time trajectory of the system in just one copy.

In quantum mechanics, states are described by wavefunctions $|\psi\rangle$ rather than points $\left\{q_{i}, p_{i}\right\}$ in phase space. To describe a quantum ensemble, imagine making many copies of the system. Let $\left|\psi^{k}\right\rangle$ be the state of the system in copy $k$.

The ensemble average of an observable operator $\hat{X}$ would then be,

$$
\begin{equation*}
\langle\hat{X}\rangle=\frac{1}{M} \sum_{k=1}^{M}\left\langle\psi^{k}\right| \hat{X}\left|\psi^{k}\right\rangle \tag{3.1.2}
\end{equation*}
$$

where in the above we took $M$ copies of the system to make our ensemble. In general we want $M \rightarrow \infty$.
In quantum mechanics it is convenient to express wavefunctions as a linear superposition of some complete set of orthonormal basis wavefunctions $\left|\varphi_{n}\right\rangle$, such that $\left\langle\varphi_{n} \mid \varphi_{m}\right\rangle=\delta_{m n}$. Define,

$$
\begin{equation*}
\left|\psi^{k}\right\rangle=\sum_{n} a_{n}^{k}\left|\varphi_{n}\right\rangle \quad \text { so that } \quad\left\langle\varphi_{m} \mid \psi^{k}\right\rangle=a_{m}^{k} \tag{3.1.3}
\end{equation*}
$$

Here $a_{n}^{k}$ is the probability amplitude for $\left|\psi^{k}\right\rangle$ to be in the state $\left|\varphi_{n}\right\rangle$. The probability for $\left|\psi^{k}\right\rangle$ to be found in state $\left|\varphi_{n}\right\rangle$ is thus $\left|\left\langle\phi_{n} \mid \psi^{k}\right\rangle\right|^{2}=\left|a_{n}^{k}\right|^{2}$.

Normalization of wavefunctions then gives,

$$
\begin{equation*}
1=\left\langle\psi^{k} \mid \psi^{k}\right\rangle=\sum_{n}\left\langle\psi^{k} \mid \varphi_{n}\right\rangle\left\langle\varphi_{n} \mid \psi^{k}\right\rangle=\sum_{n} a_{n}^{k^{*}} a_{n}^{k}=\sum_{n}\left|a_{n}^{k}\right|^{2}=1 \tag{3.1.4}
\end{equation*}
$$

where $a_{n}^{k^{*}}$ is the complex conjugate of $a_{n}^{k}$.

Now we can express $\langle\hat{X}\rangle$ in terms of the basis states $\left|\varphi_{n}\right\rangle$,

$$
\begin{align*}
\langle\hat{X}\rangle & =\frac{1}{M} \sum_{k=1}^{M}\left\langle\psi^{k}\right| \hat{X}\left|\psi^{k}\right\rangle=\frac{1}{M} \sum_{k=1}^{M} \sum_{n, m}\left\langle\psi^{k} \mid \varphi_{m}\right\rangle\left\langle\varphi_{m}\right| \hat{X}\left|\varphi_{n}\right\rangle\left\langle\varphi_{n} \mid \psi^{k}\right\rangle \\
& =\frac{1}{M} \sum_{k=1}^{M} \sum_{n, m} a_{n}^{k} a_{m}^{k^{*}}\left\langle\varphi_{m}\right| \hat{X}\left|\varphi_{n}\right\rangle=\frac{1}{M} \sum_{k} \sum_{n, m} a_{n}^{k} a_{m}^{k^{*}} X_{m n} \tag{3.1.5}
\end{align*}
$$

where $X_{m n} \equiv\left\langle\varphi_{m}\right| \hat{X}\left|\varphi_{n}\right\rangle$ are the matrix elements of $\hat{X}$ in the basis $\left|\varphi_{n}\right\rangle$.
We now define the density matrix that describes the quantum ensemble,

$$
\begin{equation*}
\rho_{n m} \equiv \frac{1}{M} \sum_{k=1}^{M} a_{n}^{k} a_{m}^{k^{*}} \tag{3.1.6}
\end{equation*}
$$

$\rho_{n m}$ are the matrix elements of the density operator $\hat{\rho}$ in the basis $\left|\varphi_{n}\right\rangle$,

$$
\begin{equation*}
\hat{\rho}=\sum_{n, m}\left|\varphi_{n}\right\rangle \rho_{n m}\left\langle\varphi_{m}\right| \quad \Rightarrow \quad \rho_{n m}=\left\langle\varphi_{n}\right| \hat{\rho}\left|\varphi_{m}\right\rangle \tag{3.1.7}
\end{equation*}
$$

We can then write for the ensemble average of $\hat{X}$,

$$
\begin{equation*}
\langle\hat{X}\rangle=\sum_{n, m} \rho_{n m} X_{m n}=\sum_{n, m}\left\langle\varphi_{n}\right| \hat{\rho}\left|\varphi_{m}\right\rangle\left\langle\varphi_{m}\right| \hat{X}\left|\varphi_{n}\right\rangle=\sum_{n}\left\langle\varphi_{n}\right| \hat{\rho} \hat{X}\left|\varphi_{n}\right\rangle=\operatorname{Tr}[\hat{\rho} \hat{X}] \tag{3.1.8}
\end{equation*}
$$

where $\operatorname{Tr}[\hat{O}]$ is the trace of the operator $\hat{O}$.
Note, $\rho_{n n}=(1 / M) \sum_{k}\left|a_{n}^{k}\right|^{2}$ is the probability that a state, selected at random from the ensemble, will be found to be in basis state $\left|\varphi_{n}\right\rangle$.

The density operator $\hat{\rho}$ obeys the property,

$$
\begin{equation*}
\operatorname{Tr}[\hat{\rho}]=\sum_{n} \rho_{n n}=\frac{1}{M} \sum_{k=1}^{M} \sum_{n} a_{n}^{k} a_{n}^{k^{*}}=\frac{1}{M} \sum_{k=1}^{M} \sum_{n}\left|a_{n}^{k}\right|^{2}=\frac{1}{M} \sum_{k=1}^{M} 1=1 \tag{3.1.9}
\end{equation*}
$$

where we used the normalization condition of Eq. (3.1.4). We also have

$$
\begin{equation*}
\rho_{n m}=\frac{1}{M} \sum_{k=1}^{M} a_{n}^{k} a_{m}^{k^{*}} \Rightarrow \rho_{m n}^{*}=\frac{1}{M} \sum_{k=1}^{M} a_{m}^{k^{*}} a_{n}^{k}=\rho_{n m} \tag{3.1.10}
\end{equation*}
$$

So $\rho_{n m}=\rho_{m n}^{*}$ and hence $\hat{\rho}$ is a Hermitian operator. This means that $\rho_{n m}$ can be diagonalized and its eigenvalues are real.

Now for a quantum mechanical ensemble described by a Hermitian density matrix $\hat{\rho}$, such that $\operatorname{Tr}[\hat{\rho}]=1$ and ensemble averages are given by $\operatorname{Tr}[\hat{\rho} \hat{X}]$, what additional conditions must $\hat{\rho}$ satisfy if it is to describe an ensemble in thermal equilibrium?

As for any quantum mechanical operator in the Heisenberg picture, the equation of motion for $\hat{\rho}$ is given by,

$$
\begin{equation*}
i \hbar \frac{\partial \hat{\rho}}{\partial t}=[\hat{\mathcal{H}}, \hat{\rho}] \tag{3.1.11}
\end{equation*}
$$

where $\hat{\mathcal{H}}$ is the Hamiltonian operator and $[\hat{A}, \hat{B}]=\hat{A} \hat{B}-\hat{B} \hat{A}$ is the commuator. This is the quantum mechanical analog of Liouville's equation!

So if $\hat{\rho}$ is to describe a time independent equilibrium ensemble, it is necessary that $\partial \hat{\rho} / \partial t=0$, and so $\hat{\rho}$ must commute with $\hat{\mathcal{H}}$, i.e. $[\hat{\mathcal{H}}, \hat{\rho}]=0$.

Since $\hat{\rho}$ commutes with $\hat{\mathcal{H}}$, we must be able to diagonalize $\hat{\rho}$ in the basis formed by the energy eigenstates. Let $|\alpha\rangle$ be the energy eigenstates. Then because $[\hat{\mathcal{H}}, \hat{\rho}]=0$ we have,

$$
\left.\begin{array}{rl}
\langle\alpha| \hat{\mathcal{H}} \hat{\rho}|\beta\rangle & =E_{\alpha}\langle\alpha| \hat{\rho}|\beta\rangle  \tag{3.1.12}\\
= & \langle\alpha| \hat{\rho} \hat{\mathcal{H}}|\beta\rangle=E_{\beta}\langle\alpha| \hat{\rho}|\beta\rangle
\end{array}\right\} \Rightarrow E_{\alpha}\langle\alpha| \hat{\rho}|\beta\rangle=E_{\beta}\langle\alpha| \hat{\rho}|\beta\rangle \Rightarrow\langle\alpha| \hat{\rho}|\beta\rangle=0 \text { unless } E_{\alpha}=E_{\beta}
$$

So $\rho_{\alpha \beta}=0$ unless $|\alpha\rangle=|\beta\rangle$, or $|\alpha\rangle$ and $|\beta\rangle$ are degenerate energy eigenstates with the same $E_{\alpha}=E_{\beta}$. Thus $\hat{\rho}$ only couples eigenstates of equal energy. But since $\rho$ is Hermitian it can always be diagonalized on any subspace of degenerate energy eigenstates; that is, if $\left\{\left|\alpha_{i}\right\rangle\right\}$ is the set of all degenerate eigenstates with energy $E_{\alpha}$, it is possible to make linear combinations of the $\left\{\left|\alpha_{i}\right\rangle\right\} \rightarrow\left\{\left|\alpha_{i}^{\prime}\right\rangle\right\}$ such that the $\left\{\left|\alpha_{i}^{\prime}\right\rangle\right\}$ span the degenerate subspace and $\hat{\rho}$ is diagonal on the $\left\{\left|\alpha_{i}^{\prime}\right\rangle\right.$.

Thus we can always find a a set of $\left\{\left|\alpha_{i}\right\rangle\right\}$ on which both $\hat{\mathcal{H}}$ and $\hat{\rho}$ are simultaneously diagonal,

$$
\begin{equation*}
\hat{\mathcal{H}}|\alpha\rangle=E_{\alpha}|\alpha\rangle, \quad \hat{\rho}|\alpha\rangle=\rho_{\alpha}|\alpha\rangle \tag{3.1.13}
\end{equation*}
$$

or

$$
\begin{equation*}
\langle\alpha| \hat{\mathcal{H}}|\beta\rangle=E_{\alpha} \delta_{\alpha \beta}, \quad\langle\alpha| \hat{\rho}|\beta\rangle=\rho_{\alpha} \delta_{\alpha \beta} \tag{3.1.14}
\end{equation*}
$$

and so,

$$
\begin{equation*}
\hat{\mathcal{H}}=\sum_{\alpha}|\alpha\rangle E_{\alpha}\langle\alpha|, \quad \hat{\rho}=\sum_{\alpha}|\alpha\rangle \rho_{\alpha}\langle\alpha| \tag{3.1.15}
\end{equation*}
$$

In terms of the basis states $|\alpha\rangle$, we can write,

$$
\begin{equation*}
\langle\hat{X}\rangle=\operatorname{Tr}[\hat{\rho} \hat{X}]=\sum_{\alpha}\langle\alpha| \hat{\rho} \hat{X}|\alpha\rangle=\sum_{\alpha} \rho_{\alpha}\langle\alpha| \hat{X}|\alpha\rangle=\sum_{\alpha} \rho_{\alpha} X_{\alpha \alpha} \tag{3.1.16}
\end{equation*}
$$

Note, even though an equilibrium $\hat{\rho}$ is diagonal in the basis of energy eigenstates, we still can always express it in terms of any other complete set of basis states $\left|\varphi_{n}\right\rangle$,

$$
\begin{equation*}
\rho_{n m}=\left\langle\varphi_{n}\right| \hat{\rho}\left|\varphi_{m}\right\rangle=\sum_{\alpha, \beta}\left\langle\varphi_{n} \mid \alpha\right\rangle\langle\alpha| \hat{\rho}|\beta\rangle\left\langle\beta \mid \varphi_{m}\right\rangle=\sum_{\alpha}\left\langle\varphi_{n} \mid \alpha\right\rangle \rho_{\alpha}\left\langle\alpha \mid \varphi_{m}\right\rangle \tag{3.1.17}
\end{equation*}
$$

In this basis, $\hat{\rho}$ need not be diagonal.
This is often useful because we might not know the exact eigenstates for $\hat{\mathcal{H}}$. If $\hat{\mathcal{H}}=\hat{\mathcal{H}}^{(0)}+\hat{\mathcal{H}}^{(1)}$, we might know the eigenstates of the simpler $\hat{\mathcal{H}}^{(0)}$, but not the full $\hat{\mathcal{H}}$. In this case it might be convenient to express $\hat{\rho}$ in terms of the eigenstates of $\hat{\mathcal{H}}^{(0)}$ and treat $\hat{\mathcal{H}}^{(1)}$ as a perturbation.

We can now state what we mean by the microcanonical, the canonical, and the grand canonical ensembles for quantum mechanical systems. With $|\alpha\rangle$ the set of energy eigenstates as above,
microcanonical ensemble:

$$
\hat{\rho}=\sum_{\alpha}|\alpha\rangle \rho_{\alpha}\langle\alpha| \quad \text { with } \quad \rho_{\alpha}=\left\{\begin{array}{ll}
\text { constant } & \text { for } E-\frac{\Delta E}{2} \leq E_{\alpha} \leq E+\frac{\Delta E}{2}  \tag{3.1.18}\\
0 & \text { otherwise }
\end{array} \quad \text { and } \quad \sum_{\alpha} \rho_{\alpha}=1\right.
$$

For non-zero $\rho_{\alpha}$, we have,

$$
\begin{align*}
& \rho_{\alpha}=\frac{1}{\Omega(E)} \text { where } \Omega(E)=\sum_{\alpha \text { such that }} 1 \quad \text { is the microcanonical partition function }  \tag{3.1.19}\\
& E-\frac{\Delta E}{2} \leq E_{\alpha} \leq E+\frac{\Delta E}{2}
\end{align*}
$$

canonical ensemble:

$$
\begin{equation*}
\hat{\rho}=\sum_{\alpha}|\alpha\rangle \rho_{\alpha}\langle\alpha| \quad \text { with } \quad \rho_{\alpha}=\frac{\mathrm{e}^{-\beta E_{\alpha}}}{Q_{N}} \quad \text { where } \quad Q_{N}=\sum_{\alpha} \mathrm{e}^{-\beta E_{\alpha}} \quad\left(\beta=1 / k_{B} T\right) \tag{3.1.20}
\end{equation*}
$$

$Q_{N}$ is the quantum canonical partition function.
It is often useful to have a representation for $\hat{\rho}$ and $\langle\hat{X}\rangle=\operatorname{Tr}[\hat{X} \hat{\rho}]$ in an operator form that is independent of its representation in any particular basis. We can therefore also write,

$$
\begin{equation*}
Q_{N}=\sum_{\alpha} \mathrm{e}^{-\beta E_{\alpha}}=\sum_{\alpha}\langle\alpha| \mathrm{e}^{-\beta \hat{\mathcal{H}}}|\alpha\rangle=\operatorname{Tr}\left[\mathrm{e}^{-\beta \hat{\mathcal{H}}}\right] \tag{3.1.21}
\end{equation*}
$$

and

$$
\begin{equation*}
\hat{\rho}=\frac{\mathrm{e}^{-\beta \hat{\mathcal{H}}}}{Q_{N}} \quad \text { with } \quad\langle\hat{X}\rangle=\operatorname{Tr}[\hat{X} \hat{\rho}]=\frac{\operatorname{Tr}\left[\hat{X} \mathrm{e}^{-\beta \hat{\mathcal{H}}}\right]}{\operatorname{Tr}\left[\mathrm{e}^{-\beta \hat{\mathcal{H}}}\right]} \tag{3.1.22}
\end{equation*}
$$

The average energy can be obtained from the quantum canonical partition function $Q_{N}$ just like we found classically,

$$
\begin{align*}
-\frac{\partial}{\partial \beta}\left[\ln Q_{N}\right] & =-\frac{1}{Q_{N}} \frac{\partial Q_{N}}{\partial \beta}=-\frac{1}{Q_{N}} \frac{\partial}{\partial \beta}\left[\sum_{\alpha} \mathrm{e}^{-\beta E_{\alpha}}\right]=-\frac{1}{Q_{N}} \sum_{\alpha} \mathrm{e}^{-\beta E_{\alpha}}\left(-E_{\alpha}\right)  \tag{3.1.23}\\
& =\sum_{\alpha} \rho_{\alpha} E_{\alpha}=\sum_{\alpha}\langle\alpha| \hat{\rho} \hat{\mathcal{H}}|\alpha\rangle=\operatorname{Tr}[\hat{\rho} \hat{\mathcal{H}}]=\langle E\rangle \tag{3.1.24}
\end{align*}
$$

Thus, like we found classically, the above gives the identification that, also quantum mechanically, $A=-k_{B} T \ln Q_{N}$. grand canonical ensemble:

With our state space being one that includes wavefunctions with any number of particles $N$, the operator $\hat{\rho}$ should commute with both $\hat{\mathcal{H}}$ (so it describes equilibrium) and with $\hat{N}$ (so it does not mix states with different $N$ - an exception to this condition occurs in the BCS theory of superconductivity!). With $|\alpha\rangle$ the set of eigenstates of both $\hat{\mathcal{H}}$ and $\hat{N}$, with energy $E_{\alpha}$ and number of particles $N_{\alpha}$, we have,

$$
\begin{equation*}
\hat{\rho}=\sum_{\alpha}|\alpha\rangle \rho_{\alpha}\langle\alpha| \quad \text { with } \quad \rho_{\alpha}=\frac{\mathrm{e}^{-\beta\left(E_{\alpha}-\mu N_{\alpha}\right)}}{\mathcal{L}}=\frac{\mathrm{e}^{-\beta E_{\alpha}} z^{N_{\alpha}}}{\mathcal{L}} \quad \text { where } z=\mathrm{e}^{\beta \mu} \text { and } \mathcal{L}=\sum_{\alpha} \mathrm{e}^{-\beta\left(E_{\alpha}-\mu N_{\alpha}\right)} \tag{3.1.25}
\end{equation*}
$$

$\mathcal{L}$ is the quantum grand canonical partition function.
More generally, we can write,

$$
\begin{equation*}
\mathcal{L}=\sum_{\alpha} \mathrm{e}^{-\beta\left(E_{\alpha}-\mu N_{\alpha}\right)}=\sum_{\alpha}\langle\alpha| \mathrm{e}^{-\beta(\hat{\mathcal{H}}-\mu \hat{N})}|\alpha\rangle=\operatorname{Tr}\left[\mathrm{e}^{-\beta(\hat{\mathcal{H}}-\mu \hat{N})}\right] \tag{3.1.26}
\end{equation*}
$$

and then,

$$
\begin{equation*}
\hat{\rho}=\frac{\mathrm{e}^{-\beta(\hat{\mathcal{H}}-\mu \hat{N})}}{\mathcal{L}} \quad \text { with } \quad\langle\hat{X}\rangle=\operatorname{Tr}[\hat{X} \hat{\rho}]=\frac{\operatorname{Tr}\left[\hat{X} \mathrm{e}^{-\beta \hat{\mathcal{H}}} \mathrm{e}^{\beta \mu \hat{N}}\right]}{\operatorname{Tr}\left[\mathrm{e}^{-\beta \hat{\mathcal{H}}} \mathrm{e}^{\beta \mu \hat{N}}\right]}=\frac{\sum_{N=0}^{\infty} z^{N} Q_{N}\langle\hat{X}\rangle_{N}}{\sum_{N=0}^{\infty} z^{N} Q_{N}} \quad\left(z=\mathrm{e}^{\beta \mu}\right) \tag{3.1.27}
\end{equation*}
$$

where $\langle X\rangle_{N}$ is the average value of $\hat{X}$ in the canonical ensemble of $N$ particles.

The average energy and average number of particles can be obtained from the quantum grand canonical partition function $\mathcal{L}$ just like we found classically. Following Eq. (2.17.12) we have,

$$
\begin{align*}
\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V, z} & =\frac{1}{\mathcal{L}} \frac{\partial}{\partial \beta}\left[\sum_{\alpha} \mathrm{e}^{-\beta\left(E_{\alpha}-\mu N_{\alpha}\right)}\right]_{V, z}=\frac{1}{\mathcal{L}} \frac{\partial}{\partial \beta}\left[\sum_{\alpha} \mathrm{e}^{-\beta E_{\alpha}} z^{N_{\alpha}}\right]_{V, z}=\frac{1}{\mathcal{L}} \sum_{\alpha} \mathrm{e}^{-\beta E_{\alpha}} z^{N_{\alpha}}\left(-E_{\alpha}\right)  \tag{3.1.28}\\
& =-\sum_{\alpha} \rho_{\alpha} E_{\alpha}=-\sum_{\alpha}\langle\alpha| \hat{\rho} \hat{\mathcal{H}}|\alpha\rangle=\operatorname{Tr}[\hat{\rho} \hat{\mathcal{H}}]=-\langle E\rangle \tag{3.1.29}
\end{align*}
$$

And following Eq. (2.17.15) we have,

$$
\begin{align*}
z\left(\frac{\partial \ln \mathcal{L}}{\partial z}\right)_{\beta, V} & =\frac{z}{\mathcal{L}} \frac{\partial}{\partial z}\left[\sum_{\alpha} \mathrm{e}^{-\beta\left(E_{\alpha}-\mu N_{\alpha}\right)}\right]_{\beta, V}=\frac{z}{\mathcal{L}} \frac{\partial}{\partial z}\left[\sum_{\alpha} \mathrm{e}^{-\beta E_{\alpha}} z^{N_{\alpha}}\right]_{\beta, V}=\frac{z}{\mathcal{L}} \sum_{\alpha} \mathrm{e}^{-\beta E_{\alpha}} z^{N_{\alpha}-1} N_{\alpha}  \tag{3.1.30}\\
& =\frac{1}{\mathcal{L}} \sum_{\alpha} \mathrm{e}^{-\beta E_{\alpha}} z^{N_{\alpha}} N_{\alpha}=\sum_{\alpha} \rho_{\alpha} N_{\alpha}=\langle N\rangle \tag{3.1.31}
\end{align*}
$$

and similarly one can show the alternative versions as in Eq. (2.17.16),

$$
\begin{equation*}
\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V, \mu}=-\langle E\rangle+\mu\langle N\rangle, \quad\left(\frac{\partial \ln \mathcal{L}}{\partial \mu}\right)_{T, V}=\beta\langle N\rangle \tag{3.1.32}
\end{equation*}
$$

Thus, as we found classically, the identification that $\Phi=-k_{B} T \ln \mathcal{L}$ holds also quantum mechanically.
Note: If we consider our classical formalism in the case where states are labeled by a discrete index $i$, then everything looks the same quantum mechanically provided we work in the basis of energy eigenstates $|\alpha\rangle$.

## Example: The Quantum Harmonic Oscillator

As a simple example, suppose we have a single harmonic oscillator of frequency $\omega$. The quantized energy eigenvalues are,

$$
\begin{equation*}
E_{n}=\hbar \omega(n+1 / 2), \quad n=0,1,2 \ldots \tag{3.1.33}
\end{equation*}
$$

The canonical partition function will then be,

$$
\begin{equation*}
Q=\sum_{n=0}^{\infty} \mathrm{e}^{-\beta E_{n}}=\sum_{n=0}^{\infty} \mathrm{e}^{-\beta \hbar \omega(n+1 / 2)}=\mathrm{e}^{-\beta \hbar \omega / 2} \sum_{n=0}^{\infty}\left(\mathrm{e}^{-\beta \hbar \omega}\right)^{n}=\frac{\mathrm{e}^{-\beta \hbar \omega / 2}}{1-\mathrm{e}^{-\beta \hbar \omega}} \tag{3.1.34}
\end{equation*}
$$

The average energy is,

$$
\begin{equation*}
\langle E\rangle=-\frac{\partial}{\partial \beta} \ln Q=-\frac{\partial}{\partial \beta}\left[-\frac{\beta \hbar \omega}{2}-\ln \left(1-\mathrm{e}^{-\beta \hbar \omega}\right)\right]=\frac{\hbar \omega}{2}+\frac{\hbar \omega \mathrm{e}^{-\beta \hbar \omega}}{1-\mathrm{e}^{-\beta \hbar \omega}}=\frac{\hbar \omega}{2}+\frac{\hbar \omega}{\mathrm{e}^{\beta \hbar \omega}-1} \tag{3.1.35}
\end{equation*}
$$

Writing,

$$
\begin{equation*}
\langle E\rangle=\hbar \omega(\langle n\rangle+1 / 2) \tag{3.1.36}
\end{equation*}
$$

where $\langle n\rangle$ is the average level of excitation of the harmonic oscillator, we then have,

$$
\begin{equation*}
\langle n\rangle=\frac{1}{\mathrm{e}^{\beta \hbar \omega}-1} \tag{3.1.37}
\end{equation*}
$$

We could have also gotten this result from a direct calculation of $\langle n\rangle$, as follows.

The probability that the oscillator is excited to energy level $n$ is,

$$
\begin{equation*}
P_{n}=\frac{\mathrm{e}^{-\beta E_{n}}}{Q} \tag{3.1.38}
\end{equation*}
$$

So the average excitation level is,

$$
\begin{align*}
\langle n\rangle & =\sum_{n=0}^{\infty} P_{n} n=\frac{\sum_{n=0}^{\infty} \mathrm{e}^{-\beta \hbar \omega(n+1 / 2)} n}{\sum_{n=0}^{\infty} \mathrm{e}^{-\beta \hbar \omega(n+1 / 2)}}=\frac{\sum_{n=0}^{\infty} \mathrm{e}^{-\beta \hbar \omega n} n}{\sum_{n=0}^{\infty} \mathrm{e}^{-\beta \hbar \omega n}}=\frac{-\frac{1}{\hbar \omega} \frac{\partial}{\partial \beta} \sum_{n=0}^{\infty} \mathrm{e}^{-\beta \hbar \omega n}}{\sum_{n=0}^{\infty} \mathrm{e}^{-\beta \hbar \omega n}}  \tag{3.1.39}\\
& =-\frac{1}{\hbar \omega} \frac{\partial}{\partial \beta}\left[\ln \left(\sum_{n=0}^{\infty}\left(\mathrm{e}^{-\beta \hbar \omega}\right)^{n}\right)\right]=-\frac{1}{\hbar \omega} \frac{\partial}{\partial \beta}\left[\ln \left(\frac{1}{1-\mathrm{e}^{-\beta \hbar \omega}}\right)\right]=\frac{1}{\hbar \omega} \frac{\partial}{\partial \beta}\left[\ln \left(1-\mathrm{e}^{-\beta \hbar \omega}\right)\right]  \tag{3.1.40}\\
& =\frac{1}{\hbar \omega} \frac{\mathrm{e}^{-\beta \hbar \omega} \hbar \omega}{1-\mathrm{e}^{-\beta \hbar \omega}}=\frac{1}{\mathrm{e}^{\beta \hbar \omega}-1} \tag{3.1.41}
\end{align*}
$$

and we get the same result as in Eq. (3.1.37).

