Thermodynamic average or thermodynamic expectation value of a quantum-mechanical quantity described by an operator $\hat{O}$,

$$\left\langle \hat{O} \right\rangle = Tr\left(\hat{O}\hat{W}\right) = Tr\left(\hat{W}\hat{O}\right) \quad (15)$$

<u>Thermodynamic average of total energy</u>

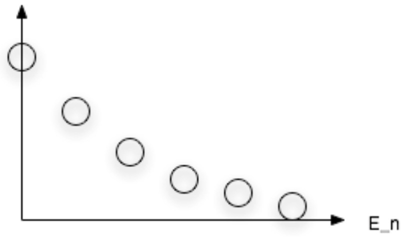
$$E = \left\langle \hat{H} \right\rangle = Tr\left(\hat{H}\hat{W}\right) = \frac{1}{Z} Tr\left(\hat{H}e^{-\beta\hat{H}}\right)$$

$$\hat{H}e^{-\beta\hat{H}}\phi_n\left(\underline{R}\right) = e^{-\beta E_n}\hat{H}\phi_n\left(\underline{R}\right) = E_n e^{-\beta E_n}\phi_n\left(\underline{R}\right)$$

Trace of $\hat{H}e^{-\beta\hat{H}}$ is the sum of its eigenvalues $E_n e^{-\beta E_n}$.

$$E = \frac{1}{Z}\sum_n E_n e^{-\beta E_n} = \sum_n E_n \frac{e^{-\beta E_n}}{Z} \quad (16)$$

with Z from equation (12).



(Probability vs. E_n)

$\frac{1}{Z}e^{-\beta E_n}$ is the probability that quantum-mechanical energy eigenstates $\phi_n\left(\underline{R}\right)$ with energy eigenvalue E_n is occupied at temperature T.

Equation (14), $\sum_n \frac{e^{-\beta E_n}}{Z} = 1$, is the unit normalization of the probability distribution $\frac{e^{-\beta E_n}}{Z}$. Equation (16) is the weighted average of the energy eigenvalues E_n.

$$E_{kin} = \left\langle \hat{T} \right\rangle = Tr\left(\hat{T}\hat{W}\right) \quad (17)$$

$$E_{pot} = \left\langle V\left(\underline{R}\right)\right\rangle = Tr\left(V\left(\underline{R}\right)\hat{W}\right) \quad (18)$$

$$\begin{aligned} E &= \left\langle \hat{H} \right\rangle = Tr\left(\hat{H}\hat{W}\right) = \left\langle \hat{T} \right\rangle + \left\langle V\left(\underline{R}\right)\right\rangle \\ &= E_{kin} + E_{pot} \end{aligned} \quad (19)$$

Entropy

$$\begin{aligned} S &= -k_B\left\langle \ln\left(\hat{W}\right)\right\rangle \\ &= -k_B Tr\left(\hat{W}\ln\left(\hat{W}\right)\right) \\ &= -k_B\sum_n \frac{e^{-\beta E_n}}{Z}\ln\left(\frac{e^{-\beta E_n}}{Z}\right) \end{aligned}$$

1.3 Density Matrix in Coordinate Space

Take equation (11):

$$e^{-\beta\hat{H}}\psi(\underline{R}) = \sum_n e^{-\beta E_n}\langle n|\psi\rangle\phi_n(\underline{R})$$

$$\hat{W}\psi(\underline{R}) = \frac{1}{Z}e^{-\beta\hat{H}}\psi(\underline{R}) = \sum_n \frac{1}{Z}e^{-\beta E_n}\langle n|\psi\rangle\phi_n(\underline{R})$$

$$= \sum_n \frac{1}{Z}e^{-\beta E_n}\phi_n(\underline{R})\int_{V^N}\phi^*{}_n(\underline{R}')\psi(\underline{R}')d\underline{R}'$$

$$\underline{R}' = (\underline{r}_1', \underline{r}_2', \ldots, \underline{r}_N')$$

$$\int_{V^N}\ldots d\underline{R}' = \int_V\int_V\ldots\int_V \ldots d\underline{r}_1' d\underline{r}_2' \ldots d\underline{r}_N'$$

There are N integrals in total.

$$\hat{W}\psi(\underline{R}) = \int_{V^N}\left\{\sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*(\underline{R}')\phi_n(\underline{R})\right\}\psi(\underline{R}')d\underline{R}'$$

$$W(\underline{R},\underline{R}') = \sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*(\underline{R}')\phi_n(\underline{R}) \quad (20)$$

This is called the Density Matrix in Coordinate Space. It is a function of two $3N$-dimensional variables, $\underline{R}$ and $\underline{R}'$; it is a function of $6N$ variables.

$$\hat{W}\psi(\underline{R}) = \int_{V^N} W(\underline{R},\underline{R}')\psi(\underline{R}')d\underline{R}' \quad (21)$$

This is an integral representation of $\hat{W}$. Take normalization (14):

$$Tr(\hat{W}) = \sum_n \frac{e^{-\beta E_n}}{Z} = 1$$

$$\frac{1}{Z}e^{-\beta E_n} = \frac{e^{-\beta E_n}}{Z}\int_{V^N}\phi_n{}^*(\underline{R})\phi_n(\underline{R})d\underline{R}$$

(This integral equals one, hence why it can be substituted in)

$$Tr(\hat{W}) = \int_{V^N}\left\{\sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*(\underline{R})\phi_n(\underline{R})\right\}d\underline{R} = 1$$

$$= \int_{V^N} W(\underline{R},\underline{R})d\underline{R}$$

$W(\underline{R},\underline{R})$ is called the diagonal elements of the density matrix.

$$W(\underline{R},\underline{R}) = \sum_n \frac{e^{-\beta E_n}}{Z}|\phi_n(\underline{R})|^2 \quad (22)$$

This is obtained by setting $\underline{R}' = \underline{R}$ in equation (20). The unit-normalization:

$$\int_{V^N} W(\underline{R},\underline{R})d\underline{R} = 1 \quad (23)$$

If the many-body system is in a pure eigenstate, i.e. in a single state $\phi_n(\underline{R})$ at $T = 0$, then $|\phi_n(\underline{R})|^2$ is the probability density that the particles are at $\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N$. This is equal to the probability density that the system is in a $3N$-dimensional configuration $\underline{R} = (\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N)$.

$|\phi_n(\underline{R})|^2 d\underline{R}$ is the probability that $3N$-dimensional spatial configuration vector $\underline{R}$ lies in an infinitesimal $3N$-dimensional volume of size $d\underline{R} = d\underline{r}_1, d\underline{r}_2, \ldots, d\underline{r}_N$ $= dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \ldots dx_N dy_N dz_N$ centered at $\underline{R}$.

$\left|\phi_n\left(\underline{r}_1,\underline{r}_2,\ldots,\underline{r}_N\right)\right|^2 d\underline{r}_1,d\underline{r}_2,\ldots,d\underline{r}_N$ is the probability that a particle is in an infinitesimal three-dimensional volume $d\underline{r}_1 = dx_1 dy_1 dz_1$ at $\underline{r}_1$, another particle in $d\underline{r}_2 = dx_2 dy_2 dz_2$ at $\underline{r}_2$, …, and an N-th particle in $d\underline{r}_N = dx_N dy_N dz_N$ at $\underline{r}_N$.

The normalization of the wavefunctions $\int_{V^N}\left|\phi_n\left(\underline{R}\right)\right|^2 d\underline{R} = 1$ means that the probabilities $\left|\phi_n\left(\underline{R}\right)\right|^2 d\underline{R}$ integrate up to certainty. Every $\underline{r}_i$ will certainly be somewhere in the volume occupied by the many-particle system.

At $T > 0$, the probability density for the $3N$-dimensional configuration vector $\underline{R}$ is given by the sum of the probability densities $\left|\phi_n\left(\underline{R}\right)\right|^2$ weighted by the probability $\frac{1}{Z}e^{-\beta E_n}$ that the quantum state $\phi_n\left(\underline{R}\right)$ is occupied at $T > 0$. This is equation (22).

$W\left(\underline{R},\underline{R}\right)d\underline{R}$ is the probability that the $3N$-dimensional configuration vector lies in an infinitesimal volume of size $d\underline{R}$ centered at $\underline{R}$.

Normalization (23) has the meaning that the probabilities $W\left(\underline{R},\underline{R}\right)d\underline{R}$ integrate up to certainty. The configuration vector $\underline{R}$ is guaranteed to lie somewhere.

<u>Equation (15) in coordinate space representation</u>

$$\left\langle\hat{O}\right\rangle = Tr\left(\hat{O}\hat{W}\right) = \sum_\lambda \int_{V^N} \chi_\lambda{}^*\left(\underline{R}\right)\hat{O}\hat{W}\chi_\lambda\left(\underline{R}\right)d\underline{R}$$

This is the sum of expectation values $\int_{V^N} \chi_\lambda{}^*\left(\underline{R}\right)\hat{O}\hat{W}\chi_\lambda\left(\underline{R}\right)d\underline{R}$ with respect to any complete orthonormalized set $\chi_\lambda\left(\underline{R}\right)$ of basis functions.

The trace is independent of the choice of complete orthonormalized set of basis functions.

Take now eigenfunctions $\phi_n\left(\underline{R}\right)$ of the Hamiltonian $\hat{H}$.

$$\hat{H}\phi_n\left(\underline{R}\right) = E_n\phi_n\left(\underline{R}\right)$$

$$\hat{W}\phi_n\left(\underline{R}\right) = \frac{e^{-\beta E_n}}{Z}\phi_n\left(\underline{R}\right) \quad (13)$$

$$\begin{aligned}\left\langle\hat{O}\right\rangle &= \sum_n \int_{V^N} \phi_n{}^*\left(\underline{R}\right)\hat{O}\hat{W}\phi_n\left(\underline{R}\right)d\underline{R} \\ &= \sum_n \int_{V^N} \phi_n{}^*\left(\underline{R}\right)\frac{e^{-\beta E_n}}{Z}\hat{O}\phi_n\left(\underline{R}\right)d\underline{R} \\ &= \int_{V^N}\left\{\sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*\left(\underline{R}\right)\hat{O}_{\underline{R}}\phi_n\left(\underline{R}\right)\right\}d\underline{R}\end{aligned}$$

where the subscript $\underline{R}$ on $\hat{O}$ is used to emphasise that this operator acts on $\underline{R}$.

$$\sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*(\underline{R})\hat{O}_{\underline{R}}\phi_n(\underline{R}) = \left\{\hat{O}_{\underline{R}}\left[\sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*(\underline{R}')\phi_n(\underline{R})\right]\right\}(\underline{R}'=\underline{R})$$
$$= \left\{\sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*(\underline{R}')\hat{O}_{\underline{R}}\phi_n(\underline{R})\right\}(\underline{R}'=\underline{R})$$
$$= \sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*(\underline{R})\hat{O}\phi_n(\underline{R})$$

$\left\{\hat{O}_R[...](\underline{R},\underline{R}')\right\}(\underline{R}'=\underline{R})$ means that we apply the operator $\hat{O}$ to the variable $\underline{R}$ only in $[...](\underline{R},\underline{R}')$ and not to variable $\underline{R}'$, and then after having carried out that operation set $\underline{R}'=\underline{R}$ in the result thus obtained.

$$\left\{\hat{O}_{\underline{R}}\left[\sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*(\underline{R}')\phi_n(\underline{R})\right]\right\}(\underline{R}'=\underline{R}) = \left\{\hat{O}_{\underline{R}}W(\underline{R},\underline{R}')\right\}(\underline{R}'=\underline{R})$$
$$= \sum_n \frac{e^{-\beta E_n}}{Z}\phi_n{}^*(\underline{R})\hat{O}_{\underline{R}}\phi_n(\underline{R})$$

$$\langle\hat{O}\rangle = \int_{V^N}\left[\hat{O}_{\underline{R}}W(\underline{R},\underline{R}')\right](\underline{R}'=\underline{R})d\underline{R} \quad (24)$$

Apply $\hat{O}$ to $\underline{R}$ in $W(\underline{R},\underline{R}')$, then set in the result $\underline{R}'=\underline{R}$, and integrate over the $3N$-dimensional configuration space.

Potential Energy

$$E_{pot} = \langle V(\underline{R})\rangle = \int_{V^N}\left[V(\underline{R})W(\underline{R},\underline{R}')\right](\underline{R}'=\underline{R})d\underline{R}$$
$$\left[V(\underline{R})W(\underline{R},\underline{R}')\right](\underline{R}'=\underline{R}) = V(\underline{R})W(\underline{R},\underline{R})$$
$$E_{pot} = \int_{V^N} V(\underline{R})W(\underline{R},\underline{R})d\underline{R} \quad (25)$$