Statistics of the various ensembles

The microcanonical ensemble

The construction of the microcanonical ensemble is based on the premise that the systems constituting the ensemble are characterized by a fixed number of particles N, a fixed volume V and an energy lying within the interval $(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$, where $\Delta \ll E$. The total number of distinct microstates accessible to a system is then denoted by the symbol $\Gamma(N, V, E; \Delta)$ and, by assumption, any one of these microstates is as likely to occur as any other. This assumption enters into our theory in the nature of a postulate, and is often referred to as the postulate of *equal a priori probabilities* for the various accessible states. Accordingly, the density matrix ρ_{mn} (which, in the energy representation, must be a diagonal matrix) will be of the form

$$\rho_{mn} = \rho_n \delta_{mn} \qquad \rho_n = \begin{cases} 1/\Gamma & \text{for each of the accessible states,} \\ 0 & \text{for all other states;} \end{cases}$$

$$\rho = \begin{pmatrix} \frac{1}{\Gamma} & 0 & 0 & \dots \\ 0 & \frac{1}{\Gamma} & 0 & \dots \\ 0 & 0 & \frac{1}{\Gamma} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}$$

$$\rho = \frac{1}{\Gamma} \begin{pmatrix} 1 & 0 & 0 & \dots \\ 0 & 1 & 0 & \dots \\ 0 & 0 & 1 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} = \frac{1}{\Gamma} I$$

The normalized condition is clearly satisfied

$$Tr(\rho) = \sum_n \rho_{nn}(t) = \sum_n \rho_n(t) = \sum_n \frac{1}{\Gamma} = \Gamma \frac{1}{\Gamma} = 1$$

As we already know, the thermodynamics of the system is completely determined from the expression for its entropy which, in turn, is given by

$$S = k \ln \Gamma$$

Since Γ, the total number of distinct, accessible states, is supposed to be computed quantum-mechanically, taking due account of the indistinguishability of the particles right from the beginning, no paradox, such as Gibbs', is now expected to arise. Moreover, if the quantum state of the system turns out to be unique ($\Gamma = 1$), the entropy of the system would identically vanish. This provides us with a sound theoretical basis for the hitherto empirical theorem of Nernst (also known as the third law of thermodynamics).

The situation corresponding to the case $\Gamma = 1$ is usually referred to as a *pure* case. In such a case, the construction of an ensemble is essentially superfluous, because every system in the ensemble has got to be in one and the same state. Accordingly, there is only one diagonal element ρ_{nn} which is nonzero (actually equal to unity), while all others are zero. The density matrix, therefore, satisfies the condition

$$\rho^2 = \rho$$

For pure case we have:

$$\Gamma = 1$$

$$\rho = \frac{1}{\Gamma}\begin{pmatrix} 0 & 0 & 0 & \ldots \\ 0 & 1 & 0 & \ldots \\ 0 & 0 & o & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & \ldots \\ 0 & 1 & 0 & \ldots \\ 0 & 0 & o & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{pmatrix}$$

$$\rho^2 = \rho$$ ☺

How about in a different representation where the density matrix may not be so longer diagonal?

We show that the above condition holds in any representation:

In a different representation, the pure case will correspond to

$$\rho_{mn}(t) = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \left\{ a_m^k(t) a_n^{k*}(t) \right\}$$

$$= \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} \left\{ a_m(t) a_n^*(t) \right\}$$

$$= \frac{1}{\mathcal{N}} \mathcal{N} a_m(t) a_n^*(t) = a_m(t) a_n^*(t)$$

$$\rho_{mn}^2(t) = \sum_l a_m(t) a_l^*(t) a_l(t) a_n^*(t) =$$

$$= a_m(t) a_n^*(t) \sum_l a_l^*(t) a_l(t) = a_m(t) a_n^*(t) \sum_l \left| a_l(t) \right|^2 = a_m(t) a_n^*(t)$$

$$= \rho_{mn}$$ ☺

$$\rho_{mn} = \rho_n \delta_{mn} \qquad \rho_n = \begin{cases} 1/\Gamma & \text{for each of the accessible states,} \\ 0 & \text{for all other states;} \end{cases}$$

A situation in which $\Gamma > 1$ is usually referred to as a *mixed* case. The density matrix, in the energy representation, is then given by eqns (1) and (2). If we now change over to any other representation, the general form of the density matrix should remain the same, namely (i) the off-diagonal elements should continue to be zero, while (ii) the diagonal elements (over the allowed range) should continue to be equal to one another. Now, had we constructed our ensemble on a representation other than the energy representation right from the beginning, how could we have possibly anticipated *ab initio* property (i) of the density matrix, though property (ii) could have been easily invoked through a postulate of *equal a priori probabilities*? To ensure that property (i), as well as property (ii), holds in *every* representation, we must invoke yet another postulate, viz. the postulate of *random a priori phases* for the probability amplitudes a_n^k, which in turn implies that the wave function ψ^k, for all k, is an *incoherent* superposition of the basis $\{\phi_n\}$. As a consequence of this postulate, coupled with the postulate of equal *a priori* probabilities, we would have in any representation

$$
\begin{aligned}
\rho_{mn} \equiv \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} a_m^k a_n^{k*} &= \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} |a|^2 e^{i(\theta_m^k - \theta_n^k)} \\
&= c\langle e^{i(\theta_m^k - \theta_n^k)} \rangle \\
&= c\delta_{mn},
\end{aligned}
$$

as it should be for a microcanonical ensemble.

Thus, contrary to what might have been expected on customary thought, to secure the physical situation corresponding to a microcanonical ensemble, we require in general two postulates instead of one! The second postulate arises solely from quantum-mechanics and is intended to ensure noninterference (and hence a complete absence of correlations) among the member systems; this, in turn, enables us to form a mental picture of each system, one at a time, completely disentangled from other systems in the ensemble.

m = n

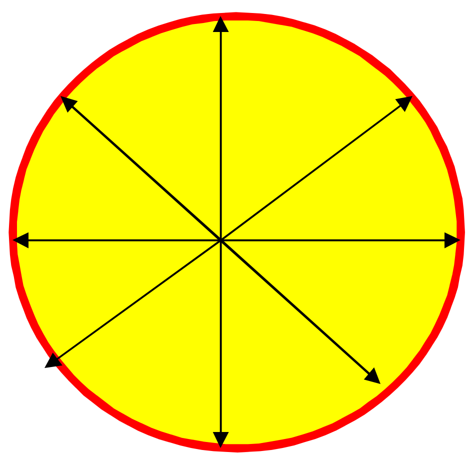
$$\rho_{mm} = c\left\langle e^{i\theta_m^k - i\theta_m^k} \right\rangle = c\langle 1 \rangle = c$$

m <> n

$$\rho_{mn} = c\left\langle e^{i\theta_m^k - i\theta_n^k} \right\rangle = c\,\frac{1}{\mathcal{N}}\sum_{k=1}^{\mathcal{N}} e^{i\theta_m^k - i\theta_n^k} = 0$$

Why?

Due to a random a priori phases



The canonical ensemble

In this ensemble the macrostate of a member system is defined through the parameters N, V and T; the energy E is now a variable quantity. The probability that a system, chosen *at random* from the ensemble, possesses an energy E_r is determined by the Boltzmann factor $\exp(-\beta E_r)$, where $\beta = 1/kT$; see Secs 3.1 and 3.2. The density matrix in the energy representation is, therefore, taken as

$$\rho_{mn} = \rho_n \delta_{mn} \qquad \rho_n = Ce^{-\beta E_n}$$

$$Tr(\rho) = \sum_n \rho_n(t) = \sum_n Ce^{-\beta E_n} = C\sum_n e^{-\beta E_n} = 1$$

$$C = \frac{1}{\sum_n e^{-\beta E_n}} = \frac{1}{Q_N(\beta, V)}$$

$$\rho = \rho \sum_n \left|\varphi_n\right\rangle\left\langle\varphi_n\right| = \sum_n \rho_n \left|\varphi_n\right\rangle\left\langle\varphi_n\right| = \sum_n \left|\varphi_n\right\rangle \rho_n \left\langle\varphi_n\right|$$

$$= \sum_n \left|\varphi_n\right\rangle \frac{e^{-\beta E_n}}{Q_N(\beta,V)} \left\langle\varphi_n\right| \qquad \rho_n = \frac{e^{-\beta E_n}}{Q_N(\beta,V)}$$

$$= \frac{e^{-\beta H}}{Q_N(\beta,V)} \sum_n \left|\varphi_n\right\rangle\left\langle\varphi_n\right| = \frac{e^{-\beta H}}{Q_N(\beta,V)}$$

$$= \frac{e^{-\beta H}}{\sum_n e^{-\beta E_n}} = \frac{e^{-\beta H}}{\sum_n \left\langle\varphi_n\right| e^{-\beta H} \left|\varphi_n\right\rangle} = \frac{e^{-\beta H}}{Tr(e^{-\beta H})}$$

$$\left\langle G\right\rangle_N = \frac{Tr\left(\rho G\right)}{Tr\left(\rho\right)} = \frac{Tr(e^{-\beta H} G)}{Tr(e^{-\beta H})}$$

The grand canonical ensemble

In this ensemble the density operator $\hat{\rho}$ operates on a Hilbert space with an indefinite number of particles. The density operator must therefore commute not only with the Hamiltonian operator $\hat{H}$ but also with a number operator $\hat{n}$ whose eigenvalues are $0, 1, 2, \ldots$. The precise form of the density operator can now be obtained by a straightforward generalization of the preceding case, with the result

$$\hat{\rho} \propto e^{-\beta\hat{H}-\alpha\hat{n}} = \frac{1}{\mathcal{Q}(\mu, V, T)} e^{-\beta(\hat{H}-\mu\hat{n})}, \tag{14}$$

where

$$\mathcal{Q}(\mu, V, T) = \sum_{r,s} e^{-\beta(E_r-\mu N_s)} = \mathrm{Tr}\left\{e^{-\beta(\hat{H}-\mu\hat{n})}\right\}. \tag{15}$$

The ensemble average $\langle G \rangle$ is now given by

$$\langle G \rangle = \frac{1}{\mathcal{Q}(\mu, V, T)} \operatorname{Tr}\left(\hat{G} e^{-\beta \hat{H}} e^{\beta \mu \hat{n}}\right)$$
$$= \frac{\sum_{N=0}^{\infty} z^N \langle G \rangle_N Q_N(\beta)}{\sum_{N=0}^{\infty} z^N Q_N(\beta)}, \tag{16}$$

where $z\,(\equiv e^{\beta\mu})$ is the *fugacity* of the system while $\langle G \rangle_N$ is the canonical-ensemble average, as given by eqn. (13). The quantity $\mathcal{Q}(\mu, V, T)$ appearing in these formulae is, clearly, the *grand partition function* of the system.

5.3. Examples

A. An electron in a magnetic field

Let us consider, for illustration, the case of a single electron which possesses an intrinsic spin $\frac{1}{2}\hbar\hat{\boldsymbol{\sigma}}$ and a magnetic moment μ_B, where $\hat{\boldsymbol{\sigma}}$ is the Pauli spin operator and $\mu_B = e\hbar/2mc$. The spin of the electron can have two possible orientations, $\uparrow$ or $\downarrow$, with respect to an applied magnetic field $\boldsymbol{B}$. If the applied field is taken to be in the direction of the z-axis, the configurational Hamiltonian of the spin takes the form

$$\hat{H} = -\mu_B(\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{B}) = -\mu_B B \hat{\sigma}_z. \tag{1}$$

In the representation that makes $\hat{\sigma}_z$ diagonal, namely

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{2}$$

Method 1

$$\rho = \frac{e^{-\beta H}}{Tr(e^{-\beta H})} = \frac{\begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}}{Tr(e^{-\beta H})} = \frac{1}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}$$

$$\langle \sigma_z \rangle = Tr(\rho\sigma_z) = \frac{e^{\beta\mu_B B} - e^{-\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} = \tanh(\beta\mu_B B)$$

Eigenvalues of σ_z are 1 and -1 with the eighevectors of $\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

Eigenvalues of H are $E_1 = \beta\mu_B B$ and $E_2 = -\beta\mu_B B$ with the above eigenvalues of $\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$$\rho = \sum_n \left| \varphi_n \right\rangle \frac{e^{-\beta E_n}}{Q_N(\beta, V)} \left\langle \varphi_n \right|$$

$$\left| \varphi_1 \right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \left| \varphi_2 \right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad \left\langle \varphi_1 \right| = \begin{pmatrix} 1 & 0 \end{pmatrix} \qquad \left\langle \varphi_2 \right| = \begin{pmatrix} 0 & 1 \end{pmatrix}$$

$$\rho = \frac{1}{Q_N(\beta, V)} \left\{ \left| \varphi_1 \right\rangle e^{-\beta E_1} \left\langle \varphi_1 \right| + \left| \varphi_2 \right\rangle e^{-\beta E_2} \left\langle \varphi_2 \right| \right\}$$

$$\rho = \frac{e^{-\beta H}}{Tr(e^{-\beta H})} = \frac{\begin{pmatrix} e^{\beta \mu_B B} & 0 \\ 0 & e^{-\beta \mu_B B} \end{pmatrix}}{Tr(e^{-\beta H})}$$

☺

Method 2

$$\sigma_z^2 = 1 \qquad \sigma_z^3 = \sigma_z$$

$$e^{-\beta H} = e^{\beta\mu_B B\sigma_z} = \sum_{j=0}^{\infty} \frac{1}{j!}(\beta\mu_B B)^j \sigma_z^j$$

$$= \sum_{j \text{ even}}^{\infty} \frac{1}{j!}(\beta\mu_B B)^j I + \sum_{j \text{ 0dd}}^{\infty} \frac{1}{j!}(\beta\mu_B B)^j \sigma_z$$

$$= \cosh(\beta\mu_B B) I + \sinh(\beta\mu_B B)\sigma_z$$

$$= \cosh(\beta\mu_B B)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \sinh(\beta\mu_B B)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \begin{pmatrix} \cosh(\beta\mu_B B) + \sinh(\beta\mu_B B) & 0 \\ 0 & \cosh(\beta\mu_B B) - \sinh(\beta\mu_B B) \end{pmatrix}$$

$$\langle \sigma_z \rangle = \frac{Tr(\rho\sigma_z)}{Tr(\rho)} = \frac{Tr\left(e^{-\beta H}\sigma_z\right)}{Tr\left(e^{-\beta H}\right)}$$

$$e^{-\beta H} = \begin{pmatrix} \cosh(\beta\mu_B B) + \sinh(\beta\mu_B B) & 0 \\ 0 & \cosh(\beta\mu_B B) - \sinh(\beta\mu_B B) \end{pmatrix}$$

$$e^{-\beta H}\sigma_z = \begin{pmatrix} \cosh(\beta\mu_B B) + \sinh(\beta\mu_B B) & 0 \\ 0 & \cosh(\beta\mu_B B) - \sinh(\beta\mu_B B) \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \begin{pmatrix} \cosh(\beta\mu_B B) + \sinh(\beta\mu_B B) & 0 \\ 0 & -\cosh(\beta\mu_B B) + \sinh(\beta\mu_B B) \end{pmatrix}$$

$$\langle \sigma_z \rangle = \frac{Tr\left(e^{-\beta H}\sigma_z\right)}{Tr\left(e^{-\beta H}\right)} = \frac{2\sinh(\beta\mu_B B)}{2\cosh(\beta\mu_B B)} = \tanh(\beta\mu_B B)$$ ☺

We now consider the case of a free particle, of mass m, in a cubical box of side L. The Hamiltonian of the particle is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right), \tag{5}$$

while the eigenfunctions of the Hamiltonian, which satisfy periodic boundary conditions

$$\begin{aligned}\phi(x+L, y, z) = \phi(x, y+L, z) = \phi(x, y, z+L) \\ = \phi(x, y, z),\end{aligned} \tag{6}$$

are given by

$$\phi_E(r) = \frac{1}{L^{3/2}} \exp\,(i\boldsymbol{k}\cdot\boldsymbol{r}), \tag{7}$$

the corresponding eigenvalues E being

$$E = \frac{\hbar^2 k^2}{2m}, \tag{8}$$

with

$$\boldsymbol{k} \equiv (k_x, k_y, k_z) = \frac{2\pi}{L}(n_x, n_y, n_z); \tag{9}$$

the quantum numbers n_x, n_y and n_z must be integers (positive, negative or zero). Symbolically, we may write for the wave vector $\boldsymbol{k}$

$$\boldsymbol{k} = \frac{2\pi}{L}\boldsymbol{n}, \tag{10}$$

where $\boldsymbol{n}$ is a vector with integral components $0, \pm 1, \pm 2, \ldots$.

We now proceed to evaluate the density matrix ($\hat{\rho}$) of this system in the canonical ensemble; we shall do so in the *coordinate* representation. In view of eqn. (5.2.11), we have

$$\begin{aligned}\langle \boldsymbol{r}|e^{-\beta\hat{H}}|\boldsymbol{r}'\rangle &= \sum_E \langle \boldsymbol{r}|E\rangle e^{-\beta E}\langle E|\boldsymbol{r}'\rangle \\ &= \sum_E e^{-\beta E}\phi_E(\boldsymbol{r})\phi_E^*(\boldsymbol{r}'). \end{aligned} \tag{11}$$

Substituting from (7) and making use of (8) and (10), we obtain

$$\begin{aligned}\langle \boldsymbol{r}|e^{-\beta\hat{H}}|\boldsymbol{r}'\rangle &= \frac{1}{L^3}\sum_{\boldsymbol{k}} \exp\left[-\frac{\beta\hbar^2}{2m}k^2 + i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')\right] \\ &\approx \frac{1}{(2\pi)^3}\int \exp\left[-\frac{\beta\hbar^2}{2m}k^2 + i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')\right] d^3k \\ &= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} \exp\left[-\frac{m}{2\beta\hbar^2}|\boldsymbol{r}-\boldsymbol{r}'|^2\right]; \end{aligned} \tag{12}$$

see eqns (B.41, 42). It follows that

$$\begin{aligned}\mathrm{Tr}\left(e^{-\beta\hat{H}}\right) &= \int \langle \boldsymbol{r}|e^{-\beta\hat{H}}|\boldsymbol{r}\rangle\, d^3r \\ &= V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}. \end{aligned} \tag{13}$$

Expression (13) is indeed the partition function, $Q_1(\beta)$, of a single particle confined to a box of volume V; see eqn. (3.5.19). Combining (12) and (13), we obtain for the density matrix in the coordinate representation

$$\langle \boldsymbol{r}|\hat{\rho}|\boldsymbol{r}'\rangle = \frac{1}{V}\exp\left[-\frac{m}{2\beta\hbar^2}|\boldsymbol{r}-\boldsymbol{r}'|^2\right] \cdot \left(\frac{m}{2\pi\beta\hbar}\right)^{3/2} = 1/V \qquad (14)$$

$$Tr(\rho) = Tr(e^{-\beta H}) = 1$$

As expected, the matrix $\rho_{\boldsymbol{r},\boldsymbol{r}'}$ is symmetric between the states $\boldsymbol{r}$ and $\boldsymbol{r}'$. Moreover, the diagonal element $\langle \boldsymbol{r}|\rho|\boldsymbol{r}\rangle$, which represents the *probability density* for the particle to be in the neighborhood of the point $\boldsymbol{r}$, is independent of $\boldsymbol{r}$; this means that, in the case of a single free particle, *all* positions within the box are equally likely to obtain. A nondiagonal element $\langle \boldsymbol{r}|\rho|\boldsymbol{r}'\rangle$, on the other hand, is a measure of the probability of "spontaneous transition" between the position coordinates $\boldsymbol{r}$ and $\boldsymbol{r}'$ and is therefore a measure of the relative "intensity" of the wave packet (associated with the particle) at a distance $|\boldsymbol{r}-\boldsymbol{r}'|$ from the centre of the packet. The spatial extent of the wave packet, which in turn is a measure of the uncertainty involved in locating the position of the particle, is clearly of order $\hbar/(mkT)^{1/2}$; the latter is also a measure of the *mean thermal wavelength* of the particle. The spatial spread found here is a purely quantum-mechanical effect; quite expectedly, it tends to vanish at high temperatures. In fact, as $\beta \to 0$, the behavior of the matrix element (14) approaches that of a delta function, which implies a return to the classical picture of a *point* particle.

Finally, we determine the expectation value of the Hamiltonian itself. From eqns (5) and (14), we obtain

$$
\begin{aligned}
\langle H \rangle = \mathrm{Tr}\,(\hat{H}\hat{\rho}) &= -\frac{\hbar^2}{2mV}\int \left\{ \nabla^2 \exp\left[-\frac{m}{2\beta\hbar^2}|\boldsymbol{r}-\boldsymbol{r}'|^2\right]\right\}_{\boldsymbol{r}=\boldsymbol{r}'} d^3r \\
&= \frac{1}{2\beta V}\int \left\{ \left[3 - \frac{m}{\beta\hbar^2}|\boldsymbol{r}-\boldsymbol{r}'|^2\right] \exp\left[-\frac{m}{2\beta\hbar^2}|\boldsymbol{r}-\boldsymbol{r}'|^2\right]\right\}_{\boldsymbol{r}=\boldsymbol{r}'} d^3r \\
&= \frac{3}{2\beta} = \frac{3}{2}kT,
\end{aligned}
\tag{15}
$$

which was indeed expected. Otherwise, too,

$$
\langle H \rangle = \frac{\mathrm{Tr}\,(\hat{H}e^{-\beta\hat{H}})}{\mathrm{Tr}\,(e^{-\beta\hat{H}})} = -\frac{\partial}{\partial\beta}\ln \mathrm{Tr}\,(e^{-\beta\hat{H}}) \tag{16}
$$

which, on combination with (13), leads to the same result.