Partition functions in other ensembles, fluctuations

Peter Košovan
peter.kosovan@natur.cuni.cz

Dept. of Physical and Macromolecular Chemistry

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If you find a mistake, kindly report it to the author :-(
Grand canonical ensemble

Constraints:

\[ A = \sum_{N} \sum_{j} a_{N,j} \]
\[ E = \sum_{N} \sum_{j} a_{N,j} E_{N,j} \]
\[ N = \sum_{N} \sum_{j} a_{N,j} N \]

Number of available states for a given distribution \( \{a_{N,j}\} \):

\[ W(\{a_{N,j}\}) = \frac{A!}{\prod_{N} \prod_{j} a_{N,j}!} \]
Grandcanonical partition function

Use most probable distribution and Lagrange multipliers (in analogy with canonical ensemble) to obtain:

\[ a^*_{N,j} = e^{-\alpha} e^{-\beta E_{N,j}(V)} e^{-\gamma N} \]

Probability of a system to have \( N \) particles and be in state \( j \):

\[ P_{N,j}(V, \beta, \gamma) = \frac{a^*_{N,j}}{A} = \frac{e^{-\beta E_{N,j}(V)} e^{-\gamma N}}{\sum_j \sum_N e^{-\beta E_{N,j}(V)} e^{-\gamma N}} \]

Partition function:

\[ \Xi = \sum_j \sum_N e^{-\beta E_{N,j}(V)} e^{-\gamma N} \]

Consider Grandcanonical ensemble as a collection of canonical ensembles with the same \( T, V \) but different \( N \). Then they have the same \( \beta = 1/k_B T \).
Averages of mechanical properties

\[
\overline{E}(V, \beta, \gamma) = \frac{1}{\Xi} \sum_{N} \sum_{j} E_{N,j}(V) e^{-\beta E_{N,j}(V)} e^{-\gamma N} = -\left( \frac{\partial \ln \Xi}{\partial \beta} \right)_{V,\gamma}
\]

\[
\overline{p}(V, \beta, \gamma) = \frac{1}{\Xi} \sum_{N} \sum_{j} \left(-\frac{\partial E_{N,j}(V)}{\partial V} \right) e^{-\beta E_{N,j}(V)} e^{-\gamma N} = \frac{1}{\beta} \left( \frac{\partial \ln \Xi}{\partial V} \right)_{\beta,\gamma}
\]

\[
\overline{N}(V, \beta, \gamma) = \frac{1}{\Xi} \sum_{N} \sum_{j} Ne^{-\beta E_{N,j}(V)} e^{-\gamma N} = -\left( \frac{\partial \ln \Xi}{\partial \gamma} \right)_{V,\beta}
\]

Evaluation of $\gamma$

Total derivative of $\overline{E}$:

\[
d\overline{E} = \sum_{N} \sum_{j} E_{N,j} dP_{N,j} + \sum_{N} \sum_{j} P_{N,j} dE_{N,j}
\]
Evaluation of $\gamma$

Total derivative of $\overline{E}$:

$$d\overline{E} = \sum_N \sum_j E_{N,j} dP_{N,j} + \sum_N \sum_j P_{N,j} dE_{N,j}$$

Identify the second term as reversible work (assume only $pdV$):

$$d\overline{E} = \sum_N \sum_j E_{N,j} dP_{N,j} - \bar{p}dV$$

Substitute $E_{N,j}$ expressed from $P_{N,j}$: $-\beta E_{N,j} = \ln P_{N,j} - \beta \mu N + \ln \Xi$

$$d\overline{E} = -\frac{1}{\beta} \sum_N \sum_j \left( \ln P_{N,j} + \gamma N + \ln \Xi \right) dP_{N,j} - \bar{p}dV$$

Use $d\overline{N} = \sum_{N,j} N dP_{N,j}$ and $\ln \Xi \sum_{N,j} dP_{N,j} = 0$ to obtain

$$d\overline{E} = -\frac{1}{\beta} \sum_N \sum_j \ln P_{N,j} dP_{N,j} - \frac{\gamma}{\beta} d\overline{N} - \bar{p}dV$$
Evaluation of $\gamma$ (continued)

Compare the last equation from previous slide

$$d\bar{E} = -\frac{1}{\beta} \sum_N \sum_j \ln P_{N,j} dP_{N,j} - \frac{\gamma}{\beta} d\bar{N} - \bar{p}dV$$

with the relation from Thermodynamics:

$$dU = TdS - pdV + \mu dN$$

and the expression for entropy

$$dS = -k_B \sum_N \sum_j \ln P_{N,j} dP_{N,j} = -k_B d\left(\sum_N \sum_j P_{N,j} \ln P_{N,j}\right)$$

to arrive at

$$\gamma = -\beta \mu = -\frac{\mu}{k_BT}$$
Entropy from $\Xi$

Integrating

$$dS = -k_B d\left( \sum_N \sum_j P_{N,j} \ln P_{N,j} \right)$$

we obtain

$$S = -k_B \sum_N \sum_j P_{N,j} \ln P_{N,j} + C$$

Setting $C = 0$ and substituting for $P_{N,j}$:

$$S = k_B \ln \Xi + k_B T \left( \frac{\partial \ln \Xi}{\partial T} \right)_{V,\mu}$$

Partition function:

$$\Xi = \sum_N \sum_j e^{-\beta E_{N,j}} e^{\beta \mu N}$$

Probability:

$$P_{N,j} = \frac{1}{\Xi} e^{-\beta E_{N,j}} e^{\beta \mu N}$$
**Digression on derivatives**

**In general:**

\[
\frac{\partial f}{\partial x} = \frac{\partial f}{\partial \ln x} \frac{\partial \ln x}{\partial x} = x \frac{\partial f}{\partial \ln x},
\]

\[
\frac{\partial f}{\partial \ln x} = \frac{1}{x} \frac{\partial f}{\partial x}.
\]

\[
\frac{\partial f}{\partial x} = \frac{\partial f}{\partial 1/x} \frac{\partial 1/x}{\partial x} = -x^2 \frac{\partial f}{\partial 1/x},
\]

\[
\frac{\partial f}{\partial 1/x} = -x^{-2} \frac{\partial f}{\partial x}.
\]

**Two special cases:**

\[
\frac{\partial f}{\partial \beta} = \frac{\partial f}{\partial 1/(k_B T)} = -\frac{1}{(k_B T)^2} \frac{\partial f}{\partial k_B T},
\]

\[
\frac{\partial f}{\partial k_B T} = \frac{1}{k_B T^2} \frac{\partial f}{\partial T}.
\]

\[
\frac{\partial \ln f}{\partial \ln T} = \frac{T}{f} \frac{\partial f}{\partial T}.
\]
Other thermodynamic functions from $\Xi$

Internal energy:

$$\overline{E} = \sum_{N} \sum_{j} E_{N,j} P_{N,j} \quad \text{where} \quad -\beta E_{N,j} = \ln P_{N,j} - \beta \mu N + \ln \Xi$$

Substitute $E_{N,j}$ from $P_{N,j}$:

$$\beta \overline{E} = -\sum_{N,j} P_{N,j} \ln P_{N,j} + \beta \mu \sum_{N,j} N P_{N,j} - \ln \Xi \sum_{N,j} P_{N,j}$$

Use

$$S = -k_B \sum_{N,j} P_{N,j} \ln P_{N,j} \quad \overline{N} = \sum_{N,j} N P_{N,j} \quad \sum_{N,j} P_{N,j} = 1$$

to substitute for $S$ and obtain:

$$\overline{E} = TS + \overline{N} \mu - k_B T \ln \Xi$$
Grandcanonical ensemble – characteristic function

From previous slide

\[ \overline{E} = TS + \overline{N}\mu - k_B T \ln \Xi \]

From first postulate

\[ \overline{E} = U, \quad \mu \overline{N} = G \]

Compare with

\[ G = U - TS + pV \]

to obtain

\[ pV = k_B T \ln \Xi \]

Characteristic function of the Grandcanonical ensemble.
We can express $\bar{N}$ as

$$\bar{N} = \frac{1}{\beta} \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T}$$

Which we substitute to

$$U = TS + \bar{N} \mu - k_B T \ln \Xi$$

to obtain

$$U = k_B T \left[ \left( \frac{\partial \ln \Xi}{\partial \ln \mu} \right)_{V,T} + \left( \frac{\partial \ln \Xi}{\partial \ln T} \right)_{V,\mu} \right]$$
Internal energy and Helmholtz free energy from $\Xi$

We can express $\overline{N}$ as

$$\overline{N} = \frac{1}{\beta} \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T}$$

Which we substitute to

$$U = TS + \overline{N} \mu - k_B T \ln \Xi$$

to obtain

$$U = k_B T \left[ \left( \frac{\partial \ln \Xi}{\partial \ln \mu} \right)_{V,T} + \left( \frac{\partial \ln \Xi}{\partial \ln T} \right)_{V,\mu} \right]$$

Finally we use

$$G = \overline{N} \mu = k_B T \left( \frac{\partial \ln \Xi}{\partial \ln \mu} \right)_{V,T}$$

and from

$$A = U - TS$$

we obtain

$$A = k_B T \left[ \left( \frac{\partial \ln \Xi}{\partial \ln \mu} \right)_{V,T} - \ln \Xi \right]$$
Overview of other ensembles (without derivations)

**Microcanonical, \((N, V, E)\)**

Total energy is fixed, all states are equally probable:

\[
P_j = \frac{1}{\Omega}, \quad \ln P_j = -\ln \Omega
\]

\[
S = -k_B \sum_j P_j \ln P_j = -k_B \sum_j P_j \ln \Omega = k_B \ln \Omega(N, V, E)
\]

- \(\Omega(N, V, E)\) is the partition function of microcanonical ensemble.
- It is proportional to the number of states available to the system with energy \(E\) (degeneracy of the energy level).
- Constant \(E\) requirement makes microcanonical ensemble inconvenient for practice.
Other ensembles (without derivations)

**Isothermal-isobaric** $(N, p, T)$

The partition function:

$$\Delta(N, p, T) = \sum_E \sum_V \Omega(N, V, E) e^{-\beta E} e^{-\beta p V}$$

**Characteristic function**

$$G = -k_B T \ln \Delta(N, p, T)$$

- Practical for chemical problems without reactions
- For other thermodynamic functions from $\Delta(N, p, T)$, see textbook.
Relation between different partition functions

\[ Q(N, V, T) = \sum_E \Omega(N, V, E) e^{-\beta E} = \sum_j e^{-\beta E_j} \]

\[ \Xi(\mu, V, T) = \sum_E \sum_N \Omega(N, V, E) e^{-\beta E} e^{\beta \mu N} = \sum_N Q(N, V, T) e^{\beta \mu N} \]

\[ \Delta(N, p, T) = \sum_E \sum_V \Omega(N, V, E) e^{-\beta E} e^{-\beta p V} = \sum_V Q(N, V, T) e^{-\beta p V} \]

- General feature for all ensembles.
$n$-th moment of a (discrete) probability distribution $P(x)$:

$$
\mu'_n = \sum_x x^n P(x), \quad \sum_x P(x) = 1
$$

First moment – mean:

$$
\bar{x} = \mu'_1 = \sum_x x P(x)
$$

Central moments:

$$
\mu_n = \sum_x \left(x - \bar{x}\right)^n P(x)
$$

Second central moment – variance

$$
\sigma^2 = \mu_2 = \sum_x \left(x - \bar{x}\right)^2 P(x) = (x - \bar{x})^2
$$

Standard deviation $\sigma$ – measure of spread of a distribution.
Fluctuations in energy (canonical ensemble)

\[ \sigma_E^2 = (\bar{E} - \bar{E})^2 = \bar{E}^2 - \bar{E}^2 \]

\[ \sigma_E^2 = \sum_j E_j^2 P_j - \bar{E}^2 \quad \text{with} \quad P_j = \frac{e^{-\beta E_j}}{Q(N, V, T)} \]

We can rewrite

\[ \sum_j E_j^2 P_j = \frac{1}{Q} \sum_j E_j^2 e^{-\beta E_j} = -\frac{1}{Q} \frac{\partial}{\partial \beta} \sum_j E_j e^{-\beta E_j} \]

\[ \ldots = -\frac{1}{Q} \frac{\partial}{\partial \beta} (\bar{E}Q) = -\frac{\partial \bar{E}}{\partial \beta} - \bar{E} \frac{\partial \ln Q}{\partial \beta} = k_B T^2 \frac{\partial \bar{E}}{\partial T} + \bar{E}^2 \]

Thus variance in \( \bar{E} \) is proportional to heat capacity

\[ \sigma_E^2 = k_B T^2 \left( \frac{\partial \bar{E}}{\partial T} \right)_{N,V} = k_B T^2 C_V \]
Scaling of relative fluctuations – thermodynamic limit

For an ideal gas:

\[
\overline{E} = \frac{3}{2} N k_B T \sim \mathcal{O}(N k_B T), \quad C_V = \frac{3}{2} N k_B \sim \mathcal{O}(N k_B)
\]

The relative magnitude of fluctuations follows as

\[
\frac{\sigma_E}{\overline{E}} = \left(\frac{k_B T^2 C_V}{\overline{E}}\right)^{1/2} \sim \frac{\mathcal{O}(N^{1/2})}{\mathcal{O}(N)} \sim \mathcal{O}(N^{-1/2})
\]

- In the thermodynamic limit \((N \to \infty)\), relative fluctuations become negligibly small.
- With \(N \to \infty\), each system of a canonical ensemble will have the same value of \(E = \overline{E}\) – it degenerates to a microcanonical ensemble.
Intermezzo: Binomial distribution for large numbers

\[(x + y)^N = \sum_{N_1=0}^{N} \frac{N!x^{(N-N_1)}y^{N_1}}{N_1!(N - N_1)!} = \sum_{N_1,N_2} * \frac{N!x^{N_2}y^{N_1}}{N_1!N_2!}, \quad N = N_1 + N_2\]

Binomial coefficients: \(f(N_1)\).

Maximum term: \(d \ln f(N_1)/dN_1 = 0\).

Expand \(\ln f(N_1)\) around its maximum at \(N_1^*\):

\[\ln f(N_1) = \ln f(N_1^*) + \frac{1}{2}(N_1 - N_1^*)^2 \left(\frac{d^2 \ln f(N_1^*)}{dN_1^2}\right) + \mathcal{O}\left((N_1 - N_1^*)^3\right)\]

with \(d^2 \ln(f(N_1^*))/dN_1^2 = -4/N\) we obtain

\[f(N_1) = f(N_1^*) \exp\left(-\frac{2(N_1 - N_1^*)^2}{N}\right)\text{ cf. Gauss: } P(x) = \frac{1}{\sigma \sqrt{2\pi}} e\left(-\frac{(x-x_0)^2}{2\sigma^2}\right)\]

Gaussian with \(\sigma \approx \mathcal{O}(N^{1/2})\) — for \(N \to \infty\) sharp peak around \(N_1^*\)
Probability of observing a certain deviation from $\overline{E}$

Most probable term $E^* \approx \overline{E}$ occurs at maximum of $P(E) \sim C\Omega(E)e^{-\beta E}$ (equivalently, maximum of $\ln P(E)$):

$$
\left( \frac{\partial \ln P(E)}{\partial E} \right)_E = \left( \frac{\partial \ln \Omega}{\partial E} \right)_E - \beta = 0
$$

The second derivative at $\overline{E}$ then follows

$$
\left( \frac{\partial^2 \ln P}{\partial E^2} \right)_E = \left( \frac{\partial^2 \ln \Omega}{\partial E^2} \right)_E = \left( \frac{\partial^2 \ln \Omega(\overline{E})}{\partial \overline{E}^2} \right)_E = \frac{\partial}{\partial \overline{E}} \left( \frac{\partial \ln \Omega(\overline{E})}{\partial \overline{E}} \right)_E
$$

$$
\ldots = \frac{\partial}{\partial \overline{E}} \left( \frac{\partial \ln \Omega}{\partial E} \right)_E = \frac{\partial \beta}{\partial \overline{E}} = -\frac{1}{k_B T^2} \frac{\partial T}{\partial \overline{E}} = -\frac{1}{k_B T^2 C_V}
$$
Probability of observing a certain deviation from $\bar{E}$

Now we use

$$\left( \frac{\partial^2 \ln P}{\partial E^2} \right)_E = -\frac{1}{k_B T^2 C_V}$$

in Taylor expansion of $\ln P(E)$ around the most probable term:

$$\ln P(E) = \ln P(\bar{E}) - \frac{(E - \bar{E})^2}{2k_B T^2 C_V} + \mathcal{O}((E - \bar{E})^3)$$

which we rewrite as

$$P(E) = P(\bar{E}) \exp\left(-\frac{(E - \bar{E})^2}{2k_B T^2 C_V}\right)$$

i.e. a Gaussian distribution with $\sigma = (k_B T^2 C_V)^{1/2}$.

1 mol of an ideal gas: probability that $(E - \bar{E})/\bar{E} > 0.1\%$ is $\mathcal{O}(e^{-10^6})$. 
...Probability of observing a certain deviation from $\overline{E}$

![Graph showing probability of fluctuation in $E$ versus number of particles, $N$, with different levels of fluctuation (10%, 1%, 0.1%, 0.01%).]
Energy fluctuations in small systems

- Same simulations of a Lennard-Jones system
- Different $N$, otherwise the same parameters: temperature, density, ...
Fluctuations in $N$ (grandcanonical ensemble)

Analogous to the case of $E$:

$$\sigma_N^2 = (\overline{N} - \overline{N})^2 = \overline{N}^2 - \overline{N}^2 = \sum_{N,j} N_j^2 P_{N,j} - \overline{N}^2 \text{ with } P_{N,j} = \frac{e^{-\beta E_{N,j}} e^{-\gamma N}}{\Xi(\nu, V, T)}$$

We can rewrite

$$\sum_{N,j} N_j^2 P_{N,j} = \frac{1}{\Xi} \sum_{N,j} N^2 e^{-\beta E_{N,j}} e^{-\gamma N} = -\frac{1}{\Xi} \frac{\partial}{\partial \gamma} \sum_{N,j} N e^{-\beta E_{N,j}} e^{-\gamma N}$$

$$\ldots = -\frac{1}{\Xi} \frac{\partial}{\partial \gamma} (\overline{N} \Xi) = -\frac{\partial \overline{N}}{\partial \gamma} - \overline{N} \frac{\partial \ln \Xi}{\partial \gamma} = k_B T \frac{\partial \overline{N}}{\partial \mu} + \overline{N}^2$$

Thus using $\kappa = -1/V (\partial V/\partial p)_{N,T}$

$$\sigma_N^2 = k_B T \left( \frac{\partial \overline{N}}{\partial \mu} \right)_{V,T} = \overline{N}^2 k_B T \kappa \frac{\kappa}{V} \text{ because } \left( \frac{\partial \mu}{\partial \overline{N}} \right)_{V,T} = -\frac{V^2}{N^2} \left( \frac{\partial p}{\partial V} \right)_{N,T}$$
Relative magnitude of fluctuations in $N$

For an ideal gas:

$$\kappa = \frac{1}{p} \quad \text{where (by definition)} \quad \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{N,T}$$

The relative magnitude of fluctuations follows as

$$\frac{\sigma_N}{N} = \frac{1}{N} \left( \frac{N^2 k_B T \kappa}{V} \right)^{1/2} = \left( \frac{k_B T \kappa}{V} \right)^{1/2} = \mathcal{O}(N^{-1/2})$$

With $V \to \infty$ (thermodynamic limit), the fluctuations in $N$ become negligibly small (except criticality)!

By procedure analogous with the derivation of $P(E)$, we obtain

$$P(N) = P(N) \exp \left( -\frac{(N - \overline{N})^2}{2k_B T (\partial \overline{N}/\partial \mu)_{V,T}} \right)$$

\[1\] See McQuarrie: Statistical Mechanics for the full derivation
Equivalence of ensembles in thermodynamic limit

In general

\[ Q(N, V, T) = \sum_{E} \Omega(N, V, E) e^{-E/k_B T} \]

With \( N \to \infty \) only the term with \( E^* = \overline{E} \) dominates the sum:

\[ Q(N, V, T) = \Omega(N, V, E) e^{-E/k_B T} \]

From

\[ A = -k_B T \ln Q(N, V, T) \]

we obtain that

\[ k_B \ln \Omega(N, V, \overline{E}) = \frac{\overline{E} - A}{T} = S \]