Lecture 18 - Thermodynamics in the NVT ensemble

Last time we got a probability mass function for the NVT ensemble. For NVE, we used our PMF to get the density of states Ω, which we related to the entropy using Boltzmann's formula. We're going to follow an analogous procedure here.

A. The Partition Function

We have a probability mass function for the canonical ensemble,

$$P(E_i) = \frac{\exp(-\beta E_i)}{\sum_{i=1}^{M} \exp(-\beta E_i)}$$

This is for the discrete case from quantum mechanics.

← Sum over all NVT ensemble.

Sometimes you will see the PMF written differently.

$$P(E_i) = \frac{\exp(-\beta E_i)}{\sum_{j=1}^{J} \Omega_j \exp(-\beta E_j)}$$

← sum over energy levels

↖ occupation # of energy levels is the # of microstates of an NVE ensemble.

Analogous to the NVE ensemble, the denominator, the "constant" that normalizes the probability plays a special role. In the NVT ensemble, this quantity is called the canonical partition function,

$$Q = \sum_{i=1}^{M} e^{-\beta E_i} = \sum_{j=1}^{J} \Omega_j e^{-\beta E_j}$$

Weighted sum of the # of microstates based on their energy

We would also like the continuous probability density that relies on classical mechanics. The naïve probability density is

$$\rho(\underline{x}) = \frac{\exp(-\beta H(\underline{x}))}{\int_{\Gamma} \exp(-\beta H(\underline{x}))\, d\underline{x}}$$

$\underline{x} = \{\underline{p}, \underline{q}\}$

$H(\underline{x})$: Hamiltonian

Γ: phase space volume.

However, this probability density has a problem. The normalization

constant (the denominator) is not the same as the partition function Q in the discrete case. We want the statistical physics to be the same regardless of whether we use classical mechanics or quantum mechanics.

To get Q for the continuous probability density to be the same as for the PMF, our phase space integrals need to account for quantum effects and overcounting,

$$\rho_{NVE} = \frac{\delta(H-E)}{\Sigma} \qquad \rho_{NVT} = \frac{e^{-\beta H}}{\int_\Gamma e^{-\beta H} d\underline{X}}$$

← overcounts small scales and double counts indistinguishable particles

$$\Omega = \frac{\Sigma}{h^{3N} N!} \qquad Q = \frac{1}{h^{3N} N!} \int_\Gamma e^{-\beta H} d\underline{X}$$

the proper count of microstates

It is useful to define a weighted probability density to make this more seamless. To do so, we require that the PMF and PDF give the same probability,

$$P(E_i) = \int_\Gamma \tilde{\rho}(H(\underline{X}))\, \delta(H-E_i)\, d\underline{X}$$

$\tilde{\rho}(X)$: corrected density

$$\tilde{\rho}(X) = \frac{\rho(X)}{w(X)}$$

$w(X)$ is the correction (a weight)

So,

$$P(E_i) = \int_\Gamma \frac{e^{-\beta H}}{\int_\Gamma e^{-\beta H} d\underline{X}} \frac{\delta(H-E_i)}{w(X)} d\underline{X} = \frac{\int_\Gamma e^{-\beta H} w^{-1} \delta(H-E_i)\, d\underline{X}}{\int_\Gamma e^{-\beta H} d\underline{X}}$$

$\int_\Gamma e^{-\beta H} d\underline{X}$ is constant and can come out of the integral

If $w^{-1}(X) = h^{3N} N!$ then,

$$P(E_i) = \frac{\int_\Gamma e^{-\beta H} \delta(H-E_i)\, d\underline{X}}{\frac{1}{h^{3N} N!} \int_\Gamma e^{-\beta H} d\underline{X}} = \frac{e^{-\beta E_i}}{Q} \quad \therefore$$

Now, we can give our weighted densities,

$$\tilde{\rho}_{NVE} = \frac{\delta(H-E)}{\Omega} \quad \text{and} \quad \int_\Gamma \tilde{\rho}_{NVE} \cdot \frac{1}{h^{3N} N!}\, d\underline{X} = 1$$

$$\tilde{\rho}_{NVT} = \frac{e^{-\beta H}}{Q} \quad \text{and} \quad \int_\Gamma \tilde{\rho}_{NVT} \cdot \frac{1}{h^{3N} N!}\, d\underline{X} = 1$$

Correct "measure" of phase space. Like spherical coordinates. We need the right way to add up things in space.

$$\rho(x) = \tilde{\rho}(x)\, \omega(x)$$

↑ Book PDF ↑ Properly weighted PDF

and we can define an ensemble average.

$$\langle M \rangle = \int_\Gamma M(\underline{X})\, \rho(\underline{X})\, d\underline{X} = \int_\Gamma M(\underline{X})\, \tilde{\rho}(\underline{X})\, \frac{1}{h^{3N} N!}\, d\underline{X}$$

Example:

$$\langle \beta H \rangle = \frac{1}{Q h^{3N} N!} \int_\Gamma \beta H\, e^{-\beta H}\, d\underline{X}$$

$\langle \beta H \rangle = \beta \langle H \rangle$ ← average energy ($\langle H \rangle = U$) ← internal energy (not potential)

$$\beta U = \frac{1}{Q h^{3N} N!} \int_\Gamma \beta H\, e^{-\beta H}\, d\underline{X}$$

B. Generalizing Boltzmann's Formula

We want to connect Q to thermodynamics. For the microcanonical ensemble, we saw that

$$S = k_B \ln \Omega$$ ← Entropy is a count of microstates. in the NVE ensemble.

How do we generalize this for a case where the number of microstates is weighted by a temperature? We need a more nuanced version of Boltzmann's equation for entropy. In our NVE interpretation of entropy, we said entropy was related to the count of microstates (with

a logarithm so that entropy is extensive, i.e. doubling volume = squaring # microstates = doubling entropy).

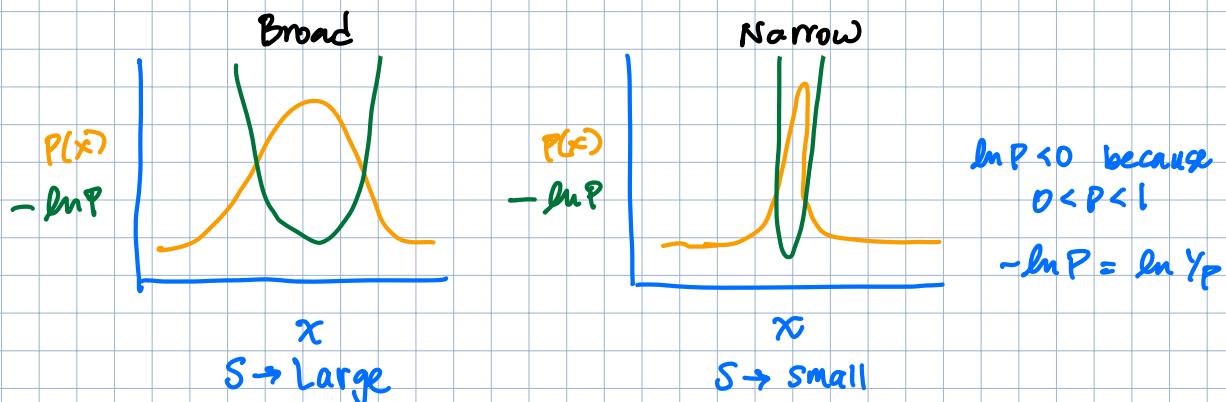
But what if we think in terms of the probability density? We can think of entropy as a measure of how broad the probability distribution is over the microstates. If the distribution is narrow (e.g. one state dominates), then the entropy is low. If the distribution is broad, then the entropy is high. In other words, if you are highly uncertain about which microstate you will observe, the entropy is high.

Using this idea, we can define entropy as,

$$S = -k_B \langle \ln P \rangle$$ ← ensemble average of ln Probability (PMF)

recall $$\langle M \rangle = \frac{1}{h^{3N} N!} \int_\Gamma M\, P(\underline{x})\, d\underline{x}$$

$$S = \frac{-k_B}{h^{3N} N!} \int_\Gamma P \ln P \, d\underline{x}$$ ← integrate over the microstates



Product of P and −lnP is moderate through a wide range of x. Have regions where both aren't small!

Product of P and −lnP is small, because −lnP cancels out P right at the peak!

This definition of entropy is equivalent to Boltzmann's formula for the NVE ensemble. But, it works for other distributions, too. A "more useful" third postulate for stat thermo.

Proof:

For the NVE ensemble $P = 1/\Omega$. Subbing into our new definition,

$$S = -\frac{k_B}{h^{3N} N!} \int_\Gamma \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) d\underline{x} = \frac{-k_B}{h^{3N} N!} \frac{1}{\Omega} \ln\frac{1}{\Omega} \int_\Gamma d\underline{x}$$

Ω is a constant $\qquad \int_\Gamma d\underline{x} = \sum = h^{3N} N! \, \Omega$

$$S = -k_B \frac{1}{\Sigma} \ln\frac{1}{\Omega} \Sigma = -k_B \ln\frac{1}{\Omega} = k_B \ln \Omega \checkmark$$

Example: Intuition about probability-defined entropy

Fair Die: $\Omega = 6$, $P = \frac{1}{6}$

$$S = k_B \ln \Omega = k_B \ln 6 \checkmark \approx 1.79\, k_B$$

$$S = -k_B \langle \ln 1/6 \rangle = -k_B \sum_i P_i \ln P_i$$

$$= -k_B \left(\frac{1}{6}\ln\frac{1}{6} + \frac{1}{6}\ln\frac{1}{6} + \dots + \frac{1}{6}\ln\frac{1}{6}\right) = -k_B \ln 1/6 = k_B \ln 6 \checkmark$$

Unfair Die:

1	2	3	4	5	6
$\frac{1}{20}$	$\frac{1}{20}$	$\frac{1}{20}$	$\frac{3}{4}$	$\frac{1}{20}$	$\frac{1}{20}$

Now we can't just count microstates.

$$S = -k_B \langle \ln P \rangle = -k_B \sum_i P_i \ln P_i$$

$$= -k_B \cdot \left(5 \cdot \frac{1}{20}\ln\frac{1}{20} + \frac{3}{4}\ln\frac{3}{4}\right) = -k_B \left(\frac{1}{4}\ln\frac{1}{20} + \frac{3}{4}\ln\frac{3}{4}\right)$$

$$= -\frac{1}{4} k_B \ln\left(\frac{1}{20}\cdot\frac{3^3}{4^3}\right) = -\frac{1}{4} k_B \ln\left(\frac{9}{1280}\right) = \frac{k_B}{4}\ln\left(\frac{1280}{9}\right) \approx 1.24\, k_B$$

Comments:

- A uniform distribution with more states is more spread out. A die with more sides has a larger entropy.
- An unfair die has a lower entropy, because we have more concentrated probability in one state. More certainty. Less uncertainty.

C. Connecting the NVT ensemble to thermodynamics

We now have a more general definition of entropy that we can apply to the canonical ensemble.

$$S = -k_B \langle \ln \tilde{\rho} \rangle \qquad \tilde{\rho} = \frac{1}{Q} e^{-\beta H}$$

$$S = -\frac{k_B}{h^{3N} N!} \int_\Gamma \tilde{\rho} \ln \tilde{\rho} \, d\underline{X} = \frac{-k_B}{h^{3N} N!} \int \frac{1}{Q} e^{-\beta H} \ln\left(\frac{1}{Q} e^{-\beta H}\right) d\underline{X}$$

$$= \frac{-k_B}{h^{3N} N! \, Q} \int_\Gamma \left[e^{-\beta H} \ln\left(\frac{1}{Q}\right) + e^{-\beta H} \ln\left(e^{-\beta H}\right) \right] d\underline{X}$$

$$= -k_B \left[\frac{-\ln Q}{Q} \frac{1}{h^{3N} N!} \int_\Gamma e^{-\beta H} \, d\underline{X} + \frac{1}{h^{3N} N!} \int_\Gamma -\beta H \, e^{-\beta H} \, d\underline{X} \right]$$

Definition of Q $\qquad$ $\langle \beta H \rangle = \beta U$ (Internal Energy)

$$= -k_B \left(-\ln Q \cdot \frac{Q}{Q} - \beta U \right) = k_B \ln Q + k_B \beta U$$

$$S = k_B \ln Q + k_B \beta U$$

This seems a little messy. There is a better relationship. Recall that the Helmholtz free energy is,

$$A = U - TS$$

$$A = U - T(k_B \ln Q + k_B \beta U) = U - k_B T \ln Q - k_B T \beta U$$

$\beta = \frac{1}{k_B T}$

$$= U - k_B T \ln Q - U$$

$$\boxed{A = -k_B T \ln Q}$$

It is useful to use thermodynamic relations to get other quantities (U, S, C_V, P) in terms of the partition function (see Appendix).

D. The Ideal Gas

We already solved the ideal gas in the NVE ensemble, so we will be quick. But it is still an important derivation to see.

Step 1: Determine the Hamiltonian

Recall that

$$H(\underline{q},\underline{p}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

Ideal Gas Hamiltonian for particles of equal mass, m.

Step 2: Compute the partition function

$$Q = \frac{1}{h^{3N} N!} \int d\underline{q} \int d\underline{p}\ \exp(-\beta H)$$

$H = H(p)$ only so we can pull out $\int d\underline{q} = V^N$

$$Q = \frac{V^N}{h^{3N} N!} \int d\underline{p}\ \exp\left(-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}\right)$$

$\exp(\sum x_i) = \prod_i \exp(x_i)$

$$= \frac{V^N}{h^{3N} N!} \prod_{i=1}^{3N} \int dp_i\ \exp\left(-\beta p_i^2/2m\right)$$

This is a Gaussian integral

$$\int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{2\sigma^2}\right) = \sqrt{2\pi}\,\sigma$$

$$\int_{-\infty}^{\infty} \exp\left(\frac{-\beta p_i^2}{2m}\right) = \sqrt{\frac{2\pi m}{\beta}} = \sqrt{2\pi m k_B T}$$

$\sigma^2 = m/\beta$

$$Q = \frac{V^N}{h^{3N} N!} \prod_{i=1}^{3N} (2\pi m k_B T)^{1/2} = \frac{V^N}{h^{3N} N!} (2\pi m k_B T)^{3N/2}$$

$$\boxed{Q = \frac{V^N}{\lambda_{th}^{3N} N!}}$$

Simpler formula than NVE

$$\lambda_{th} = \frac{h}{(2\pi m k_B T)^{1/2}}$$

thermal wavelength

$E = \frac{3}{2} N k_B T$

Step 3: Relate Q to A.

$$A = -k_B T \ln Q = -k_B T \ln\left(\frac{V^N}{\lambda_{th}^{3N} N!}\right)$$

$$= -k_B T \ln V^N + k_B T \ln \lambda_{th}^{3N} + k_B T \ln N!$$

$\ln N! \approx N \ln N - N$

$$= N k_B T \left(-\ln V + \ln \lambda_{th}^3 + \ln N - 1 \right)$$

$$\boxed{A = N k_B T \left[\ln\left(\frac{N\lambda_{th}^3}{V}\right) - 1 \right]} \qquad \lambda_{th} = \frac{h}{(2\pi m k_B T)^{1/2}} \propto T^{-1/2}$$

Step 4: Find other relevant thermodynamic functions

$$dA = -S\,dT - P\,dV \qquad S = -\left(\frac{\partial A}{\partial T}\right)_V$$

$$S = -\frac{\partial}{\partial T}\left[N k_B T \cdot \left(\ln\left(\frac{N\lambda_{th}^3}{V}\right) - 1 \right) \right]$$

$$= -N k_B \left[\ln\left(\frac{N\lambda_{th}^3}{V}\right) - 1 \right] - N k_B T \, \frac{\partial}{\partial T}\left[\ln\left(\frac{N\lambda_{th}^3}{V}\right) - 1 \right]$$

$$\left(\frac{N\lambda_{th}^3}{V}\right)^{-1} \frac{\partial}{\partial T}\left(\frac{N\lambda_{th}^3}{V}\right) = \left(\frac{N\lambda_{th}^3}{V}\right)^{-1} \frac{N}{V}\, 3\lambda_{th}^2 \, \frac{\partial \lambda_{th}}{\partial T}$$

$$\frac{\partial \lambda_{th}}{\partial T} = \frac{\partial}{\partial T}\left[\frac{h}{(2\pi m k_B T)^{1/2}} \right] = \frac{h}{(2\pi m k_B)^{1/2}} \left(-\frac{1}{2} T^{-3/2}\right) = \frac{-1}{2T} \frac{h}{(2\pi m k_B T)^{1/2}} = -\frac{\lambda_{th}}{2T}$$

$$\frac{\partial}{\partial T}\left[\ln\left(\frac{N\lambda_{th}^3}{V}\right) - 1 \right] = \left(\frac{N\lambda_{th}^3}{V}\right)^{-1} 3 \frac{N\lambda_{th}^2}{V} \left(-\frac{\lambda_{th}}{2T}\right)$$

$$= \left(\frac{N\lambda_{th}^3}{V}\right)^{-1} \cdot \left(-\frac{3}{2T}\right) \cdot \frac{N\lambda_{th}^3}{V} = -\frac{3}{2T}$$

$$S = -N k_B \left[\ln\left(\frac{N\lambda_{th}^3}{V}\right) - 1 \right] - N k_B T \left(-\frac{3}{2T}\right)$$

$$= -N k_B \left[\ln\left(\frac{N\lambda_{th}^3}{V}\right) - 1 \right] + \frac{3}{2} N k_B = N k_B \left[\ln\left(\frac{V}{N\lambda_{th}^3}\right) + \frac{5}{2} \right]$$

$$\boxed{\frac{S}{N k_B} = \ln\left(\frac{V}{N\lambda_{th}^3}\right) + \frac{5}{2}}$$

Sackur-Tetrode Equation
All else is the same as NVE.

E. Appendix – Thermodynamic Relations to the Partition Function

Internal Energy (U):

$$U = \frac{1}{h^{3N} N!} \int_\Gamma \frac{1}{Q} H e^{-\beta H} \, d\underline{X} \qquad \frac{\partial (e^{-\beta H})}{\partial \beta} = -H e^{-\beta H}$$

$$U = \frac{1}{h^{3N} N! \, Q} \int_\Gamma -\frac{\partial (e^{-\beta H})}{\partial \beta} \, d\underline{X} = \frac{-1}{h^{3N} N! \, Q} \frac{\partial}{\partial \beta} \int_\Gamma e^{-\beta H} \, d\underline{X}$$

$$U = -\frac{1}{Q} \frac{\partial}{\partial \beta} Q = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial T}{\partial \beta} \frac{\partial \ln Q}{\partial T} \qquad \beta = (k_B T)^{-1}$$

$$\frac{\partial \beta}{\partial T} = -(k_B T)^{-2} \cdot k_B = -\frac{1}{k_B T^2}$$

$$\frac{\partial T}{\partial \beta} = \left(\frac{\partial \beta}{\partial T}\right)^{-1} = -k_B T^2$$

$$\boxed{U = k_B T^2 \frac{\partial \ln Q}{\partial T} = -\frac{\partial \ln Q}{\partial \beta}}$$

Entropy (S):

$$S = k_B \ln Q + \frac{k_B}{k_B T} k_B T^2 \frac{\partial \ln Q}{\partial T}$$

$$\boxed{S = k_B \ln Q + k_B T \frac{\partial \ln Q}{\partial T}}$$

# of microstates + correction for temperature dependence

Pressure (P):

$$dA = -S\,dT - P\,dV \quad \Rightarrow \quad P = -\left(\frac{\partial A}{\partial V}\right)_T$$

$$A = -k_B T \ln Q$$

$$P = -\frac{\partial}{\partial V}\left(-k_B T \ln Q\right) = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$\boxed{P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T}$$

Heat Capacity (C_V):

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(k_B T^2 \frac{\partial \ln Q}{\partial T}\right)$$

$$= 2k_BT\left(\frac{\partial \ln Q}{\partial T}\right)_V + k_BT^2\left(\frac{\partial^2 \ln Q}{\partial T^2}\right)_V$$

This one is messy and rarely used.

People like to put it in terms of β.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{-\partial \ln Q}{\partial \beta}\right)$$

$$= \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta}\left(\frac{-\partial \ln Q}{\partial \beta}\right)$$

$\frac{\partial \beta}{\partial T} = \frac{-1}{k_BT^2}$ from above

$$\boxed{C_V = \frac{1}{k_BT^2}\left(\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_V}$$

F. Appendix: Why Gibbs Entropy formula needs $\tilde{p}$

There is a correction to the Gibbs entropy formula that Jaynes discovered in the 60's. The discrete version of Gibbs formula is correct.

$$S = -k_B \sum_i P_i \ln P_i \qquad P_i: \text{PMF} \qquad (*)$$

But when we go to the continuous probability density function, we have a problem.

$$P(a < x \leq b) = \int_a^b p(x)\,dx \qquad \text{(Assume 1D w.l.o.g.)}$$

For $\Delta x = b - a \ll 1$, this reduces to

$$P_i \approx p(x)\,\Delta x$$

Substituting into (*) gives

$$S = -k_B \sum_i p(x)\,\Delta x \ln[p(x)\,\Delta x]$$

In the limit that $\Delta x \to 0$, we get

$$S = -k_B \int p(x) \ln[p(x)\,dx]\,dx$$

As $dx \to 0$, $\ln 0 \to -\infty$!

This looks wrong. We have a problem.

To fix this, we need to divide by the "measure" or the dx, to make this cancel out. We have one more issue; we said our probability densities needed to account for quantum effects.

$$\rho_{NVE} = \frac{\delta(H-E)}{\Sigma} = \frac{\frac{1}{h^{3N}N!}\delta(H-E)}{\Omega} \qquad \Omega = \frac{\Sigma}{h^{3N}N!}$$

↖ the proper count of microstates

$$\rho_{NVT} = \frac{e^{-\beta H}}{\int_\Gamma e^{-\beta H}\, d\underline{X}} = \frac{\frac{1}{h^{3N}N!}e^{-\beta H}}{Q} \qquad Q = \frac{1}{h^{3N}N!}\int_\Gamma e^{-\beta H}\, d\underline{X}$$

So, to properly normalize our probability densities we have a weight of $\omega = 1/h^{3N}N!$ in the measure. In other words,

$$\int \tilde{\rho}(X)\, \underbrace{\omega(X)\, dx}_{\text{measure}} = 1 \qquad \omega = (h^{3N}N!)^{-1} \qquad \rho(x) = \tilde{\rho}(x)\,\omega(x)$$

So,

$$P_i \approx \tilde{\rho}(x_i)\,\omega(x_i)\,dx \quad \text{as} \quad \Delta x \to 0$$

To fix our entropy formula, we need to divide by $\omega(x)dx$ inside the log:

$$S = -k_B \int \tilde{\rho}(x)\,\omega(x)\, \ln\left[\frac{\tilde{\rho}(x)\,\omega(x)\,dx}{\omega(x)\,dx}\right] dx$$

$$S = -k_B \int \tilde{\rho}(x)\, \ln[\tilde{\rho}(x)]\, \omega(x)\, dx$$

↖ properly normalized.

$$S = -k_B \langle \ln \tilde{\rho} \rangle$$

↖ properly normalized $\tilde{\rho}(x)$ with correct $\langle\,\rangle$ with right measure

this changes the definition of the ensemble average

$$\langle M \rangle = \int_\Gamma M\, \tilde{\rho}\, \frac{1}{h^{3N}N!}\, d\underline{X}$$

So, the book gives

$$\rho_{NVE} = \frac{\delta(H-E)}{\Sigma} \quad \text{and} \quad \int \rho_{NVE}\, d\underline{X} = 1$$

$$\rho_{NVT} = \frac{e^{-\beta H}}{\int_\Gamma e^{-\beta H} d\underline{x}} \quad \text{and} \quad \int \rho_{NVT}\, d\underline{x} = 1$$

But, a more appropriate way to write the probability density is

$$\tilde{\rho}_{NVE} = \frac{\delta(H-E)}{\Omega} \quad \text{and} \quad \int \tilde{\rho}_{NVE} \cdot \frac{1}{h^{3N} N!}\, d\underline{x} = 1$$

$$\tilde{\rho}_{NVT} = \frac{e^{-\beta H}}{Q} \quad \text{and} \quad \int \tilde{\rho}_{NVT} \cdot \underbrace{\frac{1}{h^{3N} N!}\, d\underline{x}} = 1$$

correct measure of phase space!