How does one find probability distributions for arbitrary systems?

Consider a big system consisting of very many particles. Split it into <u>subsystems</u> which also have lots of particles.
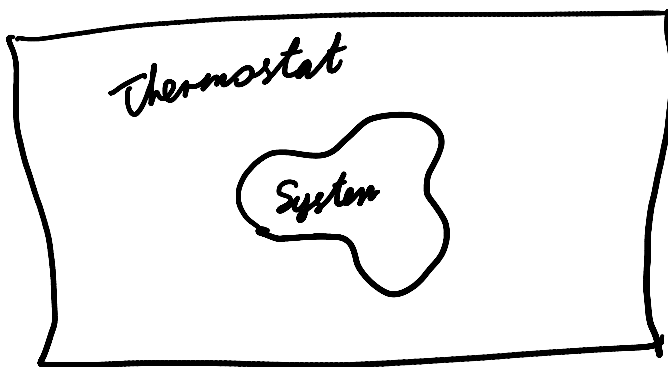
Energy of a subsystem $\mathcal{E} \propto R^3 \propto N$, N is the number of particles in each subsystem

<u>Interaction energy</u> $\mathcal{E}_{surf} \propto R^2$

$$\frac{\mathcal{E}_{surf}}{\mathcal{E}} \propto \frac{R^2}{R^3} \propto \frac{1}{R} \propto N^{-\frac{1}{3}}$$

The interaction becomes negligible when the number of particles is large. Then the subsystems are quasiindependent.

$$E \approx \sum_i \mathcal{E}_i$$

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Pick one subsystem there. While it is in equilibrium, its energy fluctuates. We want to find the

its energy fluctuates. We want to find the probability of states of this subsystem

Now Subsystem $\longrightarrow$ System
Rest of the system $\longrightarrow$ Thermostat

$$\hat{H} = \hat{H}_{Syst} + \hat{H}_{env} + \hat{V}_{Syst-env}$$

Gibbs distribution

$$w_i = \frac{1}{Z} e^{-\frac{E_i}{T}} \qquad , \quad Z = \sum_i e^{-\frac{E_i}{T}}$$

Another way to write it is

$$\hat{\rho} = \frac{1}{Z} e^{-\frac{\hat{H}}{T}}$$

// For the basis of eigenstates
$$\hat{\rho} = \sum_n \rho_{nn} |n\rangle\langle n|$$

Reminder: the density matrix is such an operator that
1) $\hat{\rho} = \hat{\rho}^+$
2) $\hat{\rho} > 0$
3) $\text{Tr}\, \hat{\rho} = 1$
4) $\forall$ observable $\hat{M}$: $\langle\hat{M}\rangle = \text{Tr}(\hat{\rho}\,\hat{M})$

$$\cdots \quad \langle i|\hat{M}|i\rangle e^{-\frac{E_i}{T}} \Big)$$

$$\langle \hat{M} \rangle = \frac{1}{Z} \text{Tr}\left(\hat{\rho}\,\hat{M}\right) \left(= \frac{1}{Z} \sum_i \langle i | \hat{M} | i \rangle e^{-\frac{E_i}{T}} \right)$$

Transition to classical statistics

$H(\vec{P}, \vec{Q})$ - the classical limit of the quantum Hamiltonian

To transition to classical mechanics, the level spacing $\Delta \varepsilon_i = \varepsilon_{i+1} - \varepsilon_i$ has to be small compared to the temperature T. Then $e^{-\frac{E_i}{T}}$ may be replaced by $e^{-\frac{E}{T}}$.

Now we will characterise the state of the system by classical $\vec{P}, \vec{Q}$. That „classical state" has the energy $E(\vec{P}, \vec{Q})$.

The number of states in the energy interval is

$$\Omega(E)\, d = \frac{\partial \Gamma}{\partial E} \frac{dE}{(2\pi \hbar)^f}$$

$$\boxed{\begin{aligned} dw &= \frac{e^{-\frac{E}{T}}}{Z} \frac{\partial \Gamma}{\partial E} \frac{dE}{(2\pi \hbar)^f} \\[2mm] Z &= \frac{1}{(2\pi \hbar)^f} \int e^{-\frac{E}{T}} \frac{\partial \Gamma}{\partial E}\, dE = \frac{1}{(2\pi \hbar)^f} \int e^{-\frac{E(\vec{P}, \vec{Q})}{T}}\, d\vec{P}\, d\vec{Q} \end{aligned}}$$
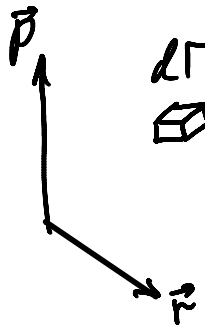
– classical Gibbs distribution

In terms of the statistical distribution function

$$\rho(\vec{P}, \vec{Q}) = \text{const} \cdot e^{-\frac{E(\vec{P}, \vec{Q})}{T}}$$

$$\left(\text{const} = \frac{1}{(2\pi \hbar)^f Z} \right)$$

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One may apply that to a classical ideal gas

One may derive Maxwell distribution from here:

$$d\Gamma = dp_x\, dp_y\, dp_z\, dx\, dy\, dz$$

$$d\Gamma = p^2 dp \, \sin\theta \, d\theta \, d\varphi \, dV$$

we could have worked in momentum representation

$$dw = const \cdot e^{-\frac{p^2}{2mT}} p^2 dp$$

$$const = \frac{1}{V} \left(\frac{1}{2\pi mT} \right)^{\frac{3}{2}}$$