The Thermodynamic Limit

- let $A(N,V,T)$ be an extensive quantity, assume

$$\lim_{\substack{N,V\to\infty \\ n \text{ finite}}} \frac{A(N,V,T)}{V} = a(n,T) = \text{finite}$$

NB: $N, V, A \to$ extensive

$\Rightarrow$ in this case the thermodynamic limit exists

- in some cases this limit does not exist

example: gravitational potential

$$-G\frac{(\rho V)^2}{V^{1/3}} \sim -\rho^2 V^{5/3}$$

$$\frac{E_G}{V} \xrightarrow[V\to\infty]{} -V^{2/3} \to -\infty$$

- ideal gas: it exists!

$$E = \frac{3NkT}{2} \rightarrow \frac{E}{V} = \epsilon = \underline{\frac{3nkT}{2}}$$

finite as $N,V\to\infty$ n finite

gravitational potential: long range

ideal gas: not even short range

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~~usually~~ the thermodynamic limit exists due to the short range nature of the interactions

<u>illustration:</u> 2D Ising model

- consider a lattice of size $2N \times 2N = 4N^2$

<u>a.)</u> assume all spins interact

$$H = -J \sum_{i \neq j} S_i S_j$$

at $T = 0$ $\quad E \sim N^4$

$$\frac{E}{4N^2} \xrightarrow[N \to \infty]{} \infty$$

thermodynamic limit does not exist

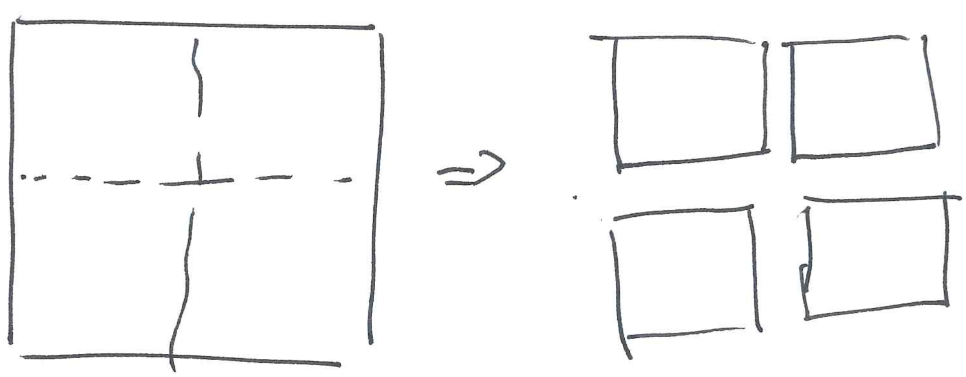
(with renormalized interaction J/N^2

thermodynamic limit exists and mean-field solution is exact) b.) Ising model with only short-range interactions (3)

$$H = -J \sum_{\langle i,j \rangle} S_i S_j$$

Sum over nearest neighbor pairs only!

consider cutting $2N \times 2N$ lattice up into 4 subsystems



boundaries of the four subsystems contribute at least $-4JN$ at most $+4JN$ to the energy

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$$(Z_N)^4 e^{-4JN\beta} \leq Z_{2N} \leq (Z_N)^4 e^{4JN\beta}$$

Z_N - partition function of one of the four blocks

Z_{2N} - partition function of $2N \times 2N$ lattice using the general result $F = -\frac{1}{\beta} \ln Z$ (4)

$$-\frac{4 \ln Z_N}{\beta} + 4JN \geq -\frac{\ln Z_{2N}}{\beta} \geq -\frac{4 \ln Z_N}{\beta} - 4JN$$

$$\Rightarrow -\frac{\cancel{4}}{\beta}\frac{\ln Z_N}{\cancel{4}N^2} + \frac{J}{N} \geq -\frac{\ln Z_{2N}}{\beta 4 N^2} \geq -\frac{4 \ln Z_N}{\beta 4 N^2} - \frac{\cancel{4}\sigma}{N}$$

$$f_N + \frac{\sigma}{N} \geq f_{2N} \geq f_N - \frac{J}{N}$$

as $N \to \infty \Rightarrow f_N = f_{2N} \Rightarrow$ thermodynamic limit exists

$\Rightarrow$ can also be cast as $(f_{2N} - f_N) \leq \frac{J}{N}$

$= \text{const} \frac{N}{N^2} \sim \frac{L}{A}$

$L \to$ length of boundary

$A \to$ area

$\Rightarrow$ in 3D we will have $\frac{\text{area}}{\text{volume}}$ for boundary contribution

Classical Statistical Mechanics

* classical limit

* in many cases classical mechanics is sufficient, and when this is the case it is also advantageous to do so, since the mathematical machinery of classical mechanics is much simpler than that of quantum mechanics
* but one must be careful! remember that even the classical partition function includes "quantal" factors, e.g. h^{3N}, $N!$ (for indistinguishable particles)
* partition functions are traces

$$\mathrm{Tr}\, e^{-\beta H}$$

the classical limit

$$\mathrm{Tr} \xrightarrow{\text{classical}} \frac{1}{N!} \int \frac{d\vec{p}_1 \dots d\vec{p}_N \, d\vec{r}_1 \dots d\vec{r}_N}{h^{3N}}$$

* based on this correspondence one can express averages, ~~based~~ and the quantal factors cancel

* average: in QM $\hat{A}$ (operator)
in CM $A(p,q)$ (function of p and q)

average:

$$\langle A\rangle = \frac{\mathrm{Tr}\, A e^{-\beta H}}{\mathrm{Tr}\, e^{-\beta H}} \longleftrightarrow \frac{\int d\vec{p}_1 \dots d\vec{p}_N\, d\vec{r}_1 \dots d\vec{r}_N\, e^{-\beta H(\vec{p},\vec{r})} A(\vec{p},\vec{r})}{\int d\vec{p}_1 \dots d\vec{p}_N\, d\vec{r}_1 \dots d\vec{r}_N\, e^{-\beta H(\vec{p},\vec{r})}}$$

($H(\vec{p},\vec{r})$ and $A(\vec{p},\vec{r})$ are functions of all momenta and all coordinates)

in $\langle A\rangle$ neither h^{3N} nor $N!$ appears

(they appear in the entropy! unusual quantity from this point of view)

* how can we tell if the classical limit is appropriate? $\lambda/d \to 0$

λ - de Broglie wave length

d - typical length scale in system (interparticle distance on average)

Maxwell distribution

classical system: momentum and coordinate contributions can be handled separately (NOT TRUE FOR A QUANTUM SYSTEM!)

$$H(\vec{p},\vec{q}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(\vec{q}_1 \dots \vec{q}_N)$$

$$Z = \frac{1}{h^{3N} N!} \int d\vec{p}_1 \dots d\vec{p}_N \, d\vec{q}_1 \dots d\vec{q}_N \, e^{-\beta \sum_i \frac{p_i^2}{2m} - \beta V(\vec{q}_1,\dots,\vec{q}_N)}$$

$$= Z_K Z_U$$

$$Z_K = \frac{V^N}{h^{3N} N!} \int d\vec{p}_1 \dots d\vec{p}_N \, e^{-\beta \sum_i \frac{p_i^2}{2m}} = \frac{V^N}{h^{3N} N!} \left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

$$Z_U = \frac{\int \dots \int d\vec{q}_1 \dots d\vec{q}_N \, e^{-\beta V(\vec{q}_1,\dots,\vec{q}_N)}}{V^N}$$

Z_K – partition function of an ideal gas

Z_U – configuration integral ($Z_U = 1$ for ideal gas)

* consider average of some momentum dependent quantity:
$$\langle g(\vec{p}_i) \rangle = \frac{\int d\vec{p}_i \, e^{-\beta p_i^2/2m} \, g(\vec{p}_i)}{\int d\vec{p}_i \, e^{-\beta p_i^2/2m}}$$

(all other momenta and all coordinates cancel)

$$\langle g(\vec{p})\rangle = \int d\vec{p}\, P(\vec{p})\, g(\vec{p})$$

$$P_p(\vec{p}) = \frac{e^{-\frac{\beta p^2}{2m}}}{\int d\vec{p}\, e^{-\frac{\beta p^2}{2m}}} = \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\frac{\beta p^2}{2m}}$$

velocity distribution

$$\langle f(\vec{v})\rangle = \frac{\int d\vec{v}\, e^{-\beta\frac{mv^2}{2}} f(\vec{v})}{\int d\vec{v}\, e^{-\beta\frac{mv^2}{2}}} = \left(\frac{\beta m}{2\pi}\right)^{3/2} \int e^{-\beta\frac{mv^2}{2}} f(\vec{v})\, d\vec{v}$$

$$\boxed{P_v(\vec{v}) = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\beta\frac{mv^2}{2}}}$$

can show that: $\langle p_x^2\rangle = mkT$ $\quad \langle v_x^2\rangle = \frac{kT}{m}$

average kinetic energy:

$$\langle \tfrac{1}{2}mv^2\rangle = \langle \tfrac{1}{2}m(v_x^2+v_y^2+v_z^2)\rangle = \frac{3kT}{2}$$

$$E = \frac{3}{2}NkT$$

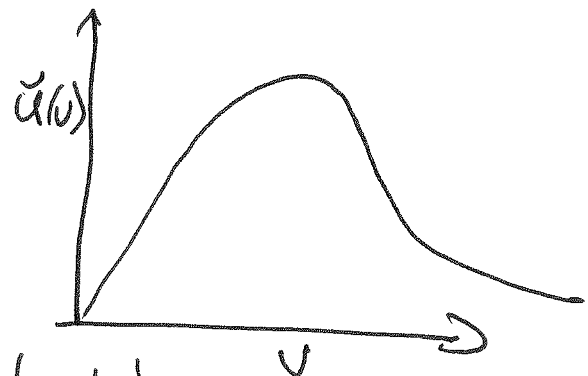
Maxwell-Boltzmann distribution $\varphi(\vec{v}) = \varphi(v)$

distribution of speeds

$$\tilde{\varphi}(v)\,dv = \int d\Omega\, v^2\, dv\, \varphi(\vec{v})$$

$$= 4\pi \underbrace{v^2 \varphi(v)}\, dv$$

$$\underline{\tilde{\varphi}_{MB}(v) = 4\pi\left(\frac{\beta m}{2\pi}\right)^{3/2} v^2 e^{-\beta\frac{mv^2}{2}}} \Rightarrow$$



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Maxwell-Boltzmann distribution