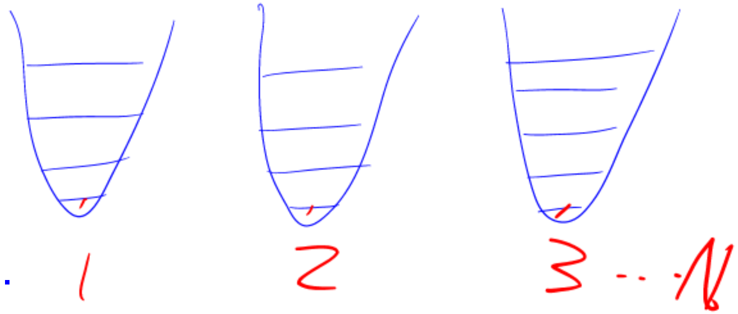
Chapter 2.4: Microcanonical Examples



Example 1: independent quantum oscillators $\varepsilon_j = \hbar\omega(n_j + \tfrac{1}{2}),\quad j = 1,2,3$.

Energy $E = \sum_j \varepsilon_j$	number of quanta $R = \sum_j n_j = \frac{E}{\hbar\omega} - \frac{3}{2}$		number of states Ω
$\|0\rangle$ $\hbar\omega\frac{3}{2}$	0	1 2 3 0 0 0	1
$\|1\rangle$ $\frac{5}{2}\hbar\omega$	1	1 0 0 0 1 0 0 0 1	3
$\|2\rangle$ $\frac{7}{2}\hbar\omega$	2	200 110 020 101 002 011	6
$\|3\rangle$ $\frac{9}{2}\hbar\omega$	3		10
$\|4\rangle$ $\frac{11}{2}\hbar\omega$	4		15

Problem: $\frac{\partial S}{\partial E}$ not easily defined since E discrete

Exercise next week!

$$\Omega(R,N) = \frac{(R+N-1)!}{(N-1)!\,R!}$$

for $N, R \gg 1$ derivative "ok"

$S = k_B \ln \Omega(E)$ increases with E

For Microcanonical ensemble to work large N and relatively large E

long molecule, but rolled up

Example 2: Polymer as a random walk

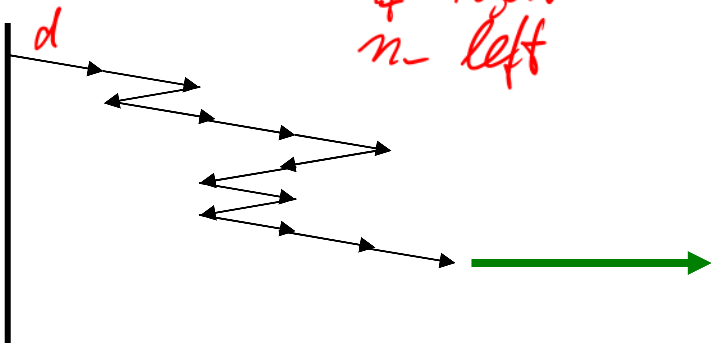
two parameters L, N

or alternatively n_+, N

Simplification: each segment can point left or right $N = n_+ + n_- \gg 1$

n_+ right

n_- left



$$F_L = \text{generalized Force to } L$$

$$= T\left(\frac{\partial S}{\partial L}\right)_{\text{rest}}$$

$$L = d(n_+ - n_-)$$

$$\Omega(L,N) = \Omega(n_+,N) = \binom{N}{n_+} = \frac{N!}{(N-n_+)!\, n_+!}$$

$=$ # of possibilities of picking n_+ elements out of N

Number of states at a given $N = n_+ + n_-$ and length $L = d(n_+ - n_-) = d(2n_+ - N)$

$dn_+ = \frac{1}{2}\left(\frac{L}{d} + N\right)$

$$\Omega(L,N) = \binom{N}{n_+} = \frac{N!}{(N-n_+)!\,n_+!}$$

Stirling

$x! \approx \sqrt{2\pi x}\, e^{-x} x^x$

$\ln x! = x\ln x - x + O(\ln x)$

Entropy: $S(L,N) \approx k_B[N\ln N - n_+ \ln n_+ - (N-n_+)\ln(N-n_+)]$

Generalized Force: $F_L = T\left(\frac{\partial S}{\partial L}\right)_N = \frac{T}{2d}\left(\frac{\partial S}{\partial n_+}\right)_N = \frac{k_B T}{2d}\left(-\ln n_+ \cancel{-1} + \ln(N-n_+) \cancel{+1}\right)$

$\partial L = 2d\,\partial n_+$

$= \frac{k_B T}{2d} \ln \frac{(N-n_+)d}{n_+ d} = \frac{k_B T}{2d} \ln \frac{Nd - L}{Nd + L}$

$\frac{\partial}{\partial x} f(y) = \frac{\partial}{\partial y} f(y) \frac{\partial y}{\partial x}$

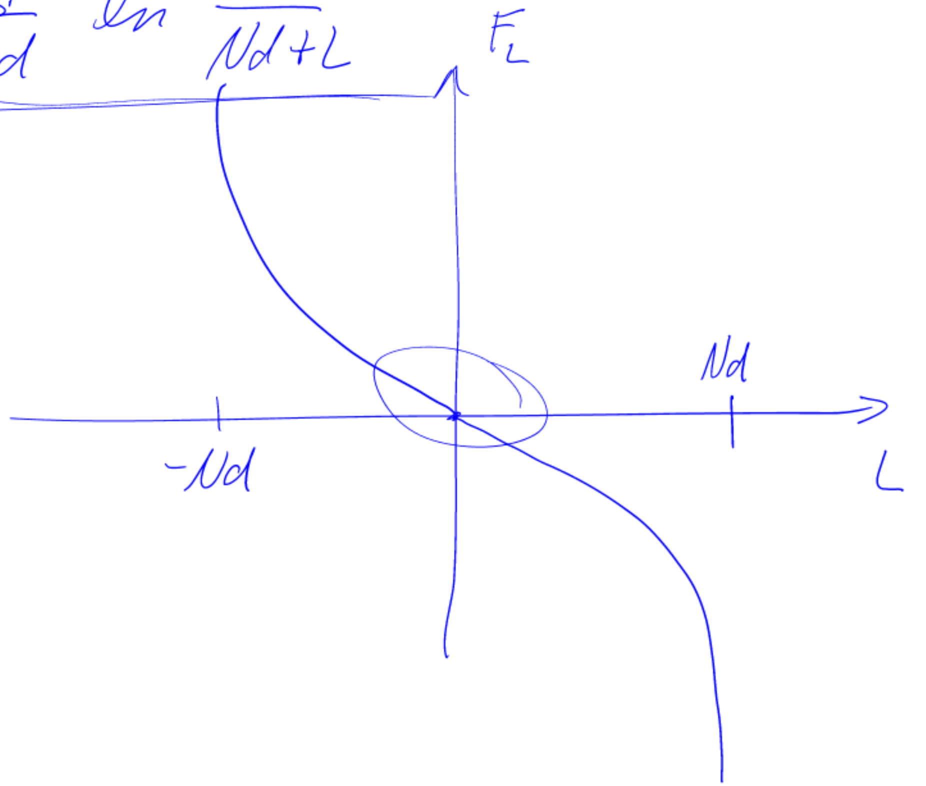
$L \ll Nd$

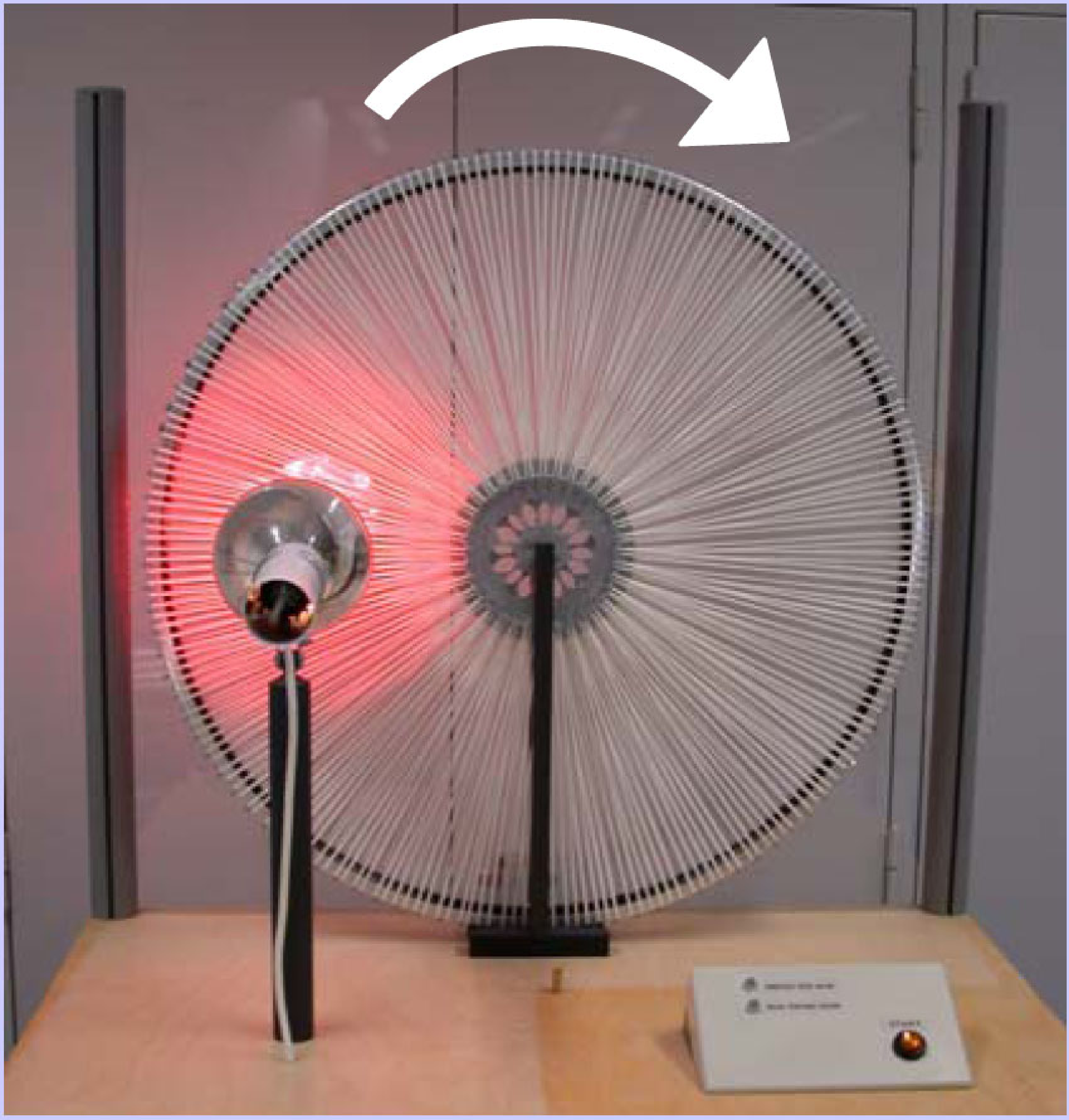
$F_L \approx \frac{k_B T}{2d} \ln\left(1 - \frac{2L}{Nd}\right)$

$\boxed{\ln(1+\varepsilon) \approx \varepsilon}$

$\approx -\frac{k_B T}{Nd^2} L$ Hook's law

$L \propto \frac{F_L}{T}$ ✓





Das Gummi-Rad. Am Anfang steht das Rad still. Wenn die Lampe die "Gummispeichen" auf der linken Seite erwärmt, verkürzen sich diese (*sog. Gough-Joule-Effekt*) und der Schwerpunkt des Rades verschiebt sich aus der Mitte auf die rechte Seite. Dadurch beginnt sich das Rad zu drehen.

Example 3: Classical ideal gas $d\Gamma = \prod_{j=1}^{N} \mathrm{d}^3\vec{r}_j \mathrm{d}^3\vec{p}_j$

$\vec{r}_1$ $\vec{p}_1$ $\vec{r}_2$ $\vec{p}_2$ ...

$$\Omega(E,V,N,....) = \int \mathrm{d}\Gamma\, \delta\big(E - \varepsilon(\{\vec{r}_j, \vec{p}_j\})\big)$$

Independent of position: $\varepsilon(\{\vec{r}_j, \vec{p}_j\}) = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} + \frac{\vec{p}_3^{\,2}}{2m} + \ldots = \frac{p_{1x}^2}{2m} + \frac{p_{1y}^2}{2m} + \frac{p_{1z}^2}{2m} + \frac{p_{2x}^2}{2m} \ldots$

indep. of $\vec{r}_j$

3N independent terms

new label $\ell = 1, \ldots, 3N$

Therefore $\int \prod_{j=1}^{N} \mathrm{d}^3\vec{r}_j = \left(\int \mathrm{d}^3\vec{r}\right)^N = V^N$

$$\Omega \propto V^N \int \prod_{\ell=1}^{3N} dp_\ell \; \delta\big(E - \varepsilon(p_\ell)\big) \quad *$$

$$\varepsilon(p_\ell) = \sum_{\ell=1}^{3N} \frac{p_\ell^2}{2m}$$

for integration: change of variable

$\rightarrow dE$

Change of variables

$$\vec{p}_{all} = (p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, p_{2z}, \ldots., p_{N,x}, p_{N,y}, p_{N,z},)$$

$$\prod_j \mathrm{d}^3 \vec{p}_j = \mathrm{d}\vec{p}_{all}^{\,3N} = \mathrm{d}p_{all}\, p_{all}^{3N-1} \mathrm{d}^{3N-1}\Omega$$

Microcanonical ensemble summary

1.) Calculate Boltzmann entropy $S = k_B \ln \Omega(E, V, N, ...)$

2.) Use $dS = \frac{1}{T} dE + \frac{p}{V} dV - \frac{\mu}{T} dN + \sum_{\alpha} \frac{F_{\alpha}}{T} d\alpha$

Therefore $$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T}$$