$$p(p_x) = \left(\frac{\sqrt{3}}{\sqrt{4\pi m}}\ e^{-1/2}\right)\left(\sqrt{N}\ e^{1/2}\right)\frac{1}{\sqrt{3N < \epsilon >}}\ e^{-\epsilon/2<\epsilon>}$$

$$= \frac{1}{\sqrt{4\pi m < \epsilon >}}\ e^{-\epsilon/2<\epsilon>}$$

Now use $\epsilon = p_x^2/2m$ and $< \epsilon > = < p_x^2 > /2m$.

$$p(p_x) = \frac{1}{\sqrt{2\pi < p_x^2 >}}\ e^{-p_x^2/2<p_x^2>}$$

Homework problem on classical harmonic oscillators

$$\boxed{\begin{aligned} p(p_i, q_i) &= \frac{1}{(2\pi/\omega) < \epsilon >} \exp[-\epsilon/ < \epsilon >] \\ &= \frac{1}{(2\pi/\omega) kT} \exp[-p_i^2/2mkT] \exp[-(m\omega^2/2kT) q_i^2] \end{aligned}}$$

$$= \cdots$$

Ensembles

- Microcanonical: E and N fixed

  Starting point for all of statistical mechanics

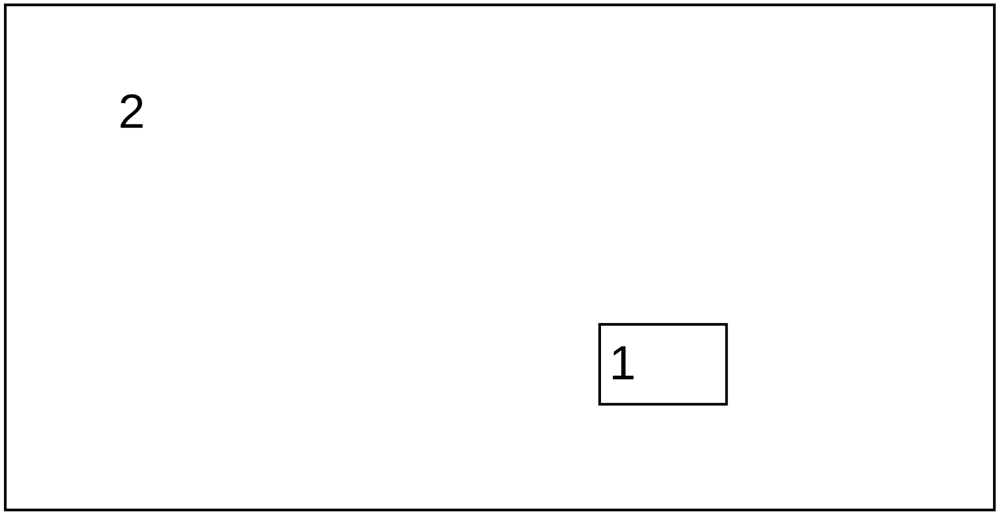
  Difficult to obtain results for specific systems

- Canonical: N fixed, T specified; E varies

  Workhorse of statistical mechanics

- Grand Canonical: T and μ specified; E and N vary

  Used when the the particle number is not fixed



1 IS THE SUBSYSTEM OF INTEREST.

2, MUCH LARGER, IS THE REMAINDER OR THE "BATH".

ENERGY CAN FLOW BETWEEN 1 AND 2.

THE TOTAL, 1+2, IS ISOLATED AND REPRESENTED BY A MICROCANONICAL ENSEMBLE.

For the entire system (microcanonical) one has

$$p(\text{system in state } X) = \frac{\text{volume of accessible phase space consistent with } X}{\Omega(E)}$$

In particular, for our case

$$p(\{p_1, q_1\}) \equiv p(\text{subsystem at } \{p_1, q_1\}; \text{remainder undetermined})$$

$$= \frac{\Omega_1(\{p_1, q_1\})\Omega_2(E - E_1)}{\Omega(E)}$$

$$k \ln p(\{p_1, q_1\}) = \underbrace{k \ln \Omega_1}_{k \ln 1 = 0} + \underbrace{k \ln \Omega_2(E - E_1)}_{S_2(E - E_1)} - \underbrace{k \ln \Omega(E)}_{S(E)}$$

$$S_2(E - E_1) \approx S_2(E) - \underbrace{\frac{\partial S_2(E_2)}{\partial E_2}}_{\text{evaluated at } E_2 = E} E_1$$

$$k \ln p(\{p_1, q_1\}) = \underbrace{-\frac{\mathcal{H}_1(\{p_1, q_1\})}{T}} + \underbrace{S_2(E) - S(E)}$$

The first term on the right depends on the <u>specific</u> state of the subsystem.

The remaining terms on the right depend on the reservoir and the <u>average</u> properties of the subsystem.

In all cases, including those where the system is too small for thermodynamics to apply,

$$
\begin{aligned}
p(\{p_1, q_1\}) &\propto \text{exp}[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}] \\
&= \frac{\text{exp}[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}]}{\int \text{exp}[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}]\{dp_1, dq_1\}}
\end{aligned}
$$

If thermodynamics does apply, one can go further.

$$S(E) = S_1(< E_1 >) + S_2(< E_2 >)$$

$$S_2(E) - S(E) =$$

$$\underbrace{S_2(E) - S_2(< E_2 >)}_{\approx (\partial S_2(E_2)/\partial E_2) < E_1 > = < E_1 > /T} \qquad -S_1(< E_1 >)$$

$$k \ln p(\{p_1, q_1\}) = -\frac{\mathcal{H}_1(\{p_1, q_1\})}{T} + \frac{< E_1 >}{T} - S_1$$

$$p(\{p_1, q_1\}) = \underbrace{\exp[\frac{(< E_1 > -TS_1)}{kT}]}_{\equiv 1/Z} \exp[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}]$$

$$< E_1 > - TS_1 = U_1 - T_1 S_1 = F_1$$

$$p(\{p,q\}) = Z^{-1} \exp[-\frac{\mathcal{H}(\{p,q\})}{kT}]$$

Z is called the partition function.

$$\begin{aligned} Z_N(T,V) &= \int \exp[-\frac{\mathcal{H}(\{p,q\})}{kT}]\{dp,dq\} \\ &= \exp[-\frac{(E-TS)}{kT}] = \exp[-\frac{F(T,V,N)}{kT}] \end{aligned}$$

In the canonical ensemble, the partition function is the source of thermodynamic information.

$$F(T,V,N) \;=\; -kT \ln Z_N(T,V)$$

$$S(T,V,N) \;=\; -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$$P(T,V,N) \;=\; -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$