Refrigerator Run cycle backwards, extract heat at cold end, dump it at hot end

$$\frac{\text{HEAT EXTRACTED (COLD END)}}{\text{WORK DONE ON SUBSTANCE}} = \frac{|Q_C|}{\Delta W} = \frac{|Q_C|}{|Q_H| - |Q_C|}$$

For the special case of a quasi-static Carnot cycle

$$= \frac{T_C}{T_H - T_C}$$

- As with engine, can show Carnot cycle is optimum.

- Practical: increasingly difficult to approach $T = 0$.

- Philosophical: $T = 0$ is point at which no more heat can be extracted.

Heat Pump Run cycle backwards, but use the heat dumped at hot end.

$$\frac{\text{HEAT DUMPED (HOT END)}}{\text{WORK DONE ON SUBSTANCE}} = \frac{|Q_H|}{\Delta W} = \frac{|Q_H|}{|Q_H| - |Q_C|}$$

For the special case of a quasi-static Carnot cycle

$$= \frac{T_H}{T_H - T_C}$$

55^o F subsurface temp. at 40^o latitude

$$\rightarrow T_C = 286K$$

70^o F room temperature

$$\rightarrow T_H = 294K$$

$$\frac{|Q_H|}{\Delta W} \leq \frac{294}{8} \sim 37$$

<u>3^{rd} law</u> $$\lim_{T \to 0} S = S_0$$

At $T = 0$ the entropy of a substance approaches a constant value, independent of the other thermodynamic variables.

- Originally a hypothesis

- Now seen as a result of quantum mechanics

Ground state degeneracy g (usually 1)
$\Rightarrow S \to k \ln g$ (usually 0)

Consequences $$\left(\frac{\partial S}{\partial x}\right)_{T=0} = 0$$

Example: A hydrostatic system

$$\underline{\alpha} \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T \to 0 \quad \text{as } T \to 0$$

$$\underline{C_P - C_V} = \frac{VT\alpha^2}{\mathcal{K}_T} \to 0 \quad \text{as } T \to 0$$

$$S(T) - S(0) = \int_{T=0}^{T} \frac{C_V(T')}{T'}\, dT' \Rightarrow \underline{C_V(T)} \to 0 \quad \text{as } T \to 0$$

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

If the density in phase space depends only on the energy at that point,

$$\rho(\{p, q\}) = \rho(\mathcal{H}\{p, q\}),$$

carrying out the indicated derivatives shows that

$$\frac{\partial \rho}{\partial t} = 0.$$

This proves that $\rho = \rho(\mathcal{H}\{p, q\})$ is a sufficient condition for an equilibrium probability density in phase space.

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

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

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

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

d) Let Ω' be the volume in a phase space for $N-1$ oscillators of total energy $E-\epsilon$ where $\epsilon = (1/2m)p_i^2 + (m\omega^2/2)q_i^2$. Since the oscillators are all similar, $<\epsilon>= E/N = kT$.

$$p(p_i, q_i) = \Omega'/\Omega$$

$$\Omega' = \left(\frac{2\pi}{\omega}\right)^{N-1} \frac{1}{(N-1)!} (E-\epsilon)^{N-1}$$

$$\frac{\Omega'}{\Omega} = \left(\frac{2\pi}{\omega}\right)^{-1} \frac{N!}{(N-1)!} \left(\frac{E-\epsilon}{E}\right)^{N} \frac{1}{E-\epsilon}$$

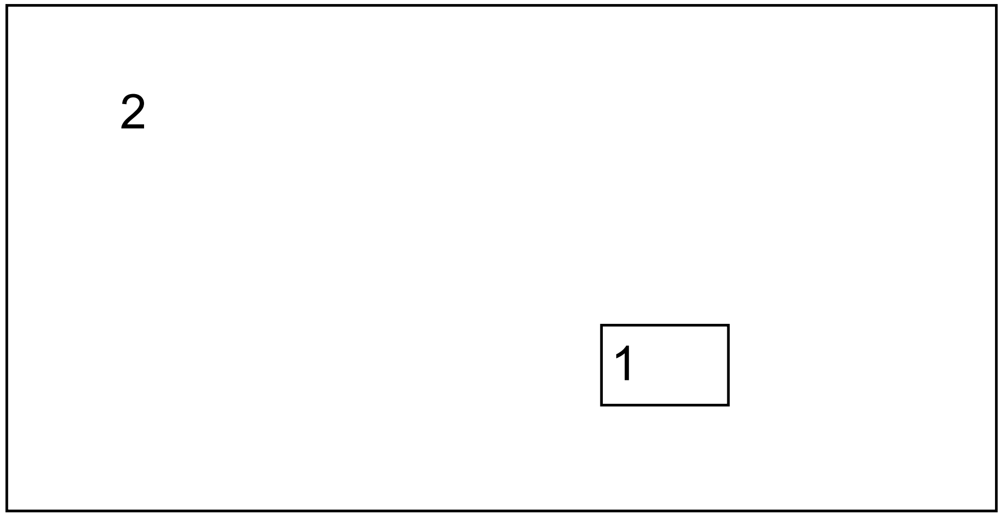
$$= \frac{\omega}{2\pi} \underbrace{\frac{N}{E-\epsilon}}_{\approx<\epsilon>^{-1}} \underbrace{\left(1-\frac{\epsilon}{E}\right)^{N}}_{\approx\exp[-\epsilon/<\epsilon>]}$$

$$p(p_i, q_i) = \frac{1}{(2\pi/\omega) < \epsilon >} \exp[-\epsilon/ < \epsilon >]$$

$$= \frac{1}{(2\pi/\omega)kT} \exp[-p_i^2/2mkT] \exp[-(m\omega^2/2kT)q_i^2]$$

$$= \underline{\left(\frac{1}{\sqrt{2\pi mkT}} \exp[-p_i^2/2mkT]\right) \left(\frac{1}{\sqrt{2\pi(kT/m\omega^2)}} \exp[-q_i^2/2(kT/m\omega^2)]\right)}$$

$$= p(p_i) \times p(q_i) \Rightarrow \; p_i \text{ and } q_i \text{ are S.I.}$$



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 specific state of the subsystem.

The remaining terms on the right depend on the reservoir and the average properties of the subsystem.

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

$$p(\{p_1, q_1\}) \propto \exp[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}]$$

$$= \frac{\exp[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}]}{\int \exp[-\frac{\mathcal{H}_1(\{p_1, q_1\})}{kT}]\{dp_1, dq_1\}}$$

If thermodynamics does apply, one can go further.

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

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

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

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

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

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

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

Z is called the partition function.

$$Z(T,V,N) \ = \ \int \exp[-\frac{\mathcal{H}(\{p,q\})}{kT}]\{dp,dq\}/h^\alpha$$

$$= \ \exp[-\frac{(E-TS)}{kT}] \ = \ \exp[-\frac{F(T,V,N)}{kT}]$$

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

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

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

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

MIT OpenCourseWare
http://ocw.mit.edu

8.044 Statistical Physics I
Spring 2013

For information about citing these materials or our Terms of Use, visit: http://ocw.mit.edu/terms.