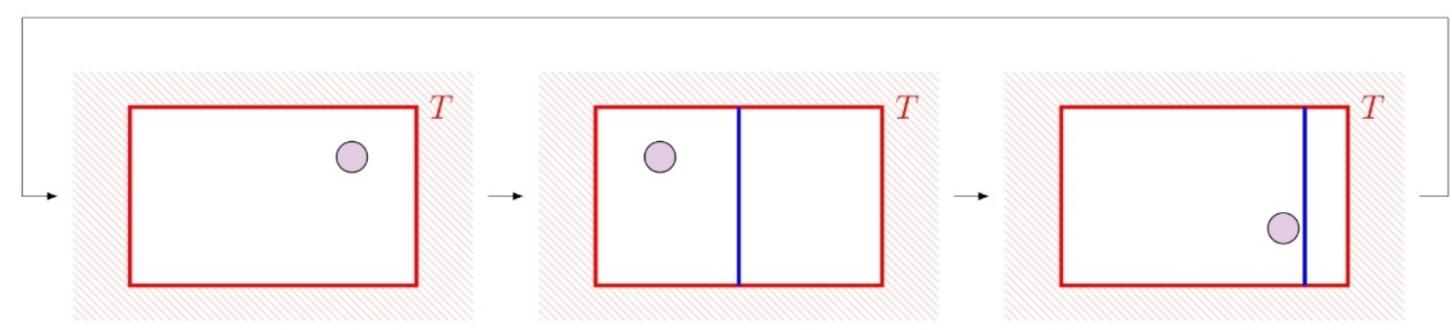


## Worksheet 6. Solutions.

### 1 Maxwell Demon.

Consider the cycle with a single ideal gas particle: (Szilard's Engine)



No change in temperature  $\rightarrow$  Isothermal compression

» Change of Volume including the wall.  
No work  
isothermal.

» Expansion making work.

» Coming back to the initial config

The way you can understand this gas, is that the particle changes its temperature everytime it touches the red walls (the reservoir) to a random velocity given by the Maxwell-Boltzmann distribution.

During an isothermal expansion from  $V$  to  $2V$  the work done by the molecule

$$W_{\text{by the molecule}} = \int_V^{2V} P dV = k_B T \int_V^{2V} \frac{dV}{V} = k_B T \ln(2)$$

To keep the temperature, and hence the internal energy, of the molecule constant, heat must flow into the box from the heat bath,  $Q = W = k_B T \ln(2)$ .

The compression, without work, adds the movable wall.

$$\Delta S_{\text{box}}^{\text{isocomp}} = k_B \ln \left( \frac{V}{2V} \right) \\ = -k_B \ln(2)$$

$\Delta S_{\text{bath}}^{\text{isocomp}} = 0 \rightarrow$  No exchange of heat nor work

During the expansion, there is work.

$$dU = dW + dQ$$

$$\Rightarrow dQ = -dW$$

$$W = k_B T \ln(2) \quad \left| \quad S_{\text{box}}^{\text{exp}} = -k_B T \ln(2) \right.$$

Then the total process

$$\left. \begin{array}{l} \Delta S_{\text{box}}^{\text{total}} = 0 \\ \Delta S_{\text{bath}}^{\text{total}} = -k_B \ln(2) \end{array} \right\} \Delta S_{\text{universe}}^{\text{total}} = k_B \ln(2)$$

→ Entropy of the universe decrease  
~ work is extracted from the Bath with  
"No Cost"  
It took years for people to find the answers to  
the question: How can this happen?

→ The solution happened to be the connection Information + Thermodynamics

look at

— Szilard's Theorem

— Landauer's principle

## 2 Ergodic System

No, an ideal gas cannot be considered Ergodic as it is non-interacting. The kinetic energies are conserved, so there is no way the system can explore the whole phase-space with a given initial condition. The kinetic energy "Stays" along every direction  $x, y$  and  $z$  will remain there.



### 3 Interstitial lattice.

We have  $M$  particles in the interstitial sites and  $N-M$  in the normal sites. The internal energy goes

$$U = (N-M) \underbrace{\text{Energy Normal Site}}_0 + M \underbrace{\text{Energy inter-sites}}_{\epsilon}$$

$$U = M\epsilon$$

Now, let us write as a function of the temperature.

The number of ways in which  $M$  atoms can be placed at  $M$  interstitial sites is

$$\Omega_{\text{inter.}} = \frac{N!}{M!(N-M)!}$$

It happens that, placing the  $N-M$  at the  $M$  normal sites is the same. Thus,

$$\Omega = \left( \frac{N!}{M!(N-M)!} \right)^2$$

$$\rightarrow S = k_B \ln (\Omega)$$

$$= 2k_B \ln \left[ \frac{N!}{M!(N-M)!} \right]$$

$$= 2k_B \left[ \ln(N!) - \ln(M!) - \ln((N-M)!) \right]$$

So, using the Stirling formula

$$\frac{S}{k_B} \approx 2[N \ln(N) - N - M \ln(M) + M - (N-M) \ln(N-M) + (N-M)]$$

$$\frac{S}{k_B} = 2 \left[ N \ln(N) - M \ln(M) - (N-M) \ln(N-M) \right]$$

So, as we have

$$\frac{1}{T} = \frac{\partial S}{\partial u} \Big|_{V,M} \quad \text{and } \mu = N\epsilon.$$

$$\frac{\partial S}{\partial u} = \frac{\partial S}{\partial M} \frac{\partial M}{\partial u} = \frac{2 k_B}{e} \left[ \ln(N-M)/M \right]$$

$$\frac{1}{T} = \frac{2 k_B}{e} \ln \left[ \frac{N-M}{M} \right] \quad M = u/e$$

Then

$$\frac{e}{2 k_B T} = \frac{N-M}{M} = \frac{N-u/e}{u/e}$$

$$e = \frac{Ne}{u} - 1$$

$$u = \frac{Ne}{e^{e/2 k_B T} + 1} \approx Ne e^{-e/2 k_B T}$$

So

$$c \approx 2 k_B N \left( \frac{e}{2 k_B T} \right)^2 e^{-e/2 k_B T}$$

$$\frac{\epsilon}{2k_B T} = \frac{U}{\mu} \frac{1}{2k_B T} = \frac{1}{2} \frac{U}{\mu} - \frac{1}{\mu}$$

3 state spin

consider each spin with magnetic moment  $\mu$ .  
we have

$$W = \frac{N!}{n_{+}! n_{-}! (N-n_{+}-n_{-})!}$$

With the Stirling formula.

$$\ln(W) \approx N \ln(N) - n_{+} \ln(n_{+}) - n_{-} \ln(n_{-}) \\ - (N-n_{+}-n_{-}) \ln(N-n_{+}-n_{-})$$

$$\frac{\partial \ln(W)}{\partial n_{+}} = 0 \quad \text{and} \quad \frac{\partial \ln(W)}{\partial n_{-}} = 0$$

$$n_{+} = (N - n_{+} - n_{-}) = n - 1$$

$$\rightarrow n_{+} = n_{-} = n_0 = \frac{N}{3}$$

Then the maximum entropy

$$S_{\max} = k N \ln(3).$$

*Classical harmonic oscillators:* Consider  $N$  harmonic oscillators with coordinates and momenta  $\{q_i, p_i\}$ , and subject to a Hamiltonian

$$\mathcal{H}(\{q_i, p_i\}) = \sum_{i=1}^N \left[ \frac{p_i^2}{2m} + \frac{m\omega^2 q_i^2}{2} \right].$$

- (a) Calculate the entropy  $S$ , as a function of the total energy  $E$ .

(Hint: By appropriate change of scale, the surface of constant energy can be deformed into a sphere. You may then ignore the difference between the surface area and volume for  $N \gg 1$ . A more elegant method is to implement this deformation through a canonical transformation.)

- *The volume of accessible phase space for a given total energy is proportional to*

$$\Omega = \frac{1}{h^N} \int_{\mathcal{H}=E} dq_1 dq_2 \cdots dq_N dp_1 dp_2 \cdots dp_N,$$

where the integration is carried out under the condition of constant energy,

$$E = \mathcal{H}(\{q_i, p_i\}) = \sum_{i=1}^N \left[ \frac{p_i^2}{2m} + \frac{m\omega^2 q_i^2}{2} \right].$$

Note that Planck's constant  $h$ , is included as a measure of phase space volume, so as to make the final result dimensionless.

The surface of constant energy is an ellipsoid in  $2N$  dimensions, whose area is difficult to calculate. However, for  $N \rightarrow \infty$  the difference between volume and area is subleading in  $N$ , and we shall instead calculate the volume of the ellipsoid, replacing the constraint  $\mathcal{H} = E$  by  $\mathcal{H} \leq E$ . The ellipsoid can be distorted into a sphere by a canonical transformation, changing coordinates to

$$q'_i \equiv \sqrt{m\omega} q_i, \quad \text{and} \quad p'_i \equiv \frac{p_i}{\sqrt{m\omega}}.$$

The Hamiltonian in this coordinate system is

$$E = \mathcal{H}(\{q'_i, p'_i\}) = \frac{\omega}{2} \sum_{i=1}^N (p'^2_i + q'^2_i).$$

Since the canonical transformation preserves volume in phase space (the Jacobian is unity), we have

$$\Omega \approx \frac{1}{h^N} \int_{\mathcal{H}_{\leq E}} dq'_1 \cdots dq'_N dp'_1 \cdots dp'_N,$$

where the integral is now over the  $2N$ -dimensional (hyper-) sphere of radius  $R = \sqrt{2E/\omega}$ . As the volume of a  $d$ -dimensional sphere of radius  $R$  is  $S_d R^d/d$ , we obtain

$$\Omega \approx \frac{2\pi^N}{(N-1)!} \cdot \frac{1}{2N} \left(\frac{2E}{h\omega}\right)^N = \left(\frac{2\pi E}{h\omega}\right)^N \frac{1}{N!}.$$

The entropy is now given by

$$S \equiv k_B \ln \Omega \approx N k_B \ln \left( \frac{2\pi e E}{N h \omega} \right).$$

(b) Calculate the energy  $E$ , and heat capacity  $C$ , as functions of temperature  $T$ , and  $N$ .

- From the expression for temperature,

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} \Big|_N \approx \frac{N k_B}{E},$$

we obtain the energy

$$E = N k_B T,$$

and the heat capacity

$$C = N k_B.$$