## Lecture 6 Examples and Problems

- Heat capacity of solids \& liquids
- Thermal diffusion
- Thermal conductivity
- Irreversibility

- Random Walk and Particle Diffusion
- Counting and Probability
- Microstates and Macrostates
- The meaning of equilibrium



## Heat Capacity and Specific Heat

Heat capacity: The heat energy required to raise the temperature of an object by $1 \mathrm{~K}\left(=1^{\circ} \mathrm{C}\right)$.
It depends on the amount of material. Units: J / K

$$
\mathrm{C}=\frac{\mathrm{Q}}{\Delta \mathrm{~T}}
$$

Specific heat: The heat capacity normalized to a standard amount of material (mass or moles).
It only depends on the kind of material.

Normalize to mass:

$$
\text { Units: } \mathrm{J} / \mathrm{kg} \cdot \mathrm{~K} \longrightarrow \mathrm{c}=\frac{\mathrm{C}}{\mathrm{~m}}
$$

Normalize to moles: "molar specific heat"

$$
\text { Units: } \mathrm{J} / \text { mole } \cdot \mathrm{K} \longrightarrow \mathrm{c}_{\mathrm{mol}}=\frac{\mathrm{C}}{\mathrm{n}}
$$

## Act 1

1 calorie* is defined to be the energy needed to raise the temperature of 1 gram of water $1^{\circ} \mathrm{C}(=1 \mathrm{~K})$. Therefore, given that $\mathrm{C}_{\mathrm{H} 2 \mathrm{O}}=4184 \mathrm{~J} / \mathrm{kg} \cdot \mathrm{K}, 1$ calorie $=4.18$ Joule.

Upper case "C"
lower case "c"
1 food Calorie $=1000$ calorie $=4180 \mathrm{~J}$
If you weigh 80 kg , consume 2000 Cal/day, and could actually convert this entirely into work, how high could you climb?
a. 1 km
b. 10 km
c. 100 km
*The amount of heat actually depends somewhat on the temperature of the water, so there are actually several slightly different "calorie" definitions.

## Solution

1 calorie is defined to be the energy needed to raise the temperature of 1 gram of water $1^{\circ} \mathrm{C}(=1 \mathrm{~K})$. Therefore, given that $\mathrm{C}_{\mathrm{H} 2 \mathrm{O}}=4184 \mathrm{~J} / \mathrm{kg} \cdot \mathrm{K}, 1$ calorie $=4.18 \mathrm{Joule}$.

1 food Calorie $=1000$ calorie $=4180 \mathrm{~J}$
If you weigh 80 kg, consume 2000 Cal/day, and could actually convert this entirely into work, how high could you climb?
a. 1 km
b. 10 km
c. 100 km
$2000 \mathrm{Cal}=8.36 \times 10^{6} \mathrm{~J}=\mathrm{mgh}$
So, $\mathrm{h}=8.36 \times 10^{6} \mathrm{~J} /\left(80 \mathrm{~kg} \times 9.8 \mathrm{~m} / \mathrm{s}^{2}\right)=10.7 \mathrm{~km}$

Note: Tour de France riders consume 6000-9000 Cal/day.

## Exercise: Spacecraft Heat Shields



This false-color view of Titan (moon of Saturn) is a composite of images captured by Cassini's infrared camera, which can penetrate some of Titan's clouds. Light and dark regions in the upper left quadrant are unknown types of terrain on Titan's surface.

The Huygens spacecraft entered the atmosphere on Jan. 14, 2005, initially traveling at $\sim 6 \mathrm{~km} / \mathrm{s}$. After decelerating from friction, the heat shield was jettisoned, and three parachutes were deployed to allow a soft landing.

What is the temperature rise on entry, assuming that half of the thermal energy goes into the ship (and half to the atmosphere)?
Assume $\mathrm{c}_{\text {steel }}=500 \mathrm{~J} / \mathrm{kg}-\mathrm{K}$.

## Solution

$\mathrm{v}=6 \mathrm{~km} / \mathrm{s}$
$\mathrm{c}=500 \mathrm{~J} / \mathrm{kg}-\mathrm{K}$

Use conservation of energy (1st law of thermodynamics).
Half of the initial kinetic energy becomes internal thermal energy.

$$
\begin{aligned}
& \frac{1}{2}\left(\frac{1}{2} m v^{2}\right)=C \Delta T=c m \Delta T \\
& \Rightarrow \Delta T=\frac{v^{2}}{4 c}=\frac{\left(6 \times 10^{3} \mathrm{~m} / \mathrm{s}\right)^{2}}{4 \times 500 \mathrm{~J} / \mathrm{kg}-\mathrm{K}}=18,000 \mathrm{~K}!
\end{aligned}
$$

Note that m cancels.

The problem is that steel melts at $\sim 1700 \mathrm{~K}$ ! For this reason, the heat shield is not made of steel, but rather a ceramic that burns off ("ablates"). Also, the ceramic has a very low thermal conductivity!

## Exercise: Heat Capacity

Two blocks of the same material are put in contact. Block 1 has $m_{1}=1 \mathrm{~kg}$, and its initial temperature is $\mathrm{T}_{1}=75^{\circ} \mathrm{C}$. Block 2 has $m_{2}=2 \mathrm{~kg}$, and $\mathrm{T}_{2}=25^{\circ} \mathrm{C}$. What is the temperature after the blocks reach thermal equilibrium?

## Solution

Two blocks of the same material are put in contact. Block 1 has $m_{1}=1 \mathrm{~kg}$, and its initial temperature is $\mathrm{T}_{1}=75^{\circ} \mathrm{C}$. Block 2 has $m_{2}=2 \mathrm{~kg}$, and $\mathrm{T}_{2}=25^{\circ} \mathrm{C}$. What is the temperature after the blocks reach thermal equilibrium?

## 2

The two blocks have the same (unknown) specific heat. However, the heat capacity of block $2, \mathrm{C}_{2}=\mathrm{cm}_{2}$, is twice as large as that of block $1, \mathrm{C}_{1}=\mathrm{cm}_{1}$.
We can use the 1st law (conservation of energy) to determine the final temperature:
$\mathrm{U}_{\mathrm{f}}=\mathrm{c}\left(\mathrm{m}_{1}+\mathrm{m}_{2}\right) \mathrm{T}_{\mathrm{f}}$
$=\mathrm{U}_{\mathrm{i}}=\mathrm{cm} \mathrm{T}_{1}+\mathrm{cm}_{2} \mathrm{~T}_{2}$.
Solve for $\mathrm{T}_{\mathrm{f}}: T_{f}=\frac{m_{1} T_{1}+m_{2} T_{2}}{m_{1}+m_{1}}=\frac{1 \times 75+2 \times 25}{3}=41.7^{\circ} \mathrm{C}$
Question:
Suppose we measure temperature in Kelvin. Will we get a different answer?

## The Diffusion Constant

The solution to the 3-D random walk, with varying $\ell$ and $v$, is similar (but the math is messier).

The mean square displacement along x is still proportional to t :

$$
\left\langle x^{2}\right\rangle=2 D t, \text { where } D=\frac{\ell^{2}}{3 \tau}=\frac{1}{3} v \ell
$$

D is called the diffusion constant*.

$$
x_{m s}=\sqrt{\left\langle x^{2}\right\rangle}=\sqrt{2 D t}
$$

The 3-D displacement (along $x, y$, and $z$ combined) is:

$$
\left\langle r^{2}\right\rangle=\left\langle x^{2}\right\rangle+\left\langle y^{2}\right\rangle+\left\langle z^{2}\right\rangle=6 D t
$$

* The numerical coefficients in general depend on the distribution of distances and time intervals. For Phys. 213 we'll use the form above.


## Exercise: <br> Impurity Diffusion in Semiconductors

Consider impurity atoms diffusing from the top surface of an aluminum film toward an interface with a semiconductor.


Assume that each impurity makes a random step of $\ell=10^{-10} \mathrm{~m}$ about once every 10 seconds.

1. Approximately what is the diffusion constant, D?
2. If the Al is $10^{-7} \mathrm{~m}$ thick, approximately how long will it take before many impurities have diffused through it?

Note: This is an important problem, because impurities affect the electrical properties of the Si, usually in a way we don't want.

## Solution

Mean free path $\quad \ell=10^{-10} \mathrm{~m}$
Time between steps $\tau=10 \mathrm{~s}$
$D \approx \frac{\ell^{2}}{3 \tau}=\frac{\left(10^{-10} \mathrm{~m}\right)^{2}}{30 \mathrm{~s}}=0.3 \times 10^{-21} \mathrm{~m}^{2} / \mathrm{s}$

We only care about motion along $x$, so use the 1-D formula:

$$
\begin{aligned}
& x_{\mathrm{rms}}=\sqrt{2 \mathrm{Dt}}=10^{-7} \mathrm{~m} \\
& \mathrm{t}=\frac{\left\langle\mathrm{x}^{2}\right\rangle}{2 \mathrm{D}} \approx \frac{\left(10^{-7} \mathrm{~m}\right)^{2}}{0.6 \times 10^{-21} \mathrm{~m}^{2} / \mathrm{s}}=1.6 \times 10^{7} \mathrm{~s} \sim 6 \text { months }
\end{aligned}
$$

## Act 2

If we make the thickness of the film twice as big, how much longer will the device last?
a) $\times 1 / 2$
b) $\times 0.71$
c) $\times 1.41$
d) $\times 2$
e) $\times 4$

## Solution

If we make the thickness of the film twice as big, how much longer will the device last?
a) $\times 1 / 2$
b) $\times 0.71$
c) $\times 1.41$
d) $\times 2$
e) $\times 4$

The diffusion time is proportional to the square of the thickness.

## Exercise: Diffusion

A perfume bottle is opened, and the molecules begin to diffuse through the air. Suppose that perfume molecules move about 10 nm between collisions with air molecules, and that their average speed is $\mathrm{v} \sim 100 \mathrm{~m} / \mathrm{s}$.

1) What is the diffusion constant of perfume in air?
2) Suppose you hold your nose 10 cm from the perfume bottle. When will you be able to smell the perfume? What about a person across the room (5 m away)?

$$
A^{n n s}{ }_{n o s e}: 1.5 \times 10^{4} \mathrm{~s}
$$

3) Are these times reasonable?

## Solution

A perfume bottle is opened, and the molecules begin to diffuse through the air. Suppose that perfume molecules move about 10 nm between collisions with air molecules, and that their average speed is $v \sim 100 \mathrm{~m} / \mathrm{s}$.

1) What is the diffusion constant of perfume in air?

$$
D=\frac{1}{3} v \ell=3.33 \times 10^{-7} \mathrm{~m}^{2} / \mathrm{s}
$$

2) Suppose you hold your nose 10 cm from the perfume bottle. When will you be able to smell the perfume? What about a person across the room ( 5 m away)?

$$
\begin{aligned}
t=\frac{\left\langle x^{2}\right\rangle}{2 D} & =1.5 \times 10^{4} \mathrm{~s} \sim 4 \text { hours } \quad \text { (nose) } \\
& =3.8 \times 10^{7} \mathrm{~s} \sim 1 \text { year } \quad \text { (across room) }
\end{aligned}
$$

3) Are these times reasonable?

These times are much too long. In this situation, conduction (air currents) is much more important than diffusion. However, in solids, where conduction is rarely important, diffusion can dominate.

## Act 3: Isotope Separation

You have the task of separating two isotopes of Uranium: ${ }^{235} \mathrm{U}$ and ${ }^{238} \mathrm{U}$. Your lab partner suggests the following: Put a gas containing both of them at one end of a long tube through which they will diffuse. Which will get to the far end first?
A) ${ }^{235} \mathrm{U}$
B) ${ }^{238} \mathrm{U}$
C) Neither (equal time)

## Solution

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A) ${ }^{235} \mathrm{U}$
B) ${ }^{238} \mathrm{U}$
C) Neither (equal time)

The diffusion time $\mathrm{t} \sim \ell^{2} / 3 \mathrm{D}$, where $\mathrm{D}=\mathrm{v} \ell / 3$.
From equipartition: $\quad \frac{1}{2} m v^{2}=\frac{3}{2} k T \Rightarrow v=\sqrt{3 k T / m}$
Therefore $t \propto 1 / D \propto 1 / \mathrm{v} \propto \sqrt{\mathrm{m}}$. The heavier isotope takes slightly longer. (This is the technique first used in the Manhattan Project. It was then found that centrifuges speed up the process.)

## ACT 4: Free Expansion of a Gas

Free expansion occurs when a valve is opened allowing a gas to expand into a bigger container.


Such an expansion is:
A) Reversible, because the gas does no work and thus loses no energy.
B) Reversible, because there is no heat flow from outside.
C) Irreversible, because the gas won't spontaneously go back into the smaller volume.

## Solution

Free expansion occurs when a valve is opened allowing a gas to expand into a bigger container.


Such an expansion is:
A) Reversible, because the gas does no work and thus loses no energy.
B) Reversible, because there is no heat flow from outside.
C) Irreversible, because the gas won't spontaneously go back into the smaller volume.
Because there are many fewer microstates.

## The Meaning of Equilibrium (1)

## An Introduction to Statistical Mechanics

Definitions:
Macrostate: The set of quantities we are interested in (e.g., p, V, T).
Microstate: A specific internal configuration of the system, with definite values of all the internal variables.

Assume:
Due to the randomness of thermal processes, every microstate is equally likely. Therefore the probability of observing a particular macrostate is proportional to the number of corresponding microstates.

$$
\mathrm{P}(\mathrm{~A})=\Omega_{\mathrm{A}} / \Omega_{\mathrm{tot}}
$$

Many systems are described by binary distributions:

- Random walk
- Coin flipping
- Electron spin

This can be solved using the binomial formula, because each particle has two choices:

$$
\begin{aligned}
& \Omega\left(N, N_{L}\right)={ }_{N} C_{N_{L}} \equiv \frac{N!}{N_{L}!\left(N-N_{L}\right)!} \\
& \Omega_{\text {tot }}=2^{N}
\end{aligned}
$$

## Example: Electron Spin

Electrons have spin and associated magnetic moment $\mu$. They can only point "up" or "down".*


Consider a system of $\mathrm{N}=9$ spins: $\uparrow \uparrow \downarrow \downarrow \uparrow \downarrow \uparrow \uparrow \downarrow$

The total magnetic moment (what we can measure) is:

$$
\mathrm{M}=\left(\mathrm{N}_{\mathrm{up}}-\mathrm{N}_{\text {down }}\right) \mu \equiv \mathrm{m} \mu \quad \mathrm{~m}=\text { "spin excess" }=\mathrm{N}_{\mathrm{up}}-\mathrm{N}_{\text {down }}
$$

A macrostate is described by m . The microstate above has $\mathrm{m}=+1$.

## Electron Spin (2)

Count microstates for each value of m :

$$
\Omega\left(N_{u p}\right)=\frac{N!}{N_{\text {up }}!N_{\text {dom }}!} \Rightarrow \Omega(m)=\frac{N!}{\left.\left(\frac{N+m}{2}\right)\right) \cdot\left(\frac{N-m}{2}\right)!} \quad P\left(N_{u p}\right)=\frac{N!}{N_{\text {up }}!N_{\text {down }}!}\left(\frac{1}{2^{N}}\right)
$$



Each macrostate is described by m . (what we measure).

This problem will become more interesting later in the course. We will put the spins in a magnetic field. The energy of spin up will not equal the spin down energy, and the probabilities will change.

## Gaussian Approximation to the Binomial Distribution

When N is large, the binomial formula becomes impossible to evaluate on a calculator.

$$
\Omega\left(N_{u p}\right)=\frac{N!}{N_{u p}!N_{\text {down }}!} \Rightarrow P\left(N_{u p}\right)=\frac{N!}{N_{\text {up }}!N_{\text {down }}!}\left(\frac{1}{2^{N}}\right)
$$

Fortunately, when N is large the shape of the distribution becomes a Gaussian:

$$
\Omega(m)=2^{N}\left(\frac{2}{\pi N}\right)^{1 / 2} e^{-m^{2} / 2 N} \Rightarrow P(m)=\left(\frac{2}{\pi N}\right)^{1 / 2} e^{-m^{2} / 2 N}
$$



This expression can be evaluated for very large N (e.g., 10 ${ }^{23}$ ).
Does it work? Try $\mathrm{N}=20, \mathrm{~m}=2$ :
Binomial: $\Omega(1)=167960, P(1)=0.160$
Gaussian: $\Omega(1)=169276, P(1)=0.161$

$$
\begin{aligned}
& \text { Ex: } \\
& N=10^{10}, m=10^{5} \\
& P(m)=8.0 \times 10^{-6}
\end{aligned}
$$

The agreement improves as N increases.

## Exercise: Random Walk

Suppose that a particle is undergoing a 1-dimensional random walk (equally likely steps in the + or minus directions.)

What is the probability:

1) that after N steps it is exactly where it started? Evaluate it for $\mathrm{N}=10$.
2) that after N steps it is within 2 steps of the maximum possible positive position? Evaluate it for $\mathrm{N}=10$.

## Solution

Suppose that a particle is undergoing a 1-dimensional random walk (equally likely steps in the + or minus directions.)

What is the probability:

1) that after N steps it is exactly where it started? Evaluate it for $\mathrm{N}=10$.

There are $2^{\mathrm{N}}$ total microstates. We want $\mathrm{N}_{+}=\mathrm{N}=\mathrm{N} / 2$. The probability that this happens is:

$$
P(0)=\frac{N!}{\left(\frac{N}{2}!\right)^{2} 2^{N}}=0.246
$$

2) that after N steps it is within 2 steps of the maximum possible positive position? Evaluate it for $\mathrm{N}=10$.

## Solution

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$$
P(0)=\frac{N!}{\left(\frac{N}{2}!\right)^{2} 2^{N}}=0.246
$$

2) that after N steps it is within 2 steps of the maximum possible positive position? Evaluate it for $\mathrm{N}=10$.
We must sum the three probabilities: $\mathrm{P}(\mathrm{N})+\mathrm{P}(\mathrm{N}-1)+\mathrm{P}(\mathrm{N}-2)$.

$$
\begin{array}{ll}
P(N)=1 / 2^{N} & \text { one microstate } \\
P(N-1)=0 & N_{+}-N \text { must be even when } N \text { is even. } \\
P(N-2)=N / 2^{N} & N \text { microstates: } N_{+}=N-1 \text { and } N-=1 .
\end{array}
$$

The sum is $P(N-2: N)=\frac{N+1}{2^{N}}=0.011$

## Exercise: Random Walk (2)

Do the previous exercise when $\mathrm{N}=10^{6}$.

For what value of $m$ is $P(m)$ half of $P(0)$ ?

## Solution

Do the previous exercise when $\mathrm{N}=10^{6}$.
There is no way that we are going to evaluate $2^{1,000,000}$.
We must use the Gaussian approximation: $P(m)=\left(\frac{2}{\pi N}\right)^{1 / 2} e^{-\mathrm{m}^{2} / 2 \mathrm{~N}}$

1) $\mathrm{m}=0: \mathrm{P}(0)=\left(\frac{2}{\pi 10^{6}}\right)^{1 / 2}=8 \times 10^{-4}$
2) $m=N$ and $m=N-2: P(N)=\left(\frac{2}{\pi 10^{6}}\right)^{1 / 2} e^{-10^{6} / 2}=0$ for all practical purposes.

For what value of $m$ is $P(m)$ half of $P(0)$ ?
We want $e^{-m^{2} / 2 N}=\frac{1}{2} \Rightarrow m=\sqrt{2 \ln (2)} \sqrt{N}=1.177 \sqrt{N}=1177$

## Example: Probability \& Microstates

The typical baseball player gets a hit $25 \%$ of the time. If this player gets several hits in a row, he is said to be "on a streak", and it's attributed to his skill.

1) What is the probability that this player will get a hit exactly $25 \%$ of the time if he tries 20 times (i.e., 5 hits and 15 misses)?
2) What is the probability that this player will get five hits (no misses) in a row?

## Solution

The typical baseball player gets a hit $25 \%$ of the time. If this player gets several hits in a row, he is said to be "on a streak", and it's attributed to his skill.

1) What is the probability that this player will get a hit exactly $25 \%$ of the time if he tries 20 times (i.e., 5 hits and 15 misses)?
The probability of obtaining a particular microstate (five hits and 15 misses, in a specific order) is $0.25^{5} \times 0.75^{15}=1.3 \times 10^{-5}$. Now, count microstates (different orderings of hits and misses): $\mathrm{N}=20!/(5!\times 15!)=15,504$. Each microstate is equally likely, so the probability is $1.3 \times 10^{-5} \times 15,504=0.20$.

Here's one microstate: MMMMMHMHMMMHHMMMMHMM
2) What is the probability that this player will get five hits (no misses) in a row?

There is only one way to do this (one microstate). The probability is: $\mathrm{P}=0.25^{5}=0.00098$. That's fairly small (about one in a thousand) for a particular player, but not unlikely to happen by chance somewhere on a particular day, if one remembers that there are more than 1000 "at bats" every day in major league baseball.

