PHY2023 Thermal Physics - Misha Portnoi Rm. 212

Core text:
Statistical Physics by
F. Mandl, various editions
'University Physics' by Young&Freedman, 11th Ed.
17. Temperature and Heat
18. Thermal Properties of Matter
19. The First Law of Thermodynamics
20. The Second Law of Thermodynamics

Supplementary texts:
Introductory Statistical Mechanics by
R. Bowley and M. Sánchez, various editions.
Heat and Thermodynamics by
M. W. Zemansky & R. H. Dittman, various editions.
*also any other **good** textbook such as*
Thermal Physics by
P. C. Riedi, various editions.

From "Statistical Mechanics Made Simple"

by D. C. Mattis (World Scientific, 2010)

Despite the lack of a reliable atomic theory of matter, the science of Thermodynamics flourished in the 19th century. Among the famous thinkers it attracted, one notes William Thomson (Lord Kelvin) after whom the temperature scale is named, and James Clerk Maxwell. The latter's many contributions include the "distribution function" and some very useful "differential relations" among thermodynamic quantities (as distinguished from his even more famous "equations" in electro-dynamics). The Maxwell relations set the stage for our present view of thermodynamics as a science based on function theory while grounded in experimental observations.

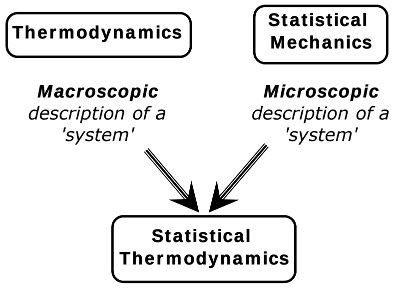
From "Statistical Mechanics Made Simple"

by D. C. Mattis (World Scientific, 2010)

The kinetic theory of gases came to be the next conceptual step. Among pioneers in this discipline one counts several unrecognized geniuses, such as J. J. Waterston who - thanks to Lord Rayleigh - received posthumous honours from the very same Royal Society that had steadfastly refused to publish his works during his lifetime. Ludwig Boltzmann committed suicide on September 5, 1906, depressed by the utter rejection of his atomistic theory by such colleagues as Mach and Ostwald. Paul Ehrenfest, another great innovator, died by his own hand in 1933. Among 20th century scientists in this field, a sizable number have met equally untimely ends. So "now it is our turn to study statistical mechanics" [D.H.Goodstein, *States of Matter*]

What is 'Thermal Physics'?

Temperature and Heat



Thermodynamics

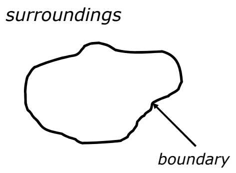
Statistical Mechanics

Macroscopic *description of a 'system'*

Microscopic *description of a 'system'*

Statistical Thermodynamics

What is 'system'?



The portion of the universe set aside for investigation is called the **system**. Everything outside the system is called the **surroundings**. The system is separated from the surroundings by a **boundary**, which may have different properties.

Types of systems

The system can be influenced (***i***) by exchanging matter, (***ii***) by doing work, (***iii***) thermally.

- ***Open system***: can exchange energy and matter.
- ***Closed system***: cannot exchange matter; can exchange energy; can have movable or stationary boundaries.
- ***Thermally isolated system***: cannot exchange energy in the form of heat; can do work.
- ***Isolated system***: cannot exchange energy and matter; stationary boundaries.

The Macroscopic View (human scale or larger)

The system is characterised by:

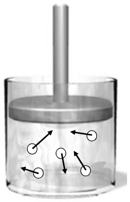
- *chemical composition*
- *volume*
- *pressure*
- *temperature*
- *density*

The macroscopic quantities that are used to specify the state of the system are called the ***state variables***; their values depend only on the condition or the state of the system.

The Microscopic View (molecular scale or smaller)

The system is considered as consisting of a large number of particles, existing in a set of energy states.

Probabilistic analysis.



Statistical Mechanics

Macroscopic *vs.* Microscopic

	Macroscopic	***Microscopic***

If the same system is considered, the two approaches **must** lead to the same conclusion!

How? Macroscopic parameters ⟷ Microscopic parameters averaged over time

e.g. Pressure ⟷ Average rate of change in momentum due to all molecular collisions on a unit area

What is Temperature?

How an intuitive concept can be developed analytically?

A
State S_A

System & **Surroundings**

State Variables

Boundary: in general, it may exchange matter and/or energy

- ❖ **Open systems**
- ❖ **Closed systems**
- ❖ **Thermally isolated systems**
- ❖ **Isolated systems**

Thermodynamic Equilibrium and Thermal Equilibrium

A
State S_A

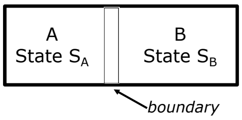
When a system suffers a change in its surroundings, it usually is seen to undergo change. After a time, the system will be found to reach a state where no further change takes place. The system has reached ***thermodynamic equilibrium***.

Similarly, if two systems are placed in thermal contact, generally changes will occur in both. When there is no longer any change, the two systems are said to be in ***thermal equilibrium***. The equilibrium state is determined by the equilibrium values of the state variables.

Definition: An equilibrium state is one in which all the state variables are uniform throughout the system and do not change in time.

Thermal Equilibrium

The equilibrium state depends on the nature of the boundary!



❖ **Adiabatic** boundary: perfectly insulating.

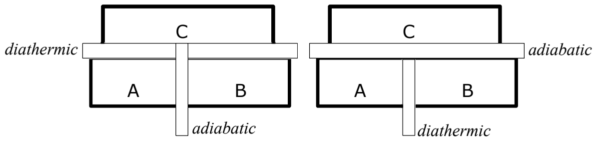
Any S_A can coexist with any S_B

❖ **Diathermic** boundary: perfectly conducting.

Change in S_A leads to change in S_B

Thermal Equilibrium: S_A and S_B are constant, but not necessary equal.

The experiment



A and **B** are insulated from each other, but are both in thermal equilibrium with **C**.

What will happen, if **A** and **B** are brought into contact via a diathermic wall?

Result: no change in the states of **A** and **B**.

This means that **A** and **B** are in thermal equilibrium: the two systems are found in such states that, if the two ***were*** connected through a diathermic wall, the combined system ***would be*** in thermal equilibrium.

The Zeroth Law of Thermodynamics

Two systems in thermal equilibrium with a third one are in thermal equilibrium with each other.

(Fowler & Guggenheim 1939)

[First Law – Helmholz 1847

Second Law – Carnot 1824]

Is this obvious?

Temperature

All systems in thermal equilibrium with each other possess a common property which we call the ***temperature.***

The temperature is that property that determines whether a system is in thermal equilibrium with other systems.

Two systems are in thermal equilibrium if and only if they have the same temperature.

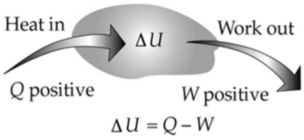
The First Law of Thermodynamics

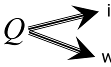
In any process where heat Q is added to the system and work W is done by the system, the net energy transfer, $Q - W$, is equal to the change, ΔU, in the internal energy of the system.

$$\Delta U = Q - W$$

$$\Delta U = U_2 - U_1$$

$$Q = \Delta U + W$$





Q
- increase internal energy
- work on surroundings

The First Law of Thermodynamics

Sign convention: In most statistical physics textbooks *W* is the work done *on* the system. Work *W* is positive if it is done *on* the system, similar to *Q,* which is positive if heat is added *to* the system.

Thus $\Delta U = Q + W$

In Joule's paddle-wheel experiment the work of gravity was indeed done *on* the system!

The First Law of Thermodynamics

$$dU = \delta Q + \delta W \qquad dU = \delta Q - PdV$$

dU is an exact differential.

U is a function of the state of the system only.

$\Delta U = U_2 - U_1$ depends only on the initial and end states and not on the path between them

The First Law states:

- Conservation of energy in thermodynamic systems
- Internal energy depends only on the state of the system, i.e. its change is path-independent

$$U = U(T,P)$$

Exact differentials

$$\mathrm{d}G = \left(\frac{\partial G(x,y)}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial G(x,y)}{\partial y}\right)_x \mathrm{d}y$$

where the notation $(\partial G(x,y)/\partial y)_x$ means differentiating $G(x,y)$ with respect to y keeping x constant. Such derivatives are called *partial derivatives*.

In general, $A(x,y)\,\mathrm{d}x + B(x,y)\,\mathrm{d}y = \mathrm{d}F$ is an exact differential and, correspondingly, $F(x,y)$ does not depend on the path only if

$$\left(\frac{\partial B(x,y)}{\partial x}\right)_y = \left(\frac{\partial A(x,y)}{\partial y}\right)_x$$

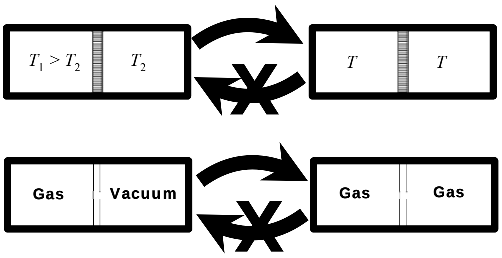
The First Law of Thermodynamics

The First Law: A perpetual motion machine of first kind is impossible.

The First Law does not explain:

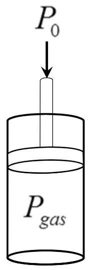
- Ease of converting work to heat but not vice versa.
- Systems naturally tend to a state of disorder, not order.
- Heat only flows DOWN a temperature gradient.

The Second Law



Although there would be no violation of the First Law, the reverse processes do not happen. Therefore, there must be a principle, dictating the ***direction*** of the processes in isolated systems: **the Second Law**

Reversible *vs.* Irreversible Processes



Irreversible processes:

- Finite changes in the state variables

$$P_0 = P_{gas} + \Delta P >> P_{gas}$$

- Existence of dissipative forces such as friction

$$P_0 = P_{gas} + P_{friction}$$

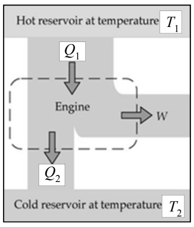
All real processes are irreversible!

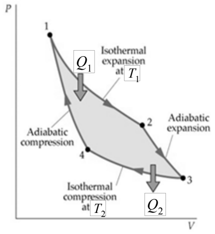
Reversible processes (idealised):

$$P_0 = P_{gas} + \delta P \approx P_{gas}$$

- Well-defined locus on P–V (or equivalent) diagram
- Can be retraced so that system **and** surrounding are restored

Carnot Cycle





$$\Delta U = Q - W$$

$$\Delta U_{\text{cyc}} = 0$$

$$Q = Q_1 + Q_2 = Q_1 - |Q_2|$$

$$W = W_{1\to2} + W_{2\to3} + W_{3\to4} + W_{4\to1}$$

$$W = Q$$

$$W = Q_1 + Q_2 = Q_1 - |Q_2|$$

$$\eta = \frac{W}{Q_1}$$ thermal efficiency of the engine

The Second Law

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - |Q_2|}{Q_1} = 1 - \frac{|Q_2|}{Q_1}$$

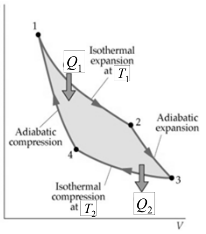
Experiment:
it is impossible to build a heat engine with η = 100 %
(i.e., a machine that converts heat completely to work).

The Second Law of Thermodynamics:

No process is possible whose **sole** result is the extraction of heat from a single reservoir and the performance of an equivalent amount of work.

Kelvin formulation

Thermal Efficiency of the Carnot Cycle



Working substance: *ideal gas*

$$\eta = 1 - \frac{|Q_2|}{Q_1} \qquad \Delta U = Q - W$$

$$\text{For } (1 \to 2): \quad \Delta U_{1\to 2} = 0$$

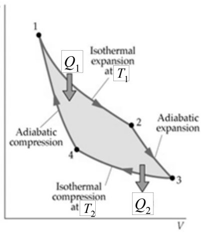
$$Q_1 = W_{1\to 2} = nRT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$\text{For } (3 \to 4): \quad \Delta U_{3\to 4} = 0$$

$$Q_2 = W_{3\to 4} = nRT_2 \ln\left(\frac{V_4}{V_3}\right) = -nRT_2 \ln\left(\frac{V_3}{V_4}\right)$$

$$\frac{|Q_2|}{Q_1} = \frac{T_2}{T_1} \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)}$$

Thermal Efficiency of the Carnot Cycle



$$\text{For } (2 \to 3): \quad T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\text{For } (4 \to 1): \quad T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

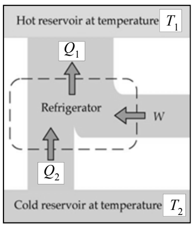
$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\frac{|Q_2|}{Q_1} = \frac{T_2}{T_1} \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} = \frac{T_2}{T_1}$$

$$\eta = 1 - \frac{|Q_2|}{Q_1} = 1 - \frac{T_2}{T_1}$$

Carnot Cycle as a refrigerator



Refrigerators extract heat from a colder reservoir and transfer it to a hotter reservoir. Experience shows that this always requires work.

$$\eta_R = \frac{|Q_2|}{|W|}$$ coefficient of performance

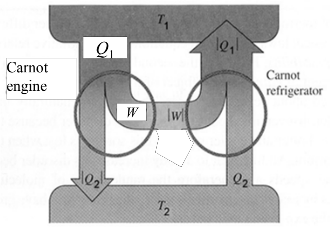
$$\eta_{HP} = \frac{|Q_1|}{|W|} = 1 + \eta_R$$ for heat pumps

The Second Law of Thermodynamics:

No process is possible whose **sole** result is the removal of heat from a reservoir at one temperature and the absorption of an equal quantity of heat by a reservoir at a higher temperature.

Clausius formulation

Thermal Efficiency of the Carnot Cycle



No engine can be more efficient than a Carnot engine operating between the same two temperatures.

$$\eta = 1 - \frac{T_2}{T_1}$$

Thermal Efficiency of the Carnot Cycle

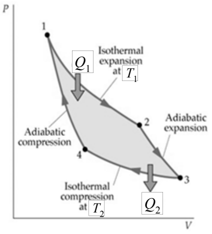
$$\eta = 1 - \frac{T_2}{T_1}$$

- Independent of working substance
- Depends only on reservoir temperatures T_1 and T_2
- Maximum possible efficiency of any heat engine
- Equal to the efficiency of any other **reversible** heat engine

Note that $\eta = 1$ when $T_2 = 0$.

Therefore, the Second Law forbids attainment of the absolute zero.

Entropy



$$\eta = 1 - \frac{|Q_2|}{Q_1} = 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \qquad \sum_i \frac{Q_i}{T_i} = 0$$

Consider any reversible cyclic process. It can be approximated by an infinite number of Carnot cycles. By summing up Q/T for each of them we obtain:

$$\sum_i \frac{Q_i^{(R)}}{T_i} = \oint \frac{\delta Q^{(R)}}{T} = 0$$

for any ***reversible*** cyclic process.

Entropy

$\oint \frac{\delta Q^{(R)}}{T} = 0$ for any reversible cyclic process.

This means that $\frac{\delta Q^{(R)}}{T}$ is an exact differential.

For an infinitesimal *reversible* change:

$$dS = \frac{\delta Q^{(R)}}{T} \qquad \delta Q^{(R)} = TdS$$

S – entropy

Reversible only!

dS is an exact differential, therefore the entropy S is a function of state.

The change in entropy ΔS between two states is determined solely by the initial and final equilibrium states and not by the path between them.

$$\Delta S = S_2 - S_1 = \int_{(1)}^{(2)} \frac{\delta Q^{(R)}}{T}$$

Entropy and irreversible processes

Remember that the reversible Carnot engine has a maximal thermal efficiency, equal to the efficiency of any other reversible heat engine.

Compare a reversible (R) and an irreversible (I) heat engine:

$$\eta_I = 1 + \frac{Q_2^{(I)}}{Q_1^{(I)}} \qquad \eta_R = 1 + \frac{Q_2^{(R)}}{Q_1^{(R)}} = 1 - \frac{T_2}{T_1} \qquad \eta_I < \eta_R$$

$$\frac{Q_2^{(I)}}{Q_1^{(I)}} < -\frac{T_2}{T_1} \qquad \frac{Q_1^{(I)}}{T_1} + \frac{Q_2^{(I)}}{T_2} < 0$$

$$\sum_i \frac{Q_i^{(I)}}{T_i} < 0 \qquad \oint \frac{\delta Q^{(I)}}{T} < 0$$

irreversible

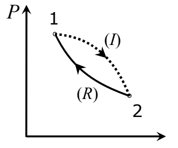
Compare with

$$\sum_i \frac{Q_i^{(R)}}{T_i} = 0 \qquad \oint \frac{\delta Q^{(R)}}{T} = 0$$

reversible

$$\boxed{\oint \frac{\delta Q}{T} \le 0}$$

Entropy and irreversible processes



$$\oint \frac{\delta Q}{T} < 0$$

$$\oint \frac{\delta Q}{T} = \int_{(1)}^{(2)} \frac{\delta Q^{(I)}}{T} + \int_{(2)}^{(1)} \frac{\delta Q^{(R)}}{T} < 0$$

$$\int_{(1)}^{(2)} \frac{\delta Q^{(I)}}{T} < -\int_{(2)}^{(1)} \frac{\delta Q^{(R)}}{T} \qquad \int_{(1)}^{(2)} \frac{\delta Q^{(I)}}{T} < \int_{(1)}^{(2)} \frac{\delta Q^{(R)}}{T} = S_2 - S_1$$

$$\Delta S > \int_{(1)}^{(2)} \frac{\delta Q^{(I)}}{T}$$

For an infinitesimal process: $dS > \frac{\delta Q^{(I)}}{T}$

$\boxed{dS \ge \frac{\delta Q}{T}}$ (*note that the equality applies only if the process is* ***reversible***)

Entropy and irreversible processes

$$dS \geq \frac{\delta Q}{T}$$

The Clausius inequality

For a system which is thermally isolated
(or completely isolated) $\delta Q = 0$:

$$\boxed{dS \geq 0}$$

The entropy of a (thermally) isolated system cannot decrease!

- Entropy distinguishes between reversible and irreversible processes.
- Helps determine the ***direction*** of natural processes and equilibrium configuration of a (thermally) isolated system: maximal entropy.
- Provides a natural direction to the time sequence of natural events.

Entropy and disorder

$dS \geq 0$ In a (thermally) isolated system, spontaneous processes proceed in the direction of increasing entropy.

Consider processes like irreversible heat flow or free expansion of a gas. They result in increased ***disorder***.

Example: Reversible (quasistatic) isothermal expansion of an ideal gas:

$$dU = 0 \Rightarrow \delta Q = \delta W = PdV = nRT\frac{dV}{V} \qquad \frac{dV}{V} \propto \frac{\delta Q}{T} = dS$$

$\frac{dV}{V}$ is a measure of the increase in disorder $\qquad \frac{dV}{V} \propto dS$

Entropy and disorder

Microscopically, the entropy of a system is a measure of the degree of molecular disorder existing in the system (much more on this later in this module):

$$S = k\ln\Omega$$

Ω is the *thermodynamic probability*

Therefore, in a (thermally) isolated system, only processes leading to greater disorder (or no change of order) will be possible, since the entropy must increase or remain constant, $dS \geq 0$.

The Fundamental Thermodynamic Relationship

$$dU = \delta Q - \delta W \qquad \delta W = PdV \qquad \delta Q = TdS$$

always *reversible* *reversible*

$$\boxed{dU = TdS - PdV}$$

Here all the variables are functions of state, so that all the differentials are exact. Therefore, it is true for all processes.

More generally

$$dU = TdS - PdV + \sum_i X_i dx_i$$

where $X_i dx_i = \begin{cases} fdl \\ \sigma dA \\ \cdots \end{cases}$

Exercises

1) A nuclear power station is designed to generate 1000 MW of electrical power. To do this it maintains a reservoir of superheated steam at a temperature of 400 K. Waste heat from the reactor is transferred by a heat exchanger to circulating sea water at 300 K. What is the minimum possible rate of nuclear energy generation needed?

Exercises

2) You are asked to design a refrigerated warehouse to maintain perishable food at a temperature of 5 C in an external environment of up to 30 C. The size of the warehouse and its degree of thermal insulation mean that the refrigeration plant must extract heat at a rate of 1000 KW. As a first step you must supply the local electricity company with an estimate for the likely electrical consumption of the proposed warehouse. What value would you suggest as a working minimum?

Exercises

3) One mole of ideal gas is maintained at a temperature T.

a) What is the minimum work needed to reduce its volume by a factor of e (=2.718…) ?

b) What is the entropy loss of the gas during this process?

4) 1 kg of water at 20C is placed in thermal contact with a heat reservoir at 80C. What is the entropy change of the total system (water plus reservoir) when equilibrium has been re-established?

Exercises

5) Demonstrate that the entropy change for *n* moles of ideal gas can also be written as

$$\Delta S = C_P \ln\left(\frac{T_2}{T_1}\right) - nR\ln\left(\frac{P_2}{P_1}\right)$$

where T_1, P_1 and T_2, P_2 are the initial and final temperatures and pressures respectively and C_P is the heat capacity at constant pressure.

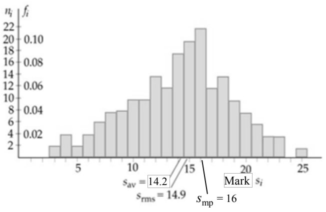
Exercises

6) Consider two identical bodies with heat capacity C initially at different temperatures T_1 and T_2. Show that the process of reaching thermal equilibrium necessarily involves a total increase in entropy. [See Supplement 1 on ELE]

Statistical Mechanics: an introduction

Preamble: distribution functions

1. Discrete distributions



n_i: number of students who received mark s_i

$$f_i = \frac{n_i}{N}$$

$n_i(s_i)$ and $f_i(s_i)$: distribution functions

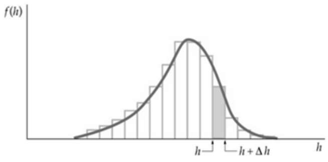
$$\sum_i f_i = \sum_i \frac{n_i}{N} = \frac{1}{N}\sum_i n_i = 1$$

$$\langle s \rangle = \frac{1}{N}\sum_i n_i s_i = \sum_i s_i f_i \qquad \langle g(s) \rangle = \frac{1}{N}\sum_i g(s_i) n_i = \sum_i g(s_i) f_i$$

$$\langle s^2 \rangle = \frac{1}{N}\sum_i s_i^2 n_i = \sum_i s_i^2 f_i \qquad s_{\mathrm{rms}} = \sqrt{\langle s^2 \rangle}$$

Statistical Mechanics: an introduction

2. Continuous distributions



$f(h)dh$: the probability of a person having a height between h and $h+dh$

$$dP = \frac{dN}{N} = f(h)dh$$

$f(h)$: distribution function

$dN = Nf(h)dh$: number of people with height between h and $h+dh$

$$\int f(h)dh = \int dP = 1$$

$$\langle h \rangle = \int h f(h) dh \qquad \langle g(h) \rangle = \int g(h) f(h) dh$$

$$\langle h^2 \rangle = \int h^2 f(h) dh$$

The Maxwell-Boltzmann distribution

What is the distribution of molecular speeds about average?

Expect:

- Mean $v_x = 0$ (no convection).
- No. of molecules with v_x = No. of molecules with $-v_x$ (even distribution function).
- No. of molecules with $v_x \rightarrow \pm\infty$ is negligible.

The Maxwell-Boltzmann distribution

Let $f(v_x)$ is the velocity distribution function.

Then the probability a molecule will have velocity between v_x and $(v_x + dv_x)$ is:

$$dP_{v_x} = \frac{dN}{N} = f(v_x)dv_x$$

The number of molecules with velocity between v_x and $(v_x + dv_x)$ is:

$$dN = Nf(v_x)dv_x$$

$$\int dN = \int_{-\infty}^{\infty} Nf(v_x)dv_x = N\int_{-\infty}^{\infty} f(v_x)dv_x = N$$

$\int_{-\infty}^{\infty} f(v_x)dv_x = 1$ as required

The Maxwell velocity distribution

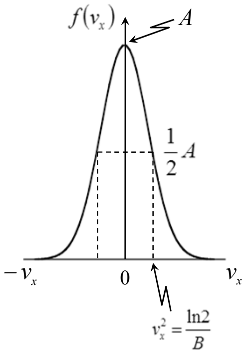
Guess that velocity distribution is Gaussian (normal distribution) [*can be derived using SM or from symmetry arguments*]:

$$f(v_x) = Ae^{-Bv_x^2}$$

Satisfies our three expectations.

A determines the height (normalisation)

B is inversely related to the width



The Maxwell velocity distribution

1. Normalisation (determines A)

$$\int_{-\infty}^{\infty} f(v_x)dv_x = \int_{-\infty}^{\infty} Ae^{-Bv_x^2}dv_x = 1$$

Remember that

$$\int_{-\infty}^{\infty} e^{-x^2}dx = \sqrt{\pi}$$

Therefore $A = \sqrt{B/\pi}$

2. Physical meaning of B

Calculate $\langle v_x^2 \rangle$: $\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x)dv_x$

The Maxwell velocity distribution

$$\langle v_x^2\rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x)\,dv_x = \sqrt{B/\pi}\int_{-\infty}^{\infty} v_x^2 e^{-Bv_x^2}\,dv_x$$

$$\boxed{\int_{-\infty}^{\infty} x^2 e^{-\beta x^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{\beta^3}}} \Rightarrow \boxed{\langle v_x^2\rangle = \frac{1}{2B}}$$

$$\langle E_x\rangle = \frac{1}{2}m\langle v_x^2\rangle = \frac{1}{2}kT \Rightarrow \boxed{B = \frac{m}{2kT}} \qquad B \propto \frac{1}{T}$$

For the distribution function we have:

$$f(v_x) = Ae^{-Bv_x^2} = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mv_x^2}{2kT}}$$

The Maxwell velocity distribution

In 3 dimensions

The probability a molecule will have velocity between v_x and $(v_x + dv_x)$, v_y and $(v_y + dv_y)$, v_z and $(v_z + dv_z)$

$$dP_{v_x,v_y,v_z} = \frac{dN}{N} = f(v_x)dv_x f(v_y)dv_y f(v_z)dv_z = $$
$$= f(v_x)f(v_y)f(v_z)dv_x dv_y dv_z$$

$$dP_{v_x,v_y,v_z} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m\left(v_x^2+v_y^2+v_z^2\right)}{2kT}} dv_x dv_y dv_z$$

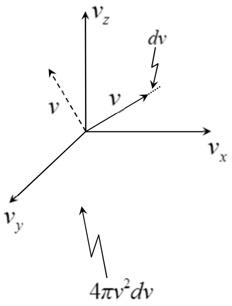
$$dP_{v_x,v_y,v_z} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} dv_x dv_y dv_z$$

$$dP_{v_x,v_y,v_z} = f_1(v)dv_x dv_y dv_z$$

The Maxwell-Boltzmann speed distribution function

What is the probability a molecule having ***speed*** between v and $v + dv$?

(remember that $v^2 = v_x^2 + v_y^2 + v_z^2$)



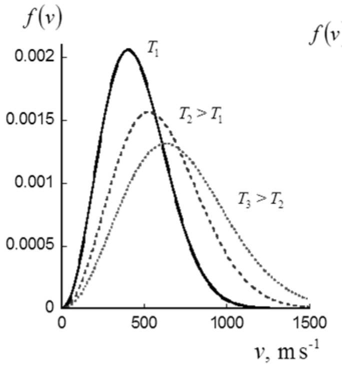
$$dP_{v_x,v_y,v_z} = f_1(v)dv_x dv_y dv_z$$

$$dP_v = f_1(v)4\pi v^2 dv$$

$$dP_v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} dv$$

$$\boxed{f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}}$$

Effect of temperature



$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

As T increases the curve flattens and the peak moves towards higher speeds.

Molecular speeds

1. Mean (average) speed

$$\langle v\rangle = \int_0^\infty v f(v)dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^3 e^{-\frac{mv^2}{2kT}}dv$$

$$\boxed{\langle v\rangle = \sqrt{\frac{8kT}{\pi m}}}$$

2. Root Mean Square (rms) speed

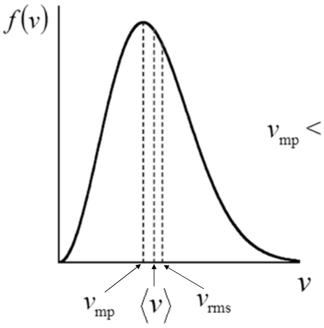
$$\langle v^2\rangle = \int_0^\infty v^2 f(v)dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^4 e^{-\frac{mv^2}{2kT}}dv$$

$$\boxed{v_{\text{rms}} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}}}$$

Molecular speeds

3. Most probable speed

Occurs at $\frac{df(v)}{dv} = 0 \Rightarrow \boxed{v_{\text{mp}} = \sqrt{\frac{2kT}{m}}}$



$$v_{\text{mp}} < \langle v\rangle < v_{\text{rms}}$$

Examples

The Maxwell-Boltzmann energy distribution function

Starting from

$$dP_v = f(v)dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}dv$$

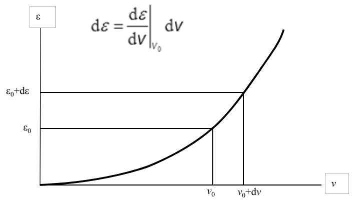
find the distribution function $F(E)$ for the energy by calculating the probability for a molecule to have energy between E and $E + dE$:

$$dP_{\mathrm{E}} = F(E)dE \quad \text{where} \quad E = \frac{mv^2}{2}$$

Answer: $F(E) = \frac{2}{\sqrt{\pi}}(kT)^{-3/2}E^{1/2}e^{-\frac{E}{kT}}$

The Maxwell-Boltzmann energy distribution function

We can exploit the 1:1 correspondence between ε and v to reformulate the speed distribution as a kinetic energy distribution :



The Maxwell-Boltzmann energy distribution function

Since a speed between v_0 and $v_0+\mathrm{d}v$ implies an energy between ε_0 and $\varepsilon_0+\mathrm{d}\varepsilon$, with , $\mathrm{d}\varepsilon = \frac{\mathrm{d}\varepsilon}{\mathrm{d}v}\mathrm{d}v$ the probability of obtaining a speed between v_0 and $v_0+\mathrm{d}v$ equals probability of obtaining an energy between ε_0 and $\varepsilon_0+\mathrm{d}\varepsilon$. hence, with

$$\varepsilon = \frac{mv^2}{2}; \mathrm{d}\varepsilon = m\,v\,\mathrm{d}v = \sqrt{2m\,\varepsilon}\,\mathrm{d}v$$

The Maxwell-Boltzmann energy distribution function

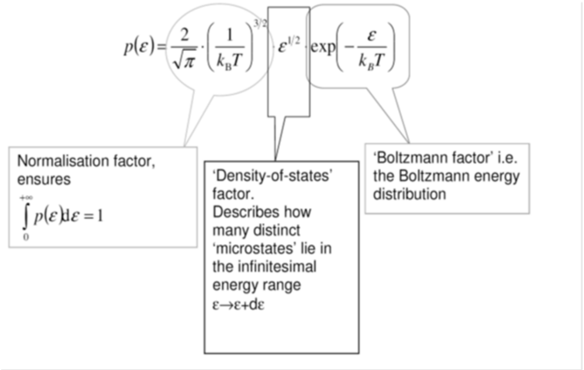
$$p(v)\mathrm{d}v = p(\varepsilon)\mathrm{d}\varepsilon = \left(\frac{2}{\pi}\right)^{1/2}\cdot\left(\frac{m}{k_{\mathrm{B}}T}\right)^{3/2}\cdot v^2\cdot\exp\left(-\frac{mv^2}{2k_{\mathrm{B}}T}\right)\cdot\mathrm{d}v$$

$$\therefore\ p(\varepsilon)\mathrm{d}\varepsilon = \left(\frac{2}{\pi}\right)^{1/2}\cdot\left(\frac{m}{k_{\mathrm{B}}T}\right)^{3/2}\cdot\frac{2\varepsilon}{m}\cdot\exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right)\cdot\frac{\mathrm{d}\varepsilon}{\sqrt{2m\varepsilon}}$$

$$= \frac{2}{(\pi)^{1/2}}\cdot\left(\frac{1}{k_{\mathrm{B}}T}\right)^{3/2}\cdot\varepsilon^{1/2}\cdot\exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right)\cdot\mathrm{d}\varepsilon$$

Exercise: What happens in a 2D case?

The Maxwell-Boltzmann energy distribution function



$$p(\varepsilon) = \frac{2}{\sqrt{\pi}}\cdot\left(\frac{1}{k_{\mathrm{B}}T}\right)^{3/2}\cdot\varepsilon^{1/2}\cdot\exp\left(-\frac{\varepsilon}{k_{\mathrm{B}}T}\right)$$

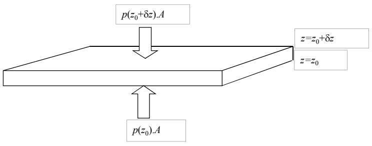
Normalisation factor, ensures $\int_0^{+\infty} p(\varepsilon)\mathrm{d}\varepsilon = 1$

'Density-of-states' factor. Describes how many distinct 'microstates' lie in the infinitesimal energy range $\varepsilon\to\varepsilon+\mathrm{d}\varepsilon$

'Boltzmann factor' i.e. the Boltzmann energy distribution

Example of the Boltzmann factor

Consider a mass of isothermal ideal gas, at temperature *T*. For a thin slab of gas at height z_0, thickness δz and cross-sectional area *A* to not fall under gravity requires :



Hydrostatic equilibrium:-

$$p(z_0)A - p(z_0+\delta z)A = \rho(z_0)A\,\delta z\,g$$

$$\therefore\ p(z_0) - p(z_0+\delta z) = \rho(z_0)\,\delta z\,g$$

Example of the Boltzmann factor

Expanding $p(z)$ in a Taylor series:

$$p(z_0+\delta z)=p(z_0)+\left.\frac{\mathrm{d}p(z)}{\mathrm{d}z}\right|_{z_0}\delta z+\frac{1}{2!}\left.\frac{\mathrm{d}^2p(z)}{\mathrm{d}z^2}\right|_{z_0}\delta z^2+\frac{1}{3!}\left.\frac{\mathrm{d}^3p(z)}{\mathrm{d}z^3}\right|_{z_0}\delta z^3+\ldots\mathrm{O}(\delta z^4)$$

In the limit that the slab thickness $\delta z \to 0$,

$$p(z_0+\mathrm{d}z)-p(z_0)=\left.\frac{\mathrm{d}p(z)}{\mathrm{d}z}\right|_{z_0}\mathrm{d}z. \quad \text{Hence,} \quad \rho(z_0)g\,\mathrm{d}z=-\left.\frac{\mathrm{d}p(z)}{\mathrm{d}z}\right|_{z_0}\mathrm{d}z,$$

$$\rho(z)g=-\frac{\mathrm{d}p(z)}{\mathrm{d}z} \qquad \therefore \frac{\mathrm{d}p(z)}{\mathrm{d}z}=-n(z)m_{\mathrm{A}}g$$

With m_{A} being the mass of one gas atom and n being the number density of gas atoms.

Example of the Boltzmann factor

Ideal gas equation of state: $pV=Nk_{\mathrm{B}}T \Rightarrow p=\frac{N}{V}k_{\mathrm{B}}T=nk_{\mathrm{B}}T,$

hence $k_{\mathrm{B}}T\frac{\mathrm{d}n(z)}{\mathrm{d}z}=-n(z)m_{\mathrm{A}}g \Rightarrow \frac{\mathrm{d}n(z)}{\mathrm{d}z}=-\frac{m_{\mathrm{A}}g}{k_{\mathrm{B}}T}n(z)$

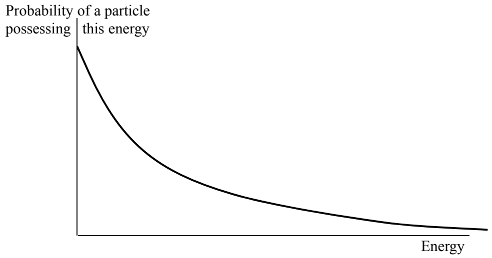
$$\therefore n(z)=n(z=0).\exp\left(-\frac{m_{\mathrm{A}}g}{k_{\mathrm{B}}T}z\right)$$

Hence $n(z)$, $\rho(z)$ and $p(z)$ all fall exponentially with height.

Here $m_{\mathrm{A}}gz$ is the gravitational potential energy of a gas atom at height z. Since $n(z) \propto$ probability of finding a gas atom at height z, suggests that the probability of finding a gas atom in an "energy level" of value $\varepsilon(z)$ is proportional to $\boxed{\exp\left(-\frac{\varepsilon(z)}{k_{\mathrm{B}}T}\right)}$ **- Boltzmann factor**

Example of the Boltzmann factor

The Boltzmann factor is of universal validity; whenever an ensemble of classical particles are in equilibrium at temperature T, the probability of an energy level of value $\varepsilon(z)$ being "occupied" by a particle of the ensemble varies as the negative exponential of $\varepsilon(z)/k\mathrm{B}T$.



Mathematical detour

Consider

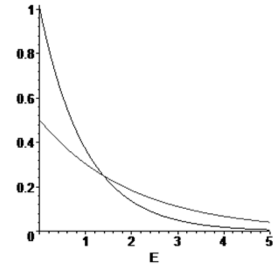
Find *A* from the "normalisation" condition:

Plot (sketch)

(a)

(b)

Mathematical detour



Example of Boltzmann energy sharing

7 identical, but distinguishable systems, each with quantized energy levels 0ε, 1ε, 2ε, 3ε … We have a total energy of 7ε to share amongst the systems. Labeling the systems A…G, some possible arrangements are :-

Note that the first two, distinct, arrangements nevertheless correspond to an identical <u>macroscopic</u> energy sharing arrangement (macrostate 'a' in the table below).

Example of Boltzmann energy sharing

Denoting the number of systems in energy level ε_i as n_i, then Ω, the number of possible microstates corresponding to this macrostate is given by

$$\Omega = \frac{7!}{n_0!\cdot n_1!\cdot n_2!\cdot n_3!\cdot n_4!\cdot n_5!\cdot n_6!\ldots} \quad \text{or in general} \quad \Omega = \frac{N!}{\prod_{i=0}^{\infty} n_i!}.$$

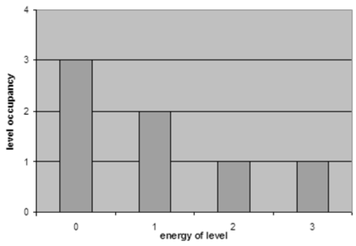
Since the n_i's must satisfy the constraints $\sum_{i=0}^{\infty} n_i = N$ and $\sum_{i=0}^{\infty} n_i \cdot \varepsilon_i = U,$ with N the total number of systems and U the total shared energy, we can complete the table of Ω for each macrostate

Example of Boltzmann energy sharing

macrostate	n_0	n_1	n_2	n_3	n_4	n_5	n_6	n_7	$n_{8,9,10\ldots}$	Ω
a	6	0	0	0	0	0	0	1	0	7
b	5	1	0	0	0	0	1	0	0	42
c	5	0	1	0	0	1	0	0	0	42
d	4	2	0	0	0	1	0	0	0	105
e	5	0	0	1	1	0	0	0	0	42
f	4	1	1	0	1	0	0	0	0	210
g	3	3	0	0	1	0	0	0	0	140
h	2	4	0	1	0	0	0	0	0	105
i	4	0	2	1	0	0	0	0	0	105
j	3	2	1	1	0	0	0	0	0	420
k	4	1	0	2	0	0	0	0	0	105
l	1	5	1	0	0	0	0	0	0	42
m	2	3	2	0	0	0	0	0	0	210
n	3	1	3	0	0	0	0	0	0	140
o	0	7	0	0	0	0	0	0	0	1
									Ω_{total}	**1716**

Example of Boltzmann energy sharing

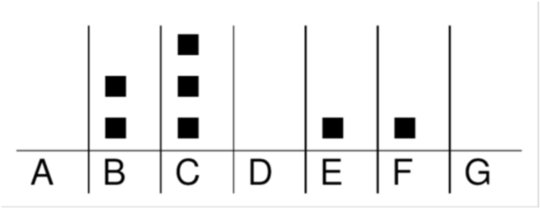
Note that, if one of the 1,716 distinct microstates were chosen at random, macrostate 'j' would occur with a probability of 420/1716 i.e. 24%. This is the most probable macrostate, and distributes the available energy roughly as a negative exponential function:



i.e. the relative occupancy of an energy level falls exponentially as the energy of that level increases. This pattern becomes clearer as the number of systems and the shared energy are increased.

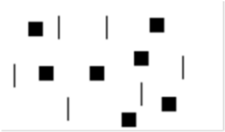
Example of Boltzmann energy sharing

In total, there are 1,716 possible ways to share 7ε amongst 7 identical systems. To calculate this directly, consider 7 distinguishable heaps A, B, C… G. How many ways can we distribute 7 identical bricks among these? One possibility is



Example of Boltzmann energy sharing

Equivalent problem. Consider a pile of 7 bricks and 6 partitions (all indistinguishable).



If we draw objects (bricks or partitions) at random, each distinct sequence of bricks and partitions corresponds to exactly one possible distribution of 7 bricks amongst 7 heaps e.g. the possible arrangement noted above corresponds to the sequence

| ■ ■ | ■ ■ ■ | | ■ | ■ |

Example of Boltzmann energy sharing

| ■ ■ | ■ ■ ■ | | ■ | ■ |

If bricks and partitions are indistinguishable, number of ways equals $\frac{(7+6)!}{7!6!} = 1{,}716$

Hence in general, we can distribute *N* packets of energy over *k* systems in

$$\frac{(N+k-1)!}{N!(k-1)!}$$ ways.

The fundamental postulates of statistical mechanics

1. An ensemble of identical but distinguishable systems can be described completely by specifying its "**microstate**". The microstate is the most detailed description of an ensemble that can be provided. For an ideal gas of *N* particles in a container, it involves specifying 6*N* co-ordinates, the position and velocity of all *N* particles. For the example of Boltzmann energy sharing, it involves specifying the energy level occupied by each individual system.

The fundamental postulates of statistical mechanics

2. Physically we observe only a corresponding "**macrostate**", specified in terms of macroscopically observable quantities. A macrostate for an ideal gas is specified fully by a few observable quantities such as pressure, temperature, volume, entropy etc. For the example of Boltzmann energy sharing, a macrostate is specified fully by the occupancies of the various energy levels e.g. [0,7,0,0,0,0,0,0…] is a macrostate of equal energy sharing.

The fundamental postulates of statistical mechanics

3. If we observe an ensemble over time, random perturbations ensure that all accessible microstates will occur with equal probability. Hence probability of a macrostate occurring =

$$\frac{\text{no. of microstates corresponding to that macrostate}}{\text{total number of microstates}}$$

4. The macrostate with the highest probability of occurrence corresponds to the equilibrium state.

Boltzmann distribution

Maximise $\Omega = \dfrac{N!}{\prod_{i=0}^{\infty} n_i!}$

subject to the constraints $\sum_{i=0}^{\infty} n_i = N \quad \sum_{i=0}^{\infty} n_i\,\varepsilon_i = U$

using Lagrange Undetermined Multipliers (see supplementary sheet).

Solution: $\dfrac{n_i}{N} = \dfrac{\exp(-\beta\varepsilon_i)}{\sum_{i=0}^{\infty}\exp(-\beta\varepsilon_i)}$ (with β undetermined)

Assigning $\beta = 1/k_\mathrm{B}T$

Boltzmann distribution

$$\boxed{\frac{n_i}{N} = \frac{\exp(-\varepsilon_i/k_\mathrm{B}T)}{\sum_{i=0}^{\infty}\exp(-\varepsilon_i/k_\mathrm{B}T)}}$$

Boltzmann distribution

NB n_i/N is the probability that a state of energy ε_i is occupied by a member of an ensemble which is in thermal equilibrium at temperature *T*.

THE BOLTZMANN DISTRIBUTION IS THE MOST IMPORTANT RESULT IN THIS COURSE !!

Examples

Ensemble of *N* gas atoms. Outer electron can reside in a "ground-state" energy level, or in an excited state, 1 eV above this. At 1000 K, what fraction of atoms lie in the excited state, relative to the ground-state?

Boltzmann distribution: $\dfrac{n_i}{N} = \dfrac{\exp(-\varepsilon_i/k_\mathrm{B}T)}{\sum_{i=0}^{\infty}\exp(-\varepsilon_i/k_\mathrm{B}T)}$

n_i is no. of systems occupying a state of energy ε_i, when ensemble of *N* such systems is in thermal equilibrium at temp *T*. For a 2-level system, energies ε_1, ε_2, relative occupancy of these levels is given by

Examples

$$\frac{n_2}{n_1} = \frac{\exp(-\varepsilon_2/k_B T)}{\sum_{i=0}^{\infty}\exp(-\varepsilon_i/k_B T)}\frac{\sum_{i=0}^{\infty}\exp(-\varepsilon_i/k_B T)}{\exp(-\varepsilon_1/k_B T)} = \exp(-(\varepsilon_2-\varepsilon_1)/k_B T)$$

$$\boxed{\frac{n_2}{n_1} = \exp(-\Delta\varepsilon/k_B T)}$$

with $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$

Useful “rule of thumb”: At room temperature (300K) the thermal energy $k_B T$ is 25 meV

Examples

Hence at 1000 K the thermal energy is
25 meV×1000/300.

$\therefore n_2/n_1 = \exp(-1/(25\times10^{-3}\times10/3)) = \exp(-12) = 6\times10^{-6}$

$$\underline{n_2/n_1 = 6\times10^{-6}}$$

Cool the gas to 300 K:-

$n_2/n_1 = \exp(-1/(25^{*}\times10^{-3})) = \exp(-40) = 4\times10^{-18}$

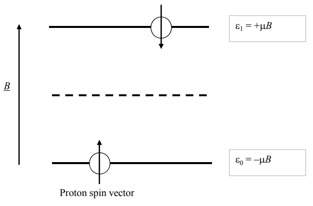
$$\underline{n_2/n_1 = 4\times10^{-18}}$$

Very strong *T*-dependence!

Examples

Ensemble of protons, magnetic moment μ, in external magnetic field *B*. Magnetostatic potential energy = +μ*B* if proton spin anti-parallel to field, −μ*B* if proton spin parallel to field.

Simple 2-level system:



In equilibrium, what is the net imbalance between spin “aligned” ($n_\uparrow$) and spin “anti-aligned” ($n_\downarrow$) protons (i.e. what is the fractional magnetization) at room temperature?

Examples

$$\frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow} = \frac{1 - n_\downarrow / n_\uparrow}{1 + n_\downarrow / n_\uparrow}$$

$$= \frac{1 - \exp\left(-\left(\varepsilon_1 - \varepsilon_0\right)/\left(k_\mathrm{B}T\right)\right)}{1 + \exp\left(-\left(\varepsilon_1 - \varepsilon_0\right)/\left(k_\mathrm{B}T\right)\right)} = \frac{1 - \exp\left(-2\mu B/\left(k_\mathrm{B}T\right)\right)}{1 + \exp\left(-2\mu B/\left(k_\mathrm{B}T\right)\right)}$$

Proton μ = 1.41×10–26 JT–1. B = 1 T (typically),
T = 300 K. Hence $2\mu B = 2.82\times10^{-26}$ J.

$k_\mathrm{B}T = 1.38\times10^{-23}\times300$ J $= 4.14\times10^{-21}$ J.

Since $2\mu B << k_\mathrm{B}T$: $\exp\left(-2\mu B/\left(k_\mathrm{B}T\right)\right) \cong 1 - 2\mu B/\left(k_\mathrm{B}T\right)$

$$\frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow} \cong \frac{1 - \left(1 - 2\mu B/\left(k_\mathrm{B}T\right)\right)}{1 + \left(1 - 2\mu B/\left(k_\mathrm{B}T\right)\right)} \cong \frac{\mu B}{k_\mathrm{B}T}$$

Examples

Hence at 300K and 1 T, the net imbalance of proton spins is 1.41×10^{-26} / 4.14×10^{-21} J

$= 3.4\times10^{-6}$

i.e. a very small imbalance.

Degeneracy

More than one 'state' can correspond to the same 'energy level'.

'State': the fullest description of a system allowed by quantum mechanics. A full set of **'quantum numbers'** must be specified, specifying e.g. the energy, orbital angular momentum and spin of the system.

'Energy level':- a quantized energy value that can be possessed by the system. Specified using a single quantum number (the 'principal' quantum number).

E.g., electron of mass m_e in a 1-D infinite potential well of width L

$$\varepsilon_n = n^2 \frac{h^2}{8m_\mathrm{e}L}$$

The integer n (=1, 2, 3…) labels the energy levels and is the principle quantum number.

Degeneracy

To fully specify the state of an electron in the well we must specify two quantum numbers *n* and *s* ($s = -½$ or ½). *s* is the "spin" quantum number and specifies whether the electron spin is found to be "up" or "down" if measured relative to a given direction in space. In the absence of an external electromagnetic field, the energies of state ($n, -½$) and ($n, ½$) are identical. Thus energy level *n* is said to be two-fold degenerate (or to have a degeneracy factor *g* equal to 2) in this example.

Degeneracy

The Boltzmann distribution gives the probability that a state i of energy ε_i is occupied, given an ensemble in equilibrium at temperature *T*. To calculate the probability that an energy level of energy ε_i, whose degeneracy factor is g_i, is occupied simply sum the probabilities for all the degenerate states corresponding to the energy level ε_i, i.e. multiply the appropriate Boltzmann factor by g_i. Hence, denoting p_i as the probability that a state i is occupied and $p(\varepsilon_i)$ the probability that an energy level ε_i is occupied, we can write the Boltzmann distribution in two ways:

Degeneracy

$$p_i = \frac{\exp\left(-\varepsilon_i/k_\mathrm{B}T\right)}{\sum\limits_{i=0}^{\text{all states}} \exp\left(-\varepsilon_i/k_\mathrm{B}T\right)}$$

$$p(\varepsilon_i) = \frac{g_i \exp\left(-\varepsilon_i/k_\mathrm{B}T\right)}{\sum\limits_{i=0}^{\text{all energy levels}} g_i \exp\left(-\varepsilon_i/k_\mathrm{B}T\right)}$$

Degeneracy

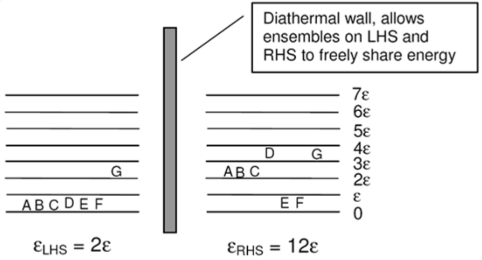
Example:

The 1st excited energy level of He lies 19.82 eV above the ground state and is 3-fold degenerate. What is the population ratio between the ground state (which is not degenerate) and the 1st excited level, when a gas of He is maintained at 10,000 K?

$$\frac{p(\varepsilon_1)}{p(\varepsilon_0)} = \frac{g_1}{g_0}\exp\left(-\frac{\Delta\varepsilon}{k_B T}\right) = 3\times\exp\left(-\frac{19.82\times1.6\times10^{-19}}{1.38\times10^{-23}\times10^4}\right)$$
$$= 3\times10^{-10}$$

Microscopic interpretation of entropy

Two identical "ensembles" each of 7 identical systems are placed in diathermal contact and share a total energy 14ε. Each system can possess energy 0, ε, 2ε, 3ε … What is the most probable distribution of energy?
One possibility :

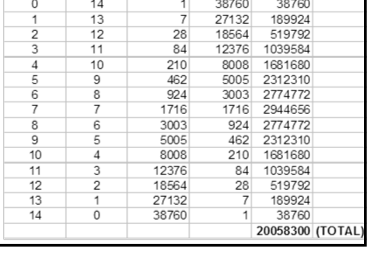


Microscopic interpretation of entropy

Total number of arrangements on LHS $\Omega_{LHS} = \Omega_{2,7} = 28$,

[$\Omega_{n,k} = \frac{(n+k-1)!}{n!(k-1)!}$]. Likewise $\Omega_{RHS} = \Omega_{12,7} = 18,564$.

Hence $\Omega_{total} = \Omega_{LHS}\times\Omega_{RHS} = 519, 792$. Tabulate this for ALL possible sharings:



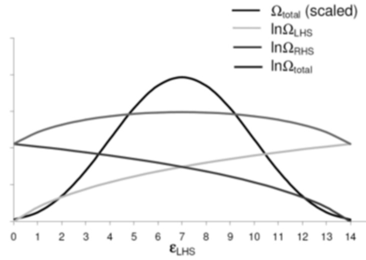
ε_{LHS}	ε_{RHS}	Ω_{LHS}	Ω_{RHS}	Ω_{total}	
0	14	1	38760	38760	
1	13	7	27132	189924	
2	12	28	18564	519792	
3	11	84	12376	1039584	
4	10	210	8008	1681680	
5	9	462	5005	2312310	
6	8	924	3003	2774772	
7	7	1716	1716	2944656	
8	6	3003	924	2774772	
9	5	5005	462	2312310	
10	4	8008	210	1681680	
11	3	12376	84	1039584	
12	2	18564	28	519792	
13	1	27132	7	189924	
14	0	38760	1	38760	
				20058300	**(TOTAL)**

The "macrostate" of equal energy sharing can be realized in the most number of ways!

Microscopic interpretation of entropy

Choosing a “microstate” at random, the macrostate of equal energy sharing would occur with 2944656/20058300 = 15% probability. Macrostate of completely uneven sharing [(0,14) or (14,0)] occurs with 2*38760/20058300 = 0.4% probability.

Plot this graphically:-



Microscopic interpretation of entropy

Over time, the ensembles will spontaneously evolve via random interactions to “visit” all accessible microstates with, *a-priori*, equal probability. If initially in a macrostate of low W_{total}, it is thus overwhelmingly likely that at a later time they will be found in a macrostate of high W_{total}.

c.f. 2nd law: systems spontaneously evolve from a state of low S to a state of higher S.

$$\boxed{S = k_{\text{B}} \ln \Omega}$$

Boltzmann/Planck hypothesis, 1905. Defines “statistical entropy”

Clausius’s S (“classical” entropy) is an “extensive” variable/function of state i.e. two ensembles a) and b), $S_{\text{total}} = S_{\text{a}} + S_{\text{b}}$.

Microscopic interpretation of entropy

Statistically $\Omega_{\text{total}} = \Omega_{\text{a}} \times \Omega_{\text{b}}$,

Hence statistical entropy is also extensive.

$$\boxed{\begin{aligned} S_{\text{total}} &= k_{\text{B}} \ln \Omega_{\text{total}} \\ &= k_{\text{B}} \ln \Omega_{\text{a}} \Omega_{\text{b}} \\ &= k_{\text{B}} \ln \Omega_{\text{a}} + k_{\text{B}} \ln \Omega_{\text{b}} \\ &= S_{\text{a}} + S_{\text{b}}. \end{aligned}}$$

Extensive variables – increase with the system size. Intensive variables do not increase with the system size.

Extensive	Intensive
Mass	Density
Energy	Temperature
Entropy	Pressure
Volume	Specific heat capacity
Heat capacity	

Microscopic interpretation of entropy

Equilibrium macrostate has the highest $\ln\Omega$, hence

$$\frac{\mathrm{d}\ln\Omega_{\text{total}}}{\mathrm{d}\varepsilon_{\text{LHS}}} = 0$$

$$\therefore \frac{\mathrm{d}\left(\ln\Omega_{\text{LHS}} + \ln\Omega_{\text{RHS}}\right)}{\mathrm{d}\varepsilon_{\text{LHS}}} = 0$$

$$\therefore \frac{\mathrm{d}\ln\Omega_{\text{LHS}}}{\mathrm{d}\varepsilon_{\text{LHS}}} + \frac{\mathrm{d}\ln\Omega_{\text{RHS}}}{\mathrm{d}\varepsilon_{\text{LHS}}} = 0$$

Microscopic interpretation of entropy

Since $\varepsilon_{\text{total}} = \varepsilon_{\text{LHS}} + \varepsilon_{\text{RHS}} = \text{constant}$

$$\therefore \mathrm{d}\varepsilon_{\text{LHS}} = -\mathrm{d}\varepsilon_{\text{RHS}}$$

$$\therefore \frac{\mathrm{d}\ln\Omega_{\text{LHS}}}{\mathrm{d}\varepsilon_{\text{LHS}}} = \frac{\mathrm{d}\ln\Omega_{\text{RHS}}}{\mathrm{d}\varepsilon_{\text{RHS}}}$$

Since $S = k_{\text{B}} \ln\Omega$

$$\frac{\mathrm{d}S_{\text{LHS}}}{\mathrm{d}\varepsilon_{\text{LHS}}} = \frac{\mathrm{d}S_{\text{RHS}}}{\mathrm{d}\varepsilon_{\text{RHS}}}$$

Microscopic interpretation of entropy

Intuitively, equilibrium implies equal 'temperature' for the ensembles. Combined with dimensional arguments ($[S]/[\varepsilon] = \text{K}^{-1}$) suggests

$\frac{\mathrm{d}S}{\mathrm{d}\varepsilon} = \frac{1}{T}$ for any system.

Since we considered the energy levels to be fixed, implicitly we assumed V = const. (QM predicts energy spacing increases as size of potential well decreases), hence formally

$$\boxed{\left(\frac{\partial S}{\partial \varepsilon}\right)_V = \frac{1}{T}}$$

Maxwell relations

Classically:-

Expect $U = U(T)$ for an ideal gas, but Joule found slight cooling during isoenergetic expansion of a real gas. Suggests we need other variables to fully define U.

Fundamental thermodynamic relationship:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

c.f. Math for Physicists for a general function $f(x,y)$:

$$\mathrm{d}f(x,y) = \left(\frac{\partial f(x,y)}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f(x,y)}{\partial y}\right)_x \mathrm{d}y$$

Maxwell relations

Suggests $U = U(S,V)$ and

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

Hence (first relation):

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad \text{c.f.} \quad \left(\frac{\partial S}{\partial \varepsilon}\right)_V = \frac{1}{T} \quad \text{found earlier.}$$

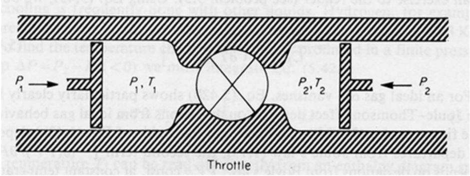
S & *V* are the "**natural variables**" of *U*

Also, since $\dfrac{\partial^2 U}{\partial V \partial S} = \dfrac{\partial^2 U}{\partial S \partial V}$ $\quad \boxed{\therefore \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V}$

1st Maxwell Relation

The Joule-Thompson process

Joule-Thompson (Joule-Kelvin) process: obstructed flow of gas from a uniform high pressure to a uniform low pressure through a semi-permeable "porous plug".



Small mass of gas Δm traverses the obstruction: initial pressure p_1, volume V_1, internal energy U_1; final pressure p_2, volume V_2, internal energy U_2.

The Joule-Thompson process: enthalpy

Total work done = $-p_1\,(0-V_1) - p_2\,(V_2-0)$. Since the process is adiabatic, 1st law implies:

$U_2 - U_1 = p_1\,V_1 - p_2\,V_2$ hence

$U_1 + p_1\,V_1 = U_2 + p_2\,V_2$.

define $H = U + pV$,

where H is "**enthalpy**".

Then $H_1 = H_2$ where H_1 is the enthalpy of the small mass of gas Δm before traversing the obstruction, ditto H_2.

Hence enthalpy is conserved in the J-T process, i.e. J-T expansion is ***isenthalpic***.

Maxwell relations: enthalpy

Differentiating:

$\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p$

Since $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$

$$\underline{\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p}$$

Hence $H = H(S, p)$.

By analogy with $U = U(S, V)$.

$$\left(\frac{\partial H}{\partial S}\right)_p = T, \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

Maxwell relations: enthalpy

Hence (by equating cross-derivatives),

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p}$$

2nd Maxwell relation

n-moles of ideal gas :-

$$U = \frac{3}{2}nRT \quad \& \quad pV = nRT$$

$$\therefore H = \frac{5}{2}nRT$$

Maxwell relations: enthalpy

Hence $H = H(T)$ for an ideal gas, hence J-T process does NOT cool an ideal gas (H=const => T=const).

Since $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$, for a reversible isobaric process ($\mathrm{d}p = 0$) $\underline{\mathrm{d}H = T\mathrm{d}S = \delta Q}$.

Hence *H* represents the heat flow during a reversible isobaric process i.e. $\underline{\mathrm{d}H = C_p \mathrm{d}T}$

c.f. $dU = C_V dT$, i.e. U represents the heat flow during an isochoric process.

H is useful when studying processes that occur at constant pressure, e.g., chemical reactions in an open container.

The Joule-Thompson process

$$\alpha_{\mathrm{JT}} \equiv \left(\frac{\partial T}{\partial p}\right)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p}.$$

Since $H = U + pV$

$$\alpha_{\mathrm{JT}} = \frac{-\left(\frac{\partial U}{\partial p}\right)_T - \left(\frac{\partial (pV)}{\partial p}\right)_T}{C_p}.$$

However, $(\partial U/\partial p)_T$ in this relation can not be obtained from measurements or from the equation of state. Therefore, a more convenient form for α_{JT} follows from the relation:

The Joule-Thompson process

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p.$$

The derivation is left as an exercise (non-trivial).

Therefore, $$\alpha_{\mathrm{JT}} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right].$$

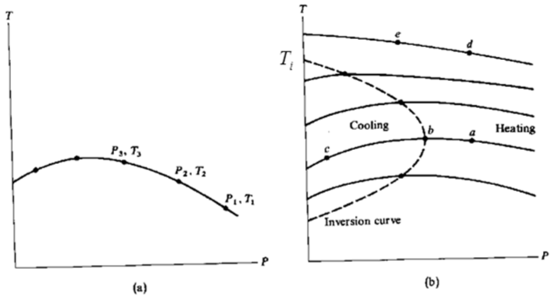
It is easy to see that for an ideal gas α_{JT} vanishes.

The equation of state for one mole of a real gas can be written as (virial expansion): $$pV = RT\left[1 + \frac{B_2}{V} + \frac{B_3}{V^2} + \cdots\right].$$

For a gas of low density (keeping terms up to B_2 only) $pV = RT + B_2(T)\,p$,

whence $$\boxed{\alpha_{\mathrm{JT}} = \frac{T\frac{\mathrm{d}B_2(T)}{\mathrm{d}T} - B_2(T)}{C_p}.}$$

The Joule-Thompson process



Curves of constant enthalpy. The dashed curve is the inversion curve. On it $(\partial T/\partial p)_H = 0$. Inside (outside) it, the gas is cooled (warmed) on expansion.

The Joule-Thompson process

Inversion temperature of some gases

gas	He	H_2	N_2	A	O_2
T_i(K)	23.6	195	621	723	893

JT process can cool (ultimately liquefy) O_2 and N_2 directly. Must pre-cool H_2 and He e.g. by heat exchange with liquefied N_2.

JT expansion is a step in the "Linde Liquefaction Cycle". Very widely used to manufacture cryogens, rocket fuel etc.

Exercise: Show that $\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$.

Thermodynamic potentials

For a simple fluid system of fixed size (i.e. fixed N) there are four thermodynamic potentials :-

1. Internal energy U
2. Enthalpy $H = U + pV$
3. Helmholtz Free Energy $F = U - TS$
4. Gibbs Free Energy $G = U - TS + pV$

By analogy with U and H :-

$$dF = dU - TdS - SdT = -pdV - SdT$$

Hence $F = F(T,V)$, i.e. T and V are the natural variables of F.

Thermodynamic potentials: Helmholtz Free Energy

Also $\left(\frac{\partial F}{\partial V}\right)_T = -p \quad \left(\frac{\partial F}{\partial T}\right)_V = -S$

hence

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T}$$

3rd Maxwell Relation

Since $\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T$ the change in F represents the work done on/by a system during an isothermal ($\mathrm{d}T = 0$) process.

Thermodynamic potentials: Helmholtz Free Energy

Also, $\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T$ in general, but $T\mathrm{d}S = \mathrm{d}U + p\mathrm{d}V$ only for changes between equilibrium states. For changes between non-equilibrium states $T\mathrm{d}S > \mathrm{d}U + p\mathrm{d}V$ [recall example sharing 14ε between 2 ensembles: $\mathrm{d}U = \text{zero}$ (total energy constant), $\mathrm{d}V = \text{zero}$ (fixed energy levels) but $\mathrm{d}S > 0$ except when equilibrium reached].

Hence $\mathrm{d}F = \text{zero}$ when equilibrium reached, $\mathrm{d}F < \text{zero}$ as equilibrium is approached. Hence

For a system evolving at constant volume and temperature, equilibrium corresponds to a minimum of the system's Helmholtz free energy.

Thermodynamic potentials: Gibbs Free Energy

$$\mathrm{d}G = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T + p\mathrm{d}V + V\mathrm{d}p = -S\mathrm{d}T + V\mathrm{d}p$$

Hence $G = G(T, p)$ i.e. T and p are the natural variables of G.

Also $\left(\frac{\partial G}{\partial p}\right)_T = V \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$

hence

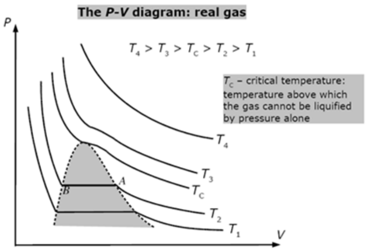
$$\boxed{\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T}$$

4th Maxwell Relation

For a system evolving at constant pressure and temperature, equilibrium corresponds to a minimum of the system's Gibbs free energy.

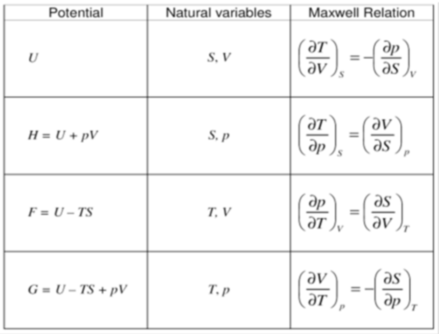
Thermodynamic potentials: Gibbs Free Energy

For a reversible process occurring at constant pressure and temperature (e.g. a phase change between gas and liquid such as from *A* to *B* in the figure below), the Gibbs free energy is a conserved quantity.



Thermodynamic potentials

THERMODYNAMIC POTENTIALS AND MAXWELL RELATIONS SUMMARY TABLE



Potential	Natural variables	Maxwell Relation
U	S, V	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$H = U + pV$	S, p	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$F = U - TS$	T, V	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
$G = U - TS + pV$	T, p	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

The Joule process

The free expansion of a gas into a vacuum, the whole system being thermally insulated: the total energy conserved.

$$\alpha_J = \left(\frac{\partial T}{\partial V}\right)_U$$

For $U = U(T,V)$, chain rule for partial derivatives (see PHY1026):

$$\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U \left(\frac{\partial V}{\partial U}\right)_T = -1$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V}$$

$$(\partial U/\partial T)_V = C_V$$

$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$, hence (divide by $\mathrm{d}V$ treating T as a constant): $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$

The Joule and Joule-Thompson processes

$$\therefore \alpha_J = \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(T\left(\frac{\partial S}{\partial V}\right)_T - p\right)$$

3rd Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$, hence

$$\boxed{\alpha_J = -\frac{1}{C_V}\left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right)}$$

Similarly

$$\alpha_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left(T\left(\frac{\partial V}{\partial T}\right)_p - V\right)$$

The Joule and Joule-Thompson processes

Hence calculate α_J and α_{JT} from the equation of state $p = p(V,T)$, e.g. n moles of ideal gas: $pV = nRT$, hence $\left(\partial p/\partial T\right)_V = nR/V = p/T$ and hence $\alpha_J = \alpha_{JT} = \text{zero}$.

Real gas virial equation of state (see PHY1024):

$$\frac{pV}{nRT} = \left(1 + B_2(T)\left(\frac{n}{V}\right) + B_3(T)\left(\frac{n}{V}\right)^2 + B_4(T)\left(\frac{n}{V}\right)^3 + \cdots\right)$$

Usually only first 2 terms are needed for good accuracy, hence

The Joule process

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}\frac{\mathrm{d}}{\mathrm{d}T}\left(T + \left(\frac{n}{V}\right)B_2(T)T\right) = \frac{nR}{V}\left(1 + \left(\frac{n}{V}\right)\left(T\frac{\mathrm{d}B_2(T)}{\mathrm{d}T} + B_2(T)\right)\right)$$

$$\therefore T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{nRT}{V}\left(1 + \left(\frac{n}{V}\right)(T + B_2(T))\right) - \frac{nRT}{V}\left(1 + \left(\frac{n}{V}\right)B_2(T)\right) +$$

$$+\frac{n^2T^2R}{V^2}\frac{\mathrm{d}B_2(T)}{\mathrm{d}T} = R\left(\frac{nT}{V}\right)^2\frac{\mathrm{d}B_2(T)}{\mathrm{d}T}$$

$$\boxed{\therefore \alpha_J = -\frac{R}{C_V}\left(\frac{nT}{V}\right)^2\frac{\mathrm{d}B_2(T)}{\mathrm{d}T}}$$

For all real gases $\frac{\mathrm{d}B_2(T)}{\mathrm{d}T} > 0$ (see Mandl sec 5.5), hence $\alpha_J < 0$, i.e. Joule expansion always cools.

The Joule-Thompson process

In the limit of low pressure (i.e. $p \to 0$)

$$\alpha_{\mathrm{JT}} = \frac{n}{C_p}\left(T\frac{\mathrm{d}B_2(T)}{\mathrm{d}T} - B_2(T)\right)$$

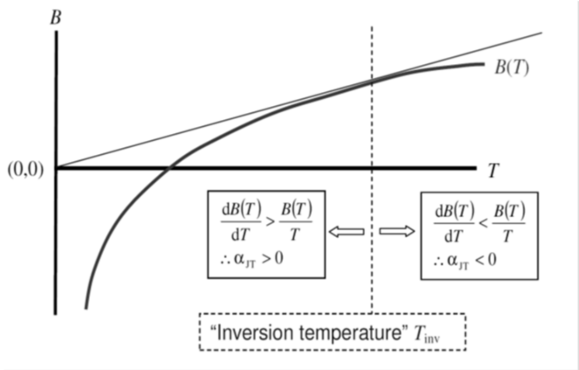
Hence $\alpha_{\mathrm{JT}} > 0$ (i.e. JT expansion cools) if

$$\mathrm{d}B_2(T)/\mathrm{d}T > B_2(T)/T$$

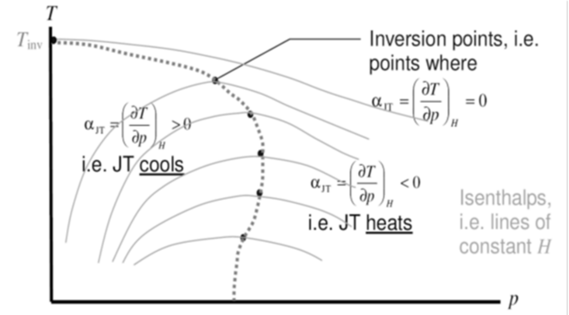
but $\alpha_{\mathrm{JT}} < 0$ (i.e. JT expansion heats) if

$$\mathrm{d}B_2(T)/\mathrm{d}T < B_2(T)/T$$

The Joule-Thompson process



The Joule-Thompson process



T_{inv} (inversion temperature) is maximum temperature a gas can have and still be cooled by J-T expansion.

The partition function

Boltzmann distribution $p_i = \frac{\exp\left(-\beta\varepsilon_i\right)}{Z}$,

where $Z = \sum_{i=0}^{\text{all states}} \exp\left(-\beta\varepsilon_i\right) = \sum_{i=0}^{\text{all energy levels}} g_i \exp\left(-\beta\varepsilon_i\right)$

with $\beta = \frac{1}{k_B T}$

Z is the "partition function".

a) It ensures that the p_i's are normalized, i.e.

$$\sum_{i=0}^{\text{all states}} p_i = 1.$$

The partition function

b) It describes how energy is "partitioned" over the ensemble i.e. states making a large contribution to Z have a high p_i hence a large share of the energy.

c) Links microscopic description of an ensemble to its macroscopic variables/ functions of state.

E.g., for an ensemble of N identical systems:

$$U = N\,\bar{\varepsilon} = N\sum_{i=0}^{\infty} \varepsilon_i p_i .$$

The partition function

In equilibrium at temp T

$$\begin{aligned} U &= N\sum_{i=0}^{\infty} \varepsilon_i \frac{\exp\left(-\beta\varepsilon_i\right)}{Z} = \frac{N}{Z}\sum_{i=0}^{\infty} \varepsilon_i \exp\left(-\beta\varepsilon_i\right) \\ &= -\frac{N}{Z}\sum_{i=0}^{\infty} \frac{\partial\left(\exp\left(-\beta\varepsilon_i\right)\right)}{\partial\beta} = -\frac{N}{Z}\frac{\partial}{\partial\beta}\sum_{i=0}^{\infty} \exp\left(-\beta\varepsilon_i\right) \\ &= -\frac{N}{Z}\frac{\partial Z}{\partial\beta} = -N\frac{\partial \ln Z}{\partial\beta} = -N\frac{\partial \ln Z}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}\beta}. \end{aligned}$$

$$\boxed{U = Nk_B T^2 \frac{\partial \ln Z}{\partial T}}$$ (in equilibrium)

The partition function

In general: $S = k_\mathrm{B} \ln \Omega$

with $$\Omega = \frac{N!}{\prod_{i=0}^{\infty} n_i!}.$$

Hence $$\ln \Omega = \ln N! - \sum_{i=0}^{\infty} \ln n_i!$$

Stirling's approximation:- for large x

$$\ln x! \approx x \ln x - x$$

The partition function

$$\therefore \ln \Omega = N \ln N - N - \sum_{i=0}^{\infty} \left(n_i \ln n_i - n_i\right)$$

$$= N \ln N - N - \sum_{i=0}^{\infty} n_i \ln n_i + \sum_{i=0}^{\infty} n_i$$

$$= N \ln N - \sum_{i=0}^{\infty} n_i \ln n_i \quad \left(\text{as} \sum_{i=0}^{\infty} n_i = N\right)$$

$$= N \ln N - \sum_{i=0}^{\infty} N p_i \ln (N p_i) = N \ln N - \sum_{i=0}^{\infty} N p_i (\ln N + \ln p_i)$$

$$= N \ln N - N \ln N \sum_{i=0}^{\infty} p_i - N \sum_{i=0}^{\infty} p_i \ln p_i$$

$$= -N \sum_{i=0}^{\infty} p_i \ln p_i \quad \left(\text{as} \sum_{i=0}^{\infty} p_i = 1\right)$$

The partition function

$\boxed{S = -N k_\mathrm{B} \sum_{i=0}^{\infty} p_i \ln p_i}$ (in general, for N and all n_i's large)

In equilibrium :-

$$S = -N k_\mathrm{B} \sum_{i=0}^{\infty} p_i \ln \left(\frac{\exp(-\beta \varepsilon_i)}{Z} \right)$$

$$= -N k_\mathrm{B} \sum_{i=0}^{\infty} p_i (-\beta \varepsilon_i - \ln Z) = N k_\mathrm{B} \beta \sum_{i=0}^{\infty} p_i \varepsilon_i + N k_\mathrm{B} \ln Z \sum_{i=0}^{\infty} p_i$$

$$= k_\mathrm{B} \beta U + N k_\mathrm{B} \ln Z = \frac{U}{T} + N k_\mathrm{B} \ln Z$$

$$\boxed{\therefore U - TS = -N k_\mathrm{B} T \ln Z}$$

The partition function

$U - TS$ is the Helmholtz Free Energy F, hence

$\boxed{F = -Nk_\mathrm{B}T\ln Z}$ (valid in equilibrium)

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk_\mathrm{B}\left(\frac{\partial(T\ln Z)}{\partial T}\right)_V$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = Nk_\mathrm{B}T\left(\frac{\partial \ln Z}{\partial V}\right)_T$$

Einstein solid

Einstein solid – crystal of N atoms, each free to perform SHM about its equilibrium position in x, y and z directions.

Classical equipartition theorem (PHY1024) – in thermal equilibrium at temperature T, ensemble will possess a mean internal energy U given by

$$U = \frac{k_\mathrm{B}T}{2}\nu$$

With ν being the number of degrees of freedom, i.e. the number of squared terms appearing in the expression for the total internal energy when expressed in generalized co-ordinates of position and velocity: q and $\dot{q}$.

Einstein solid

E.g., for a point particle of mass m moving in 3-D

$$E = \mathrm{KE} = \enclose{circle}{\frac{1}{2}m\dot{x}^2} + \enclose{circle}{\frac{1}{2}m\dot{y}^2} + \enclose{circle}{\frac{1}{2}m\dot{z}^2}$$

Hence $\nu = 3$.

For a classical harmonic oscillator of mass m, spring constant k in 3-D,

$$E = \mathrm{KE} + \mathrm{PE} = \enclose{circle}{\frac{1}{2}m\dot{x}^2} + \enclose{circle}{\frac{1}{2}kx^2} + \enclose{circle}{\frac{1}{2}m\dot{y}^2} + \enclose{circle}{\frac{1}{2}ky^2} + \enclose{circle}{\frac{1}{2}m\dot{z}^2} + \enclose{circle}{\frac{1}{2}kz^2}$$

i.e. $\nu = 6$

Einstein solid

Hence classically, $U = 3Nk_\mathrm{B}T$ for the solid and

$$C_\mathrm{v} = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_\mathrm{B}$$ (Dulong-Petit law 1822),

predicts that C_v is independent of T. However, experimentally it is found that $C_\mathrm{v} \to 0$ as $T \to 0$.

Einstein (1907): quantize the allowed energies of each of the N harmonic oscillators, such that

$$\varepsilon_l = (l + 1/2)\hbar\omega,$$

with $\omega = \sqrt{k/m}$ being the natural frequency of the oscillator.

Einstein solid

Hence, for each oscillator

$$Z = \sum_{l=0}^{\infty} \exp(-\varepsilon_l / k_\mathrm{B}T) = \sum_{l=0}^{\infty} \exp(-(l+1/2)\hbar\omega / k_\mathrm{B}T)$$

Define the Einstein temperature $\theta_\mathrm{E} = \hbar\omega / k_\mathrm{B}$

$$Z = \sum_{l=0}^{\infty} \exp(-(l+1/2)\theta_\mathrm{E}/T)$$

$$= \exp(-\theta_\mathrm{E}/2T) \sum_{l=0}^{\infty} \exp(-l\,\theta_\mathrm{E}/T)$$

Summation on RHS is a convergent geometric series, first term $a = 1$, common ratio $r = \exp(-\theta_\mathrm{E}/T) < 1$.

Einstein solid

The sum tends to $a/(1-r)$ as the number of terms tends to ∞ (see, e.g., Stroud Engineering Mathematics Programme 13), hence

$$Z = \frac{\exp(-\theta_\mathrm{E}/2T)}{1 - \exp(-\theta_\mathrm{E}/T)}$$

Hence (exercise)

$$U = 3Nk_\mathrm{B}T^2 \frac{\partial \ln Z}{\partial T} = 3Nk_\mathrm{B}\theta_\mathrm{E}\left(\frac{1}{2} + \frac{1}{\exp(\theta_\mathrm{E}/T) - 1}\right)$$

Why factor of '3'?

Einstein solid

Hence (exercise)

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B\theta_E \frac{d}{dT}\left(\frac{1}{2} + \frac{1}{\exp(\theta_E/T)-1}\right)$$

$$\boxed{C_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E/T)}{(\exp(\theta_E/T)-1)^2}}$$

As $T \to \infty$, $\exp(\theta_E/T)-1 \to \theta_E/T$, hence $C_V \to 3Nk_B$, i.e. tends to the classical result for high T.

As $T \to 0$, $\exp(\theta_E/T)-1 \to \exp(\theta_E/T)$,

hence $C_V \to (\theta_E/T)^2/\exp(\theta_E/T) \to 0$ because $\exp(x)$ diverges more rapidly than x^n for any finite n.

Quantum gases: momentum space

Single particle mass m confined to a cubic container (3-D ∞ potential well) side length L.

Describe particle via a wavefunction $\Psi(x,y,z)$ satisfying the energy eigenvalue equation :-

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z) + V(x,y,z)\Psi(x,y,z) = E\Psi(x,y,z)$$

Solutions E and $\Psi(x,y,z)$ are the energy eigenvalues and stationary states of the particle.

Boundary conditions:
$\Psi(0,y,z) = \Psi(L,y,z) = \Psi(x,0,z) = \Psi(x,L,z) = \Psi(x,y,0) = \Psi(x,y,L) = 0$

Quantum gases: momentum space

Solution :-

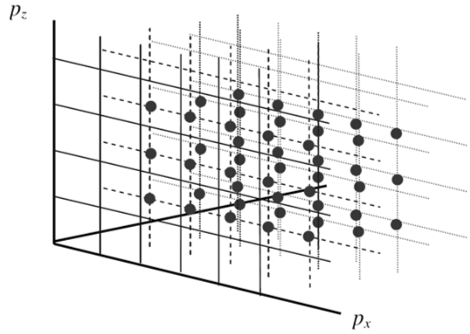
$$\Psi_{n_x,n_y,n_z}(x,y,z) = A\sin\left(n_x\frac{\pi x}{L}\right)\sin\left(n_y\frac{\pi y}{L}\right)\sin\left(n_z\frac{\pi z}{L}\right)$$

$$E_{n_x,n_y,n_z} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$p_x = n_x\frac{\hbar\pi}{L}$ (ditto y,z); $n_x = 1, 2, 3$ … (ditto n_y, n_z)

Quantum gases: momentum space

Momentum space picture :-



Quantum gases: momentum space

Allowed states form a cubic lattice, lattice constant $\frac{\hbar\pi}{L}$.

Hydrogen atom at room temp confined to 1m^3:

$$\langle \varepsilon \rangle = \frac{\langle p^2 \rangle}{2m} \approx k_B T$$

$$p \approx \sqrt{2mk_B T}$$

$$\approx \sqrt{2 \times 1.6 \times 10^{-27} \times 1.4 \times 10^{-23} \times 300} \approx 3.7 \times 10^{-24} \text{kg m s}^{-1}$$

Compare with $\frac{\hbar\pi}{L} = \frac{10^{-34} \times 3}{1} = 3 \times 10^{-34} \text{kg ms}^{-1}$

Hence momentum states are very finely spaced ⇨ can often treat as forming a continuum.

Quantum gases

Gas of N particles in a cubic container, side length L.

If $N/n_{\text{states}} << 1$ we have a 'classical' gas.

If $N/n_{\text{states}} \sim 1$ we have a 'quantum' (or 'quantal') gas.

Behaviour of a quantum gas is strongly determined by the Pauli Exclusion Principle:

Any number of bosons can occupy a given quantum state but only one fermion can occupy a given quantum state.

Half-integer spin particles (e.g. e, p, n) are '**Fermions**'. Integer-spin particles (e.g. γ, phonon) are '**Bosons**'.

Quantum gases

Consider $\langle\varepsilon\rangle$, the mean energy of each of the N particles in the container:

$$\langle\varepsilon\rangle = \frac{(p_{\text{mean}})^2}{2m}$$

$n_{\text{states}} \approx$ volume of momentum space enclosed by an octant of radius p_{mean} / volume occupied by one state

$$n_{\text{states}} \approx \frac{1}{8}\frac{4}{3}\pi p_{\text{mean}}^3\left(\frac{L}{\hbar\pi}\right)^3 \sim V\left(\frac{p_{\text{mean}}}{h}\right)^3 \sim V\left(\frac{1}{\lambda_{\text{deBroglie}}}\right)^3$$

Hence $\dfrac{N}{n_{\text{states}}} \sim \dfrac{N}{V}\lambda_{\text{deBroglie}}^3 \sim \left(\dfrac{\lambda_{\text{deBroglie}}}{\text{mean particle spacing}}\right)^3$

Quantum gases

Hence a gas becomes quantum when the mean inter-particle spacing becomes comparable with the particles' de Broglie wavelength.

Consider Hydrogen at STP, molar volume 22.4×10^{-3} m^3.
Mean spacing = $(22.4\times10^{-3}/6\times10^{23})^{1/3} = 3\times10^{-9}$ m.
At room temp,

$$\lambda_{\text{deBroglie}} = \frac{h}{\sqrt{2m\langle\varepsilon\rangle}} = \frac{h}{\sqrt{2mk_{\text{B}}T}}$$

$$= \frac{6.6\times10^{-34}}{\sqrt{2\times1.6\times10^{-27}\times1.4\times10^{-23}\times300}} = 0.2\times10^{-9}\ \text{m}$$

Only 1 in 1000 states typically occupied hence it is safe to treat as a "classical" gas i.e. rules for filling states are unimportant.

Quantum gases

Now consider gas of conduction electrons in a metal, density typically 10^{28} m^{-3}.
Mean spacing = $(10^{28})^{-1/3} = 0.5\times10^{-9}$ m.

$$\lambda_{\text{deBroglie}} = \frac{6.6\times10^{-34}}{\sqrt{2\times10^{-30}\times1.4\times10^{-23}\times300}} = 6\times10^{-9}\ \text{m}$$

Hence, conduction electrons form a quantum gas, i.e., the rules for filling states are important. Electrons are fermions so only one particle can occupy a given quantum state.

As $T\rightarrow0$ the electrons will crowd into the lowest available energy level. Unlike a classical ensemble they cannot all move into the ground state, because only one particle is allowed per state. Instead they will fill all available states up to some maximum energy, the Fermi energy E_{F}

Fermi gas

As $T \rightarrow 0$, fermions will fill all available states up to some maximum energy E_F or equivalently a maximum momentum p_F, the Fermi momentum.

Hence number of states contained within an octant of momentum space, radius $p_F = N/2$ (because each translational momentum state actually comprises TWO distinct quantum states, with the electron spin 'up' and spin 'down' respectively).

$$\frac{1}{8}\frac{4\pi}{3}p_F^3 \Big/ \left(\frac{\hbar\pi}{L}\right)^3 = \frac{N}{2}$$

$$\therefore p_F^3 = \frac{3}{8\pi}\frac{N}{V}h^3$$

Fermi gas

Writing $N/V = n$, the particle number density,

$$\boxed{E_F = \frac{p_F^2}{2m} = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3}}.$$

E.g., for the conduction electrons in a metal

$$E_F = \frac{\left(6.6\times10^{-34}\right)^2}{2\times10^{-30}}\left(\frac{3\times10^{28}}{8\pi}\right)^{2/3} \sim 1.5\text{eV}$$

Fermi-Dirac distribution

Equilibrium distribution of energy U over N particles when

a) only ONE particle per state is allowed (c.f. Boltzmann distribution, any number of particles per state were allowed).

b) the particles are indistinguishable (c.f. Boltzmann distribution, the particles were distinguishable).

Quantum states form a densely-spaced near-continuum. Divide these states into "bands" of nearly identical energy. Hence band i has a characteristic energy E_i, number of states ω_i and holds n_i particles.

Total number of microstates Ω_{total} is given by

$$\Omega_{\text{total}} = \prod_{i=1}^{\text{all bands}} \Omega_i$$

where Ω_i = the total number of ways to choose n_i indistinguishable objects from ω_i possibilities (c.f. coin-flipping).

Fermi-Dirac distribution

Hence $$\Omega_{\text{total}} = \prod_{i=1}^{\text{all bands}} \frac{\omega_i!}{(\omega_i - n_i)!n_i!}$$

As with the Boltzmann distribution, we obtain the equilibrium distribution by seeking the n_i's that maximise $\ln \Omega_{\text{total}}$ subject to the constraints

$$\sum_{i=1}^{\text{all bands}} n_i = N \qquad \sum_{i=1}^{\text{all bands}} n_i E_i = U$$

Solution (see supplement sheet 4):

$$\boxed{\frac{n_i}{\omega_i} = \frac{1}{\exp[(E_i - E_F)/k_{\mathrm{B}}T] + 1}}$$ - Fermi-Dirac distribution

Here E_F is a constant (the Fermi Energy).

Bose-Einstein distribution

Bosons, unlike fermions, are not subject to the Pauli exclusion principle: an unlimited number of particles may occupy the same state at the same time. This explains why, at low temperatures, bosons can behave very differently from fermions; all the particles will tend to congregate at the same lowest-energy state, forming what is known as a Bose–Einstein condensate.

Bose-Einstein statistics was introduced for photons in 1924 by Bose and generalized to atoms by Einstein in 1924-25.

$$\boxed{\frac{n_i}{\omega_i} = \frac{1}{\exp[(E_i - \mu)/k_{\mathrm{B}}T] - 1}}$$ - Bose-Einstein distribution

Bose-Einstein distribution

For bosons $$\Omega_{\text{total}} = \prod_{i=1}^{\text{all bands}} \frac{(n_i + \omega_i - 1)!}{n_i!(\omega_i - 1)!}$$

| ■ ■ | ■ ■ ■ | | ■ | ■ |

As with the Boltzmann and Fermi distributions, we obtain the equilibrium distribution by seeking the n_i's that maximise $\ln \Omega_{\text{total}}$ subject to the constraints

$$\sum_{i=1}^{\text{all bands}} n_i = N; \qquad \sum_{i=1}^{\text{all bands}} n_i E_i = U.$$

Classical limit

Fermi-Dirac and Bose-Einstein distributions:

$$\boxed{\frac{n_i}{\omega_i} = \frac{1}{\exp\left[\left(E_i - \mu\right)/k_\mathrm{B}T\right] \pm 1}}$$

+Fermi-Dirac distribution

- Bose-Einstein distribution

Classical limit, $n_i/\omega_i \ll 1$, requires $\exp[(E_i - \mu)/k_\mathrm{B}T] \gg 1$.

Thus, $\frac{n_i}{\omega_i} \approx e^{\mu/k_\mathrm{B}T} \times e^{-E_i/k_\mathrm{B}T} \Rightarrow \frac{n_i}{N} \propto \exp\left(-E_i/k_\mathrm{B}T\right).$

This corresponds to the Boltzmann distribution.