

Intro to Thermodynamics

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- matter in the aggregate can exist in well-defined states

"equilibrium" states:

- defined by properties: color, texture, size, etc.
- properties appear to change systematically as the system is heated/compressed/etc.
- state (set of properties) reproduced when system is brought back to original state
- if system is not perturbed: will remain forever in the same state

equilibrium: characterized by stability & reproducibility

- thermodynamics: describes macroscopic behaviour of a large variety of systems over a large range of temperatures (10^{-4} K to 10^6 K).

based on four laws:

0th law: it is possible to build a gauge for thermodynamic properties (temperature, pressure, etc.)

1st law: energy is conserved

2nd law: not all heat can be converted into work

3rd law: can never reach absolute zero in a finite number of reversible steps

- 2nd law: gives definition of entropy + criteria of stability of equilibrium states

thermodynamic potentials: describe behaviour of system ②

under different types of constraints

example: system can be isolated from the rest of the universe, or could be coupled thermally, kept at constant pressure, etc.
⇒ different set of constraints ⇒ different thermodynamic potentials

response functions: experimentally accessible quantities

- change one parameter of the system, monitor how another quantity changes under very controlled conditions ⇒ thermal/mechanical response functions

maximum entropy principle: equilibrium states are maximum

entropy states → fluctuations must decrease entropy

- constraints on other thermodynamic potentials
→ stability conditions

State Variables

- system has many degrees of freedom ($6 \cdot 10^{23}$) ^{chaotic motion}
- thermodynamics describes behaviour in terms of a few variables: state variables
- many state variables can be used, but only a few are independent → objective is to obtain relations between state variables → equation of state

state variables can be extensive or intensive (3)

extensive - changes as a function of system size

intensive - independent of system size

in thermodynamic definitions pairs of extensive and intensive variables often occur together

- generalized force / displacement

examples: pressure, volume

H-field, magnetization

tension, length

surface tension, area

electric ~~polarization~~ ^{field}, electric polarization

temperature, entropy

chemical potential, number of particles

(of a chemical component)

response functions are also state variables:

→ heat capacity, compressibility, susceptibility

thermodynamic potentials are also state variables:

→ internal energy, free energies (Helmholtz, Gibbs)
grand potential

~~to~~ to postulate that extensive state variables are additive
and independent of the shape of the system

→ equivalent to the assumption of the existence of

the thermodynamic limit

Exact Differentials

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- given a function $F(x_1, x_2)$

define
$$dF = \left(\frac{\partial F}{\partial x_1} \right)_{x_2} dx_1 + \left(\frac{\partial F}{\partial x_2} \right)_{x_1} dx_2$$

$\left(\frac{\partial F}{\partial x_1} \right)_{x_2}$ - derivative of F with respect to x_1 , holding x_2 fixed

$$\left[\frac{\partial}{\partial x_1} \left(\frac{\partial F}{\partial x_2} \right)_{x_1} \right]_{x_2} = \left[\frac{\partial}{\partial x_2} \left(\frac{\partial F}{\partial x_1} \right)_{x_2} \right]_{x_1}$$

→ in this case dF is an exact differential

denote: $c_1(x_1, x_2) = \left(\frac{\partial F}{\partial x_1} \right)_{x_2}$ $c_2(x_1, x_2) = \left(\frac{\partial F}{\partial x_2} \right)_{x_1}$

$$dF = c_1(x_1, x_2) dx_1 + c_2(x_1, x_2) dx_2$$

- consequences of "exactness":

a.) $F(B) - F(A) = \int_A^B dF = \int_A^B (c_1 dx_1 + c_2 dx_2)$

value of the integral is independent of the path taken, depends only on the endpoints A, B .

b.) $\oint_{\text{closed}} dF = \oint_{\text{closed}} (c_1 dx_1 + c_2 dx_2) = 0$

integral around a closed path is zero

c.) if one knows only the differential dF

→ F can be found to within an additive constant

can be generalized to more than two variables

(9)

$$dF = \sum_{i=1}^n \left(\frac{\partial F}{\partial x_i} \right)_{\{x_j \neq i\}} dx_i$$

$$\left[\frac{\partial}{\partial x_e} \left(\frac{\partial F}{\partial x_e} \right)_{x_{j \neq e}} \right]_{x_{j \neq e}} = \left[\frac{\partial}{\partial x_e} \left(\frac{\partial F}{\partial x_e} \right)_{\{x_{j \neq e}\}} \right]_{x_{j \neq e}}$$

differentials of all state variables are exact differentials

identities:

- given four state variables $\rightarrow x, y, z$, and w , where w is a function of any two variables of x, y , and z , one can obtain the relations along paths for which $F(x, y, z) = 0$

$$(A) \quad \left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z}$$

$$(B) \quad \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$

$$(C) \quad \left(\frac{\partial x}{\partial w} \right)_z = \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial w} \right)_z$$

$$(D) \quad \left(\frac{\partial x}{\partial y} \right)_z = \left(\frac{\partial x}{\partial y} \right)_w + \left(\frac{\partial x}{\partial w} \right)_y \left(\frac{\partial w}{\partial y} \right)_z$$

- demonstrations:

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz$$

$$dy = \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz$$

$$dx = \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x dz + \left(\frac{\partial x}{\partial z} \right)_y dz$$

$$\left[\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z - 1 \right] dx + \left[\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x + \left(\frac{\partial x}{\partial z} \right)_y \right] dz = 0 \quad (B)$$

$$\begin{aligned} &\Rightarrow \left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z} \quad \checkmark \quad \text{and} \quad \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 \quad \checkmark \\ (A) &\rightarrow \end{aligned}$$

Ideal Gas Law

⑦

⑥

$PV = nRT$ P - pressure, V - volume, n - number of moles
for m types of particles T - temperature

$$PV = \sum_{i=1}^m n_i RT$$

n_i - number of moles of i th constituent

Virial Expansion

$$P = \left(\frac{nRT}{V} \right) \left[1 + \frac{n}{V} B_2(T) + \left(\frac{n}{V} \right)^2 B_3(T) + \dots \right]$$

equation of state of a gas as an expansion in density $\left(\frac{n}{V} \right)$

- virial coefficients depend on molecular details (inter-particle potential)

- useful in checking force constants

$HD, HC \Rightarrow$ can calculate equation of state and compare to experiment

- $B_2(T)$ depends on temperature

- at low temperature $\Rightarrow$ attractive forces dominate, hence pressure is reduced

$$\Rightarrow B_2(T) < 0$$

- at high temperature $\Rightarrow$ repulsive forces dominate

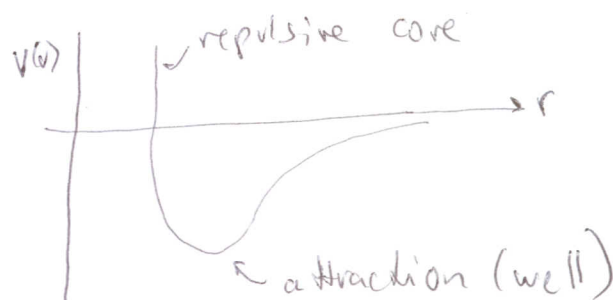
$$\Rightarrow B_2(T) > 0$$

- at very very high temperature $\Rightarrow$ even the ~~attractive~~ ^{repulsive} core can be penetrated

$$\Rightarrow B_2(T) \rightarrow 0 \text{ after a maximum}$$

- this is in connection with what one expects from knowing (8)

the potential $\rightarrow$
between atomic
constituents



- ideal classical gas = all virial coefficients are zero
- ideal quantum gases have finite virial coefficients due to quantum statistics
 - for example: Pauli repulsion is like a repulsive core, etc...

van der Waals Equation of State

- applies to both gas and liquid and exhibits a phase transition
- corrections to ideal gas equation of state, which take account of molecular (microscopic) detail

ideal gas: $PV = nRT \rightarrow P = \frac{nRT}{V}$

- (i) due to repulsion at close range expect that volume available to atoms is reduced
 - expect that this reduction is proportional to number of atoms (number of moles)

$$\rightarrow P = \frac{nRT}{V - nb}$$

(2) attractive region of potential causes

(9)

"cohesion" between atoms/molecules

→ expect a reduction of pressure

- since attraction occurs between two atoms
(or pairs of atoms)

expect that this effect is proportional to
the number of pairs in the system

→ proportional to $a \left(\frac{N}{V}\right)^2$

$$P = \frac{nRT}{V-nb} - a \left(\frac{N}{V}\right)^2$$

$$B_2^w(T) = \left(b - \frac{a}{RT}\right) \rightarrow \begin{array}{l} \text{negative at low } T \\ \text{positive at high } T \\ \text{does not exhibit maximum} \end{array}$$

Solids

relevant response functions

- thermal expansion coefficient: $\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$

$$V = \frac{V}{n}$$

- isothermal compressibility: $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

molar
volume

$$V = V_0 (1 + \alpha_P T - \kappa_T P)$$

example: solid silver (Ag): $\kappa_T = \frac{1.3 \times 10^{-10}}{\text{Pa}}$

solid sodium (Na): $\alpha_P = \frac{2 \times 10^{-4}}{\text{K}}$

(typical values)

Curie's law

(10)

- paramagnetic solid at constant pressure
- specify state in terms of applied H-field and induced magnetization

magnetic induction: $\vec{B} = \mu_0 \vec{H} + \mu_0 \vec{M}$

$\vec{H}$ - applied field

$\vec{M}$ = magnetization (magnetic moment per unit volume)

equation of state: Curie's law $\rightarrow \vec{M} = \frac{nD}{T} \vec{H}$

Other examples

elastic wire, surface tension, electric polarization

The laws of Thermodynamics

- some introductory concepts
- thermodynamic equilibrium: if mechanical variables do not change in time and no macroscopic flow processes are present
- insulating wall: prevents transfer of matter, heat, and mechanical work between two systems
 - thermodynamic variables of one system can be changed without changing the thermodynamic variables of the other system
- conducting wall: allows transfer of heat
 - $\rightarrow$ so changing thermodynamic variables of one will cause changes in the thermodynamic variables of the other system

types of thermodynamic systems: separate system + surroundings (Ad)

- isolated system: surrounded by an insulating wall
no heat no matter can be exchanged with surroundings
- closed system: surrounded by a conducting wall
heat can be exchanged, but matter can not

types of thermodynamic processes:

- thermodynamic process $\rightarrow$ change from one equilibrium state to another
- reversible (or quasi-static) process: system remains infinitesimally close to equilibrium
 $\rightarrow$ changes can be reversed in this case, and the system can be brought back to its original state in such a way that no change occurs in the thermodynamic state of the surroundings (universe)
- irreversible: not reversible $\rightarrow$ state variables do not have a precise meaning for intermediate states (states along the path)

Zeroth Law: Two bodies^{each} in thermal equilibrium with a third body are in equilibrium with each other

First Law: Energy is conserved

(12)

- write in the form: $dU = \delta Q - \delta W$
- change in internal energy is the sum of heat and work generated in the process
- notation $d \rightarrow$ not an exact differential
- negative sign $\rightarrow$ system ~~do~~ does work on surroundings
convention! some textbooks use $+ \delta W$
- work and heat are different forms of energies
- roughly speaking $\rightarrow$ work is an 'organized' ^{transfer} ~~transfer~~ of energy, i.e. the process may cause the motion of an object (microscopic) hence all constituent atoms of the system would move in the same direction
- heat ~~is~~ 'disorganized' transfer of energy, i.e. causes a change in ^{the} random motion of atoms in the surroundings

$$\delta W = P dV - T dL - \sigma dA - \vec{E} \cdot d\vec{P} - \vec{H} \cdot d\vec{M} - d\epsilon - \sum_j \mu_j' dN_j$$

usually: introduce generalised force / displacement

$$dU = \delta Q + Y dX + \sum_j \mu_j' dN_j$$

Y - force

X - displacement

Second Law: Heat Flows Spontaneously from (12) High Temperatures to Low Temperatures

other equivalent versions

- * the spontaneous tendency of a system to go to equilibrium cannot be reversed without at the same time changing some organized energy, work, into disorganized energy, heat.
- * in a cyclic process, it is not possible to convert heat into work without at the same time transferring some heat to a colder reservoir
- * the entropy change of any system and its ~~surrounding~~ surroundings, considered together, is positive and approaches zero for any process which approaches irreversibility