Thermodynamics

Deals with macroscopic, time-averaged properties of systems <u>at equilibrium</u>:

(1) properties do not change with time

(2) properties do not depend on how a system was prepared (history), but only on $C+2$ [$C \equiv$ number of chemical species] independent variables, e.g. P, T, N for $C=1$

Definitions

System: a specified, contiguous volume within defined physical or conceptual boundaries

Environment: {Universe} − {System}

Isolated system: no interactions between system + environment

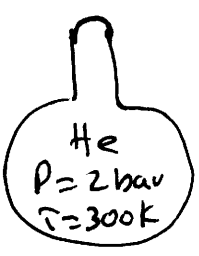
Closed/open: boundaries impermeable/permeable to mass

Adiabatic/diathermal: boundaries impermeable/permeable to heat

Time Scales

Even though thermodynamics deals with time-independent properties, some implied time scales are required for setting boundary conditions – e.g.

Hemetically sealed glass bottle containing He gas @ 2 bar, 300K



Environment
P=1 bar
300 K
air

Is this an open or closed system?

Diffusion of He through glass $D \simeq 10^{-8}\ cm^2/s$

$L \simeq 0.2\ cm$ $\quad t = L^2/D = 46$ days

Depending on time scale of interest:

$t \ll 50$ days $\rightarrow$ closed system
$t \gg 50$ days $\rightarrow$ open system
} both valid!

In the first case, $t \ll 50$ days $\rightarrow$ $P_{"final"} = 2$ bar

In the second case $P_{"final"} = ?$

Thermodynamic reasoning, by itself, cannot tell you which one is the "better" description - only comparison to experiment will tell you if assumptions are correct.

Key Quantity

Entropy $S = S(E, V, N)$ for $c=1$ mathematical function of 3 variables

energy, volume, mass

$[S = S(E, V, N_1, N_2, \ldots N_c)$ for multicomponent systems$]$

How does it arise? In classical thermodynamics, the entropy changes are defined through exchanges of heat in reversible processes,

$$\Delta S = \int_A^B \frac{(\delta Q)_{rev}}{T}$$

but here we will just assume that such a function exists for systems at equilibrium, with the following key properties:

Derivatives: $\left(\partial S/\partial E\right)_{V,N} = \frac{1}{T}$ [defines temperature]

$\left(\partial S/\partial V\right)_{E,N} = \frac{P}{T}$

$\left(\partial S/\partial N\right)_{E,V} = -\mu/T$ [defines chemical potential μ]

Extensivity: $S(\lambda E, \lambda V, \lambda N) = \lambda S(E,V,N)$

Concavity: $\left(\partial^2 S/\partial x^2\right)_{Y,Z} \leq 0$ $\{x,y,z\}$ any of $\{E,V,N\}$

$\therefore \quad dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$

or $dE = TdS - PdV + \mu dN$

} Fundamental Equations in S or E representation

Example 2.1 $P = NK_BT/V \rightarrow S = S(V,E,N)$?

$$\frac{P}{T} = \frac{NK_B}{V} \Rightarrow \left.\frac{\partial S}{\partial V}\right)_{E,N} = \frac{NK_B}{V} \Rightarrow S = K_B \ln V + f(E,N)$$

STATISTICAL MECHANICS

Connects macroscopic properties to microscopic interactions - key relationship

Boltzmann's Equation $S = K_B \ln \Omega(E,V,N)$

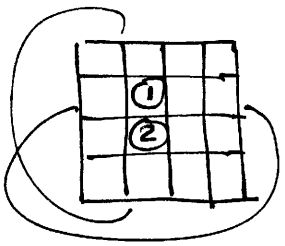
$K_B = R/N_A$

$8.314 \frac{J}{mol\,K} \cdot \frac{mol}{6.022 \cdot 10^{23}}$

$= 1.38 \cdot 10^{-23} \frac{J}{K}$

Density of states → number of distinct molecular arrangements consistent with a given E,V,N

Example 2.2.



V lattice sites
- periodic B.C.
- nearest-neighbor interactions $-\varepsilon$
- excluded volume

distinguishable

$$\begin{cases} \Omega(E=-\varepsilon) = 4V \\ \Omega(E=0) = V(V-1) - 4V \end{cases}$$

If ① and ② indistinguishable, number of states is lower by a factor of 2

Comparison of thermodynamics and Stat. mech.

Macroscopic

E, V, N, P, T, μ

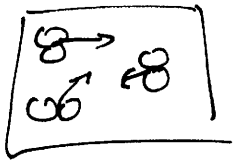
- no need to assume molecules exist
- fixed properties given $C+2$ independent variables
- connects properties to each other –

e.g. $C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

- many empirical / semitheoretical correlations developed in engineering
- Undetermined constants,

e.g. $S = N k_B \ln V + f(E,N)$ for ideal gases

Microscopic



- molecular viewpoint assume / measure interactions
- properties fluctuate
- connects properties to interactions + fundamental constants

e.g. $S = N k_B \ln\left[\left(\frac{4\pi m E}{3h^2}\right)^{3/2} \frac{V e^{5/2}}{N^{5/2}}\right]$ for ideal gases

- Very hard to get exact results!