

Thermodynamics

Xinyu Zhong
Wolfson College

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Abstract

Abstract of this course

1 Basic of thermodynamics

2 Thermodynamics equilibrium

2.1 Open systems

Open system is a system that is linked to a reservoir.

Equilibrium condition is to maximize the total entropy of the system and the reservoir.

Hence, introducing the ideal of **availability**, which is minimized when the entropy of the universe is maximized with respect to the state of the system.

2.1.1 Availability

For thermally isolated system thermodynamic equilibrium is defined as the state of maximum entropy for a given total energy, or minimum total energy for a given entropy. However, for an open system, in contact with reservoir, there is alternative, availability (of the system) that is minimised when the entropy of the universe is maximised. Availability A is defined as:

$$dA = -T_R dS_{tot}$$

Note: $dA \leq 0$ and equilibrium is achieved at $dA = 0$

Given that:

$$\begin{aligned} dS_{tot} &= dS + dS_R \geq 0 \\ &= dS + \frac{dU_R + p_R dV_R - \mu_R dN_R}{T_R} \\ &= \frac{T_R dS - dU - p_R dV + \mu_R dN}{T_R} \end{aligned}$$

Here we used the fact that $dU_R = -dU$.etc Note that $-dA$ is the negative denominator.

$$A = U - T_R S + p_R V - \mu_R N$$

2.1.2 Boltzmann expression for entropy

$$S_{\text{Boltz}} = k_B \ln \Omega$$

2.1.3 Availability is equivalent to useful work

Availability is the the maximum amount of work that can be extracted from a system by bringin the system in contact with equilibrium: Proof:

2.2 Close systems

The method we used to study closed system is to play **imaginary partition** to partition it into two or more systems.

Equilibrium condition is to find the maximized S given a fixed value of U , or alternatively minimized U for a given S .

2.2.1 Constant temperature at equilibrium

2.2.2 Constant chemical potential at equilibrium

2.3 Overview of thermodynamics potentials

Energy conservation is not sufficient to determine the equilibrium state, we need to introduce Thermodynamics potential to determine the equilibrium state.

internal energy	$U = TS - pV + \mu N$	$dU = TdS - pdV + \mu dN$
enthalpy	$H = U + pV$	$dH = TdS + Vdp + \mu dN$
Helmholtz free energy	$F = U - TS$	$dF = -SdT - pdV + \mu dN$
Gibbs free energy	$G = U - TS + pV$	$dG = -SdT + Vdp + \mu dN$
grand potential	$\Phi = F - \mu N$	$d\Phi = -SdT - pdV - Nd\mu$

Here are some thermodynamics potential examples:

Internal energy: $dU = TdS - pdV + \mu dN$

Enthalpy: $dH = TdS + Vdp + \mu dN$

Helmholtz Free energy: $dF = -TdS - pdV + \mu dN$

...see discussion in mechanical equilibrium

Gibbs Free energy: $dG = -SdT + Vdp + \mu dN$

...see discussion in phase equilibrium

Grand potential : $d\phi = -SdT - pdV - Nd\mu$

...see discussion in Fermion and Boson Gas

For given external conditions, the appropriate thermodynamic potential is a minimum in equilibrium: the minimization of these thermodynamic potential of the system is a direct consequence of the maximization of global energy.

2.3.1 Detailed discussion about each thermodynamic potential

Example: Energy U for equilibrium at constant V , S and N

[A schematic flow process](#) Handout page 33 - 35

2.4 Phase Equilibrium

In this section, we consider a one component system at constant temperature, pressure and particle number. The equilibrium is that the Gibbs free energy is minimised. i.e. the total Gibbs free energy is minimized, $dS = 0$ in a mixture of gas and liquid.

Condition for equilibrium is such that chemical potential is the same: Prove:

2.4.1 Phase Equilibrium in Van de Waal gas

Two shaded areas have equal areas.

2.4.2 Clausius-Clapeyron Equation

2.5 Mixture of ideal gas

In ideal gas, particles do not interact with each other, the thermodynamics properties are the sum of individual contribution of each species of "component". ...

2.5.1 Chemical Equilibrium

2.5.2 Equilibrium Constant

3 Statistical Mechanics

Sterling Approximation::

$$\ln(n!) = n \ln n - n$$

$$\frac{d \ln(n!)}{dn} = \ln(n).$$

4 Classical Ideal Gas

In classical ideal gas, we have the probability density function and the associated partition function:

$$\rho = \frac{e^{-\beta E(p_i, q_i)}}{Z}$$

$$Z_{\text{classical}} = \int e^{-\beta E(p_i, q_i)} \frac{d^3 x d^3 p}{(2\pi\hbar)^3}$$

Note that this is 3-dimensional case.

Trick to compute the integral, in example of a free particle:

$$\begin{aligned} Z_1 &= \int e^{-\beta E(p_i, r_i)} \frac{d^3 p d^3 r}{(2\pi\hbar)^3} \\ &= \int d^3 r \int e^{-\beta E(p_i, r_i)} \frac{d^3 p}{(2\pi\hbar)^3} \\ &= V \left(\sqrt{\frac{k_B T m}{2\pi\hbar^2}} \right)^3 \\ &= V/\lambda^3 \end{aligned}$$

where λ is also known as the thermal de Broglie wavelength

4.1 Chemical equilibrium

4.2 High-T limit

4.3 Chemical potential

4.4 Cross-over to quantum limit

Continues on quantum ideal gas

5 Fermi gas

5.1 Fermi gas in low/medium/high Temperature

6 Bose gas

Bose gas : quantum limit, Boson particles can take up any energy state instead of two
Grand partition function:

$$\Xi_k = \sum_{n=0}^{\infty} e^{-\beta(\epsilon_k - \mu)n}$$

$$= \frac{1}{1 - e^{-\beta(\epsilon_k - \mu)}}$$

Here k specifies the energy level.

The grand partition function for the whole system The grand potential is then

6.1 Quasi-particle excitation

6.2 Photons

6.3 Spin Waves

6.4 Phonon and Debye model

7 Non-ideal Gas and Liquids

7.1 2 particle probability

7.2 Radial distribution function

7.3 Mean Energy

7.4 Virial

Virial ν is defined as:

$$\nu = -\frac{1}{2} \sum_i \mathbf{r}_i \cdot \mathbf{f}_i$$

Virial Theorem: Virial Theorem states that the mean virial is equal to the mean kinetic energy.

7.4.1 ν_{ext}

7.4.2 ν_{int}

7.5 Virial Expansion

Virial Expansion

8 Phase Equilibrium and Transition

8.1 Ising model

8.2 Landau Theory

8.2.1 Critical behavior

8.2.2 External field

8.3 2nd order transition

8.4 1st order transition

8.4.1 Calculation of T^*, T_1 and latent heat

9 Fluctuation

$$\langle \Delta x^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{Z} \sum_i x_i^2 e^{-E_i/k_B T} - \left(\frac{1}{Z} \sum_i x_i e^{-E_i/k_B T} \right)^2$$

If there is a simple dependence of energy on the variable, e.g. if such dependence is linear, $E_i = -f x_i$, then a general trick applies:

$$\begin{aligned} \langle x \rangle &= \frac{1}{Z} \sum_i x_i e^{f x_i / k_B T} = \frac{1}{\beta Z} \left(\frac{\partial Z}{\partial f} \right) \\ \langle x^2 \rangle &= \frac{1}{Z} \sum_i x_i^2 e^{f x_i / k_B T} = \frac{1}{\beta^2 Z} \left(\frac{\partial^2 Z}{\partial f^2} \right) \end{aligned}$$

We realize that: $\langle \Delta x^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 = \dots = k_B T \left(\frac{\partial \langle x \rangle}{\partial f} \right)$

Definition response function:

$$\frac{\partial \langle \Delta x^2 \rangle}{\partial y}$$

as the response function. **Example: Spring with a force f and displacement x**

[... see notes.](#) **Example: The fluctuation in the magnetisation of a subsystem consisting of a paramagnet in an external field B , in and contact with a reservoir at time T .**

[... see handout](#)

9.1 Thermodynamics

In a large system, the curvature of the availability function is related to the size of the fluctuations. Probability density function can be written as an exponential function of A .

We can then The probability distribution is actually a Gaussian approximation w.r.t

10 Stochastic physics

White noise properties: $\langle \xi(t) \rangle = 0$ but $\langle \xi(t)^2 \rangle = 0$ and $\langle \xi(t_1) \xi(t_1) \rangle = 0$ if $t_1 \neq t_2$.

$$\langle \xi(t) \xi(t') \rangle = \Gamma \delta(t - t')$$

Fluctuation dissipation theorem: ???

10.1 Damped Oscillator

10.1.1 Langevin equation

Langevin equation: Fluctuating system obeys the damped single harmonic oscillator equation with random force $\epsilon(t)$

$$m\ddot{x} + \lambda\dot{x} + kx = \epsilon(t)$$

10.2 Diffusion

10.3 Diffusion in external potentials

10.4 Kramers problem: escape over a potential barrier