Thermodynamics

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Contents

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 enenrgy for a given entropy. However, for an open system, in contact with reservior, 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:

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

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

Availiabily 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:

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

Note that this is 3-dimensional case.
Trick to compute the integral, in example of a free particle:

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

where λ is also known as the thermal de Broglie wavelength

4.1 Thermodynamic properties of ideal gas

We can derive thermodynamic properties of ideal gas from the partition function:

1. Partition function: $Z = \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N$

2. Mean energy: $U = -\frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} N k_B T$

3. Free energy: $F = -k_B T \ln Z = N k_B T \ln \left(\frac{N\lambda^3}{Ve}\right)$

4. Pressure: $p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_B T}{V}$

5. Chemical potential:$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_B T}{V}$

4.2 Equipartition Theorem

Equipartition Theorem:
Each squared, separable degree of freedom in the Hamiltonian has a mean energy of $k_B T/2$
Equipartition holds only in classical limit, for example harmonic oscillator the condition is $k_B T >> \hbar\omega$

4.3   Gas of diatomic molecules

Vibration of diatomic molecules is approximated by a harmonic oscillator with frequency ω_0.

4.4   Cross-over to quantum limit

The classical limit is when $N\lambda^3/V \ll 1$, we can move to quantum region by increase N, T or reduce m. In such way, their waypackets of size $\approx \lambda$ starts to interfere with each other.

4.5   Chemical equilibrium

4.6   High-T limit

4.7   Chemical potential

4.8   Cross-over to quantum limit

Continues on quantum ideal gas

5   Fermi gas

5.1   Fermi gas in low/medium/high Temperature

5.2   Fermi gas//Bose gas

Property	Fermion	Bose gas
Grand partition function	$\Xi_{\mathbf{k}} = \sum^1 \left(e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right)^n = 1 + e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}$	$\frac{1}{1-e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}}$
Average occupation$\langle n_{\mathbf{k}}\rangle$	$-\left(\frac{\partial\Phi_{\mathbf{k}}}{\partial\mu}\right)_{T,V} = \frac{1}{e^{\beta(\varepsilon_{\mathbf{k}}-\mu)}+1}$	$-\left(\frac{\partial\Phi_{\mathbf{k}}}{\partial\mu}\right)_{T,V} = \frac{1}{e^{\beta(\varepsilon_{\mathbf{k}}-\mu)}-1}$
Entropy $S_{\mathbf{k}}(T,\mu)$	$-k_B\left[\langle n_{\mathbf{k}}\rangle \ln\langle n_{\mathbf{k}}\rangle + (1-\langle n_{\mathbf{k}}\rangle)\ln(1-\langle n_{\mathbf{k}}\rangle)\right]$	$-k_B\left[\langle n_{\mathbf{k}}\rangle \ln\langle n_{\mathbf{k}}\rangle - (1+\langle n_{\mathbf{k}}\rangle)\ln(1 -$

6   Bose gas

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

$$\Xi_k = \sum_{n=0}^{\inf} e^{-\beta(\epsilon_k-\mu)^n}$$
$$= \frac{1}{1-e^{-\beta(\epsilon_k-\mu)}}$$

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.

N-particle system   Consider a liquid consisting of N particles in a container of volume V. The value of $\mathbf{r}_i \cdot \mathbf{v}_i$ can only fluctuate between finite limits. Over a long period, its time derivative must therefore average to zero, which leads to

$$\langle \mathcal{V} \rangle = \sum_i \frac{1}{2}m_i \left\langle v_i^2 \right\rangle = \langle \text{ K.E. } \rangle = \frac{3}{2}Nk_BT.$$

The mean virial is equal to the mean kinetic energy. This is Clausius' virial theorem.

7.4.1 ν_{ext}

7.4.2 ν_{int}

7.5   Virial Expansion

Virial expansion   Virial Expansion: If we start off with a very dilute gas, interactions are unimportant, and the equation of state will approach the ideal gas law. As density increases, we may expect increasing corrections to the ideal gas law. This is the motivation for the virial expansion, which expresses the equation of state in terms of increasing powers of density:

$$\frac{p}{k_BT} = n + B_2(T)n^2 + B_3(T)n^3 + \cdots$$

The mth virial coefficient, $B_m(T)$, reflects the m-body correlations in the equation of state. Mayer developed a diagrammatic recipe which (in principle) allows each coefficient to be calculated.

radial distribution   The radial distribution function $g(r)$ likewise depends on the density. If we expand it in powers of $n = N/V$,

$$g(r) = g_0(r) + g_1(r)n + g_2(r)n^2 + \cdots,$$

where when N is Large, $g_0(r) = e^{-\beta\phi(r)}$ and substitute into the virial equation of state $p = nk_BT - \frac{n^2}{6}\int_0^\infty r\frac{d\phi}{dr}g(r)4\pi r^2 dr$, we can link the coefficients B_m in the virial expansion to coefficients g_{m-2} in the expansion of the radial distribution function. We substitute $g_0(r)$ into the equation above, and integrate by parts:

$$\frac{p}{k_BT} = n - \frac{n^2}{6k_BT}\int_0^\infty 4\pi r^3 \frac{d\phi}{dr}e^{-\phi/k_BT}dr$$

$$= n + \frac{n^2}{6}\left\{ 4\pi r^3 e^{-\phi/k_BT}\Big|_0^\infty - \int_0^\infty 12\pi r^2 e^{-\phi/k_BT}dr \right\}$$

$$= n + \frac{n^2}{6}\left\{ \int_0^\infty 12\pi r^2 dr - \int_0^\infty 12\pi r^2 e^{-\phi/k_BT}dr \right\}$$

$$= n + n^2\left\{ \int_0^\infty 2\pi r^2 \left(1 - e^{-\phi/k_BT}\right)dr \right\}$$

where to get from the second to third step we have used the fact that $e^{-\phi/k_BT}$ is equal to 1 at $r = \infty$. Comparing with equation of states we see that the second virial coefficient is

$$B_2(T) = \int_0^\infty 2\pi r^2 \left(1 - e^{-\phi/k_BT}\right)dr$$

Boyle's temperature   One significant quantity in Virial expansion is the **Boyle temperature**, defined as the temperature at which the second virial coefficient B2(T) passes through zero. At this point, the gas behaves like ideal gas as te long range and short range effects cancels out with each other

8   Phase Equilibrium and Transition

A phase transition is the occurrence of an abrupt change in the physical properties of a system when a thermodynamic variable, such as the temperature or pressure, is changed by a small amount.

8.1   Ising model

Consider N spins, σ_i, which can either point up ($\sigma = 1$) or down ($\sigma = -1$). The energy (Hamiltonian) for this model is

$$H = -m_0 B \sum_i^N \sigma_i - J \sum_{ij,nn} \sigma_i\sigma_j,$$

where B is an external magnetic field, m_0 is the magnetic moment of the spin, J is the interaction energy between nearest-neighbour spins, and $\sum_{ij,nn}$ means the sum over all pairs of spins which are nearest neighbours. $J > 0$ favours parallel spins and can lead to the phenomenon of spontaneous magnetisation, that is, a non-zero magnetisation, M, which occurs even when $B = 0$, due to the potential energy of interaction between the spins.

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

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

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

$$\langle x \rangle = \frac{1}{Z} \sum_i x_i e^{fx_i/k_B T} = \frac{1}{\beta Z}(\frac{\partial Z}{\partial f})$$

$$\langle x \rangle = \frac{1}{Z} \sum_i x_i^2 e^{fx_i/k_B T} = \frac{1}{\beta^2 Z}(\frac{\partial^2 Z}{\partial f^2})$$

We realize that: $\langle \Delta x^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 = ... = k_B T(\frac{\partial <x>}{\partial f})$
Definition response function:

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

as the response function.   **Example: Spring with a force f and displacment x**
... see notes.   **Example: The fluctuation in the magnetization of a subsystem consisting of a paramagnet in an external filed 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.

The probability distribution is a Gaussian approximation First expand availability function around x_0:

$$A(x) = A(x_0) + (x - x_0)\left(\frac{\partial A}{\partial x}\right)_{x=x_0} + \frac{1}{2}(x - x_0)^2 \left(\frac{\partial^2 A}{\partial x^2}\right)_{x=x_0} + \dots$$

We compare that with the Gaussian Function:

$$P(x) = \frac{1}{\sqrt{2\pi \langle \Delta x^2 \rangle}} \exp\left[-\frac{\Delta x^2}{2 \langle \Delta x^2 \rangle}\right]$$

We get the fluctuation around equilibrium value x, for in other cases V

$$\langle \Delta x^2 \rangle = \langle (x - x_0)^2 \rangle = \frac{k_B T_R}{(\partial^2 A/\partial x^2)_{x=x_0}}$$

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