Statistical Mechanics

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Contents

convention, notation, and units

- 使用 Planck units, 此时 $G, \hbar, c, k_B = 1$, 因此:

names/dimensions	expressions/values
Planck length (L)	$l_P = \sqrt{\frac{\hbar G}{c^3}} = 1.616 \times 10^{-35}\,\mathrm{m}$
Planck time (T)	$t_P = \frac{l_P}{c} = 5.391 \times 10^{-44}\,\mathrm{s}$
Planck mass (M)	$m_P = \sqrt{\frac{\hbar c}{G}} = 2.176 \times 10^{-8}\,\mathrm{kg} \simeq 10^{19}\,\mathrm{GeV}$
Planck temperature (Θ)	$T_P = \sqrt{\frac{\hbar c^5}{G k_B^2}} = 1.417 \times 10^{32}\,\mathrm{K}$

- 时空维度用 $d = D + 1$ 表示.

- 下面是 *Statistical Field Theory*, David Tong, 中引言的一部分.

> ... This phenomenon is known as *universality*.
> All of this makes phase transitions interesting. They involve violence, universal truths and competition between rival states. The story of phase transitions is, quite literally, the song of fire and ice.
> ...
> ... This leads us to a paradigm which now underlies huge swathes of physics, far removed from its humble origin of a pot on a stove. This paradigm revolves around two deep facts about the Universe we inhabit: **Nature is organised by symmetry. And Nature is organised by scale.**

其中 symmetry 指 Landau's approach to phase transitions, scale 是指 renormalization group.

Part I

basic theory

Chapter 1

the statistical basis of thermodynamics

1.1 statistics and thermodynamics

- macrostates, microstates, the postulate of ”equal *a priori* probabilities”.
- 通过考虑 two physical systems, A_1, A_2, brought into thermal contact, 达到平衡态时 $\Omega_1\Omega_2$ 处于最大值, 得到
$$\begin{cases} S = k_B \ln \Omega(E, V, N) \\ TdS = dU + PdV - \mu dN \end{cases}, \tag{1.1.1}$$
其中 $U = \langle E \rangle$.
- 对于 homogeneous systems, 有
$$SdT = VdP - Nd\mu \iff TS = U + PV - \mu N. \tag{1.1.2}$$

homogeneity relations:

对于 homogeneous systems, 有
$$S(\alpha U, \alpha V, \alpha N) = \alpha S(U, V, N) \Longrightarrow TS = \cdots \tag{1.1.3}$$

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a function $f(x_1, \cdots, x_n)$ satisfying
$$f(\alpha x_1, \cdots, \alpha x_n) = \alpha^k f(x_1, \cdots, x_n) \tag{1.1.4}$$
is called a homogeneous function of degree k.
consider
$$\frac{\partial f(\alpha \vec{x})}{\partial \alpha} = \sum_i x_i \frac{\partial f}{\partial x_i}\Big|_{\alpha \vec{x}} = \frac{\partial \alpha^k f(\vec{x})}{\partial \alpha} = k\alpha^{k-1} f(\vec{x}), \tag{1.1.5}$$
and by setting $\alpha = 1$, we have Euler’s homogeneous function theorem,
$$kf(\vec{x}) = \sum_i x_i \frac{\partial f}{\partial x_i}\Big|_{\vec{x}}. \tag{1.1.6}$$

- 可以定义各种 free energies 如下:

names	expressions	for homogeneous sys.	differentials
internal energy	U	$U = TS - PV + \mu N$	$dU = TdS - PdV + \mu dN$
Helmholtz f.e.	$F = U - TS$	N/A	$dF = -SdT - PdV + \mu dN$
enthalpy	$H = U + PV$	N/A	$dH = TdS + VdP + \mu dN$
Gibbs f.e.	$G = U - TS + PV$	$G = \mu N$	$dG = -SdT + VdP + \mu dN$
grand potential	$\Phi_{\mathrm{G}} = U - TS - PV$	$\Phi_{\mathrm{G}} = -PV$	$d\Phi_{\mathrm{G}} = -SdT - PdV - Nd\mu$

- the specific heats are

$$C_V \equiv T\Big(\frac{\partial S}{\partial T}\Big)_{V,N} = \Big(\frac{\partial U}{\partial T}\Big)_{V,N}, \quad C_P \equiv T\Big(\frac{\partial S}{\partial T}\Big)_{P,N} = \Big(\frac{\partial H}{\partial T}\Big)_{P,N}, \tag{1.1.7}$$

并存在关系

$$\begin{cases} C_V - C_P = \Big(P + \Big(\frac{\partial U}{\partial V}\Big)_{T,N}\Big)\Big(\frac{\partial V}{\partial T}\Big)_{P,N} = TV\frac{\alpha^2}{\kappa_T} \\ \frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S} \end{cases}, \tag{1.1.8}$$

其中

$$\begin{cases} \kappa_T = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_{T,N} \\ \kappa_S = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_{S,N} \\ \alpha = \frac{1}{V}\Big(\frac{\partial V}{\partial T}\Big)_{P,N} \end{cases}. \tag{1.1.9}$$

1.2 classical ideal gas

- consider a classical (粒子波包不重叠) system composed of noninteracting particles.
  - 这两个条件导致每个粒子的分布不受其它粒子的影响, 所以

$$\Omega(E,V,N) = f(E,N)V^N \Longrightarrow \Big(\frac{\partial \ln \Omega}{\partial V}\Big)_{E,N} = \frac{N}{V}, \tag{1.2.1}$$

  得到 equation of state,

$$\frac{P}{T} = \Big(\frac{\partial S}{\partial V}\Big)_{E,N} = k_B\frac{N}{V}. \tag{1.2.2}$$

- 考虑方形势阱 ($L^3 = V$) 中的能量本征值,

$$E = \sum_{i=1}^{3N}\epsilon_i, \quad \text{where} \quad \epsilon_i = \frac{h^2}{8mL^2}n_i^2, n_i = 1,2,\cdots, \tag{1.2.3}$$

那么

$$\Omega(E,V,N) = \frac{1}{2^{3N+1}}\frac{3N\pi^{\frac{3N}{2}}}{(\frac{3N}{2})!}\Big(\frac{8mV^{2/3}}{h^2}\Big)^{\frac{3N}{2}}E^{\frac{3N}{2}-1}\Delta E = \frac{\frac{3N}{2}}{(\frac{3N}{2})!}(2\pi mE)^{\frac{3N}{2}}\Big(\frac{V}{h^3}\Big)^N\frac{\Delta E}{E}, \tag{1.2.4}$$

因此 (忽略 $O(\ln N), O(\ln\frac{\Delta E}{E})$ 项)

$$\ln\Omega \approx \frac{3N}{2} + N\ln\Big(\frac{V}{h^3}\Big(\frac{4\pi mE}{3N}\Big)^{3/2}\Big). \tag{1.2.5}$$

  - 注意, 计算中认为每个粒子都是可区分的 (distinguishable).
  - 这个结果与 homogeneous system 的性质矛盾.

calculation:

用到 n-sphere 的面积和体积公式,

$$V_n = \frac{\pi^{n/2}}{(n/2)!}, \quad S_{n-1} = \frac{n\pi^{n/2}}{(n/2)!}, \tag{1.2.6}$$

其中

$$(z)! \equiv \Gamma(z+1) = z\Gamma(z), \quad \Gamma(\frac{1}{2}) = \sqrt{\pi}. \tag{1.2.7}$$

Stirling's formula is

$$\ln N! \approx N\ln N - N. \tag{1.2.8}$$

1.3 Gibbs paradox

- 我们已经注意到 (1.2.5) 与 homogeneous system 的性质矛盾.
- Gibbs 为解决这个问题修改了 number of microstates,
$$\Omega(E,V,N) \mapsto \frac{\Omega(E,V,N)}{N!}, \tag{1.3.1}$$
因此
$$S(E,V,N) = k_B\left(N\ln\left(\frac{V}{N}\left(\frac{4\pi mE}{3h^2N}\right)^{3/2}\right) + \frac{5}{2}N\right). \tag{1.3.2}$$
- 结论: ideal gas 中的粒子是 identical and indistinguishable.
  - 系数 $\frac{1}{N!}$ 只有在所有粒子都处于不同状态时才正确, 这种条件称为 classical limit.

- 理想气体的化学势为
$$\mu = E\left(\frac{5}{3N} - \frac{2S}{3N^2k_B}\right) = k_BT\ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mk_BT}\right)^{3/2}\right). \tag{1.3.3}$$

Chapter 2

elements of ensemble theory

- 本章从经典力学角度讨论 ensemble theory

Part II

more advanced topics

Part III

phase transition