

Notes of JU Guoxing TD&SP

hebrewsnabla

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4 Temperature and Boltzmann Factor

4.1 Thermal Equilibrium

4.2 温度计

compact - 紧致（数学译法） - 致密（物理译法）

4.3 Microstates and Macrostates

4.4 Description of Dynamic states of particles

4.4.1 Classic Description

4.4.2 Quantum Description

4.4.3 Identical Particle System

Identity Principle

Identical particles in quantum physics is indistinguishable.

Boson & Fermion

光子的自旋简并度为2，不满足 $2s + 1$

光子的静质量为0不是显然的，而是外推的结果。

Bose, Fermi & Boltzmann System

Fermion - Pauli Exclusion - Fermi-Dirac Distribution

Boson - no exclusion - Bose-Einstein Condensation (BEC)

就量子本性来说不可分辨，但可以根据位置加以区分 - Localized system / Boltzmann system - Maxwell-Boltzmann Distribution.

4.4.4 Number of Microstates

ε_l energy level

ε_s energy of state

ω_l degeneracy of energy level

a_l number of particles of energy level

For systems w/ constant N, V, E

$$\sum_l a_l = N \quad \sum_l \varepsilon_l a_l = E \quad (4.4.1)$$

Boltzmann System

4.5

4.6 Ensemble

Mar 27

S.Weinberg 还原论

P.W.Anderson "More is different"

Wilczek

4.7 Canonical Ensemble & Boltzmann Distribution

Canonical Ensemble

Constant N, V, T

与大热源(heat source, heat reservoir, heat bath; with huge heat capacity)仅有能量交换的平衡系统

ε = energy of system

E_r = energy of reservoir

$\varepsilon + E_r = E$ (Cons.) $\varepsilon \ll E$

11 Energy

11.1

11.2 First Law

$$dU = dQ + dW \quad (11.2.1)$$

$$dW = -pdV \quad (\text{对系统做功为正}) \quad (11.2.2)$$

11.3 Capacity

$$\begin{aligned} dQ &= dU + pdV \\ &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV \end{aligned} \quad (11.3.1)$$

thus

$$C_v \equiv \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (11.3.2)$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p \quad (11.3.3)$$

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p \quad (11.3.4)$$

For ideal gas (one atom, per mol)

$$C_v = \frac{3}{2}R \quad (11.3.5)$$

$$C_p = C_v + [0 + p] \frac{R}{p} = \frac{5}{2}R \quad (11.3.6)$$

Def: adiabatic index

$$\gamma = \frac{C_p}{C_v} \quad (11.3.7)$$

12 Isothermal & Adiabatic Processes

12.1

12.2 Isothermal Process of Ideal Gas

Attention: 能够在p-V图上表示出来的，一定是平衡态或近似为平衡态，这样才有确定的p, T, 否则画不出来的。

$$dT = 0 \Rightarrow dU = 0 \quad (12.2.1)$$

$$\Delta Q = \int dQ = - \int dW = RT \ln \frac{V_2}{V_1} \quad (12.2.2)$$

12.3 Adiabatic Process of Ideal Gas

$$dQ = 0 \quad (12.3.1)$$

$$dU = dW \quad (12.3.2)$$

$$C_V dT = -pdV = -\frac{RT}{V} dV \quad (12.3.3)$$

$$\ln \frac{T_1}{T_2} = -\frac{RT}{C_V} \ln \frac{V_2}{V_1} \quad (12.3.4)$$

while

$$\gamma = 1 + \frac{R}{C_V} \quad (12.3.5)$$

thus

$$TV^{\gamma-1} = Cons. \quad (12.3.6)$$

or

$$pV^\gamma = Cons. \quad (12.3.7)$$

Attention: $pV = nRT$ is a state fxn, while $pV^\gamma = Cons.$ is a process fxn. (Although state fxn and process fxn may not be differed in Mechanics)

12.4 Adiabatic Atmosphere

13 Heat Engine and the 2nd Law

13.1 The 2nd Law

13.1.1 Kelvin's Statement

Discussion:

1)

2)

13.1.2 Clausius' Statement

Discussion:

1)

2)

13.2 The Carnot Cycle

Cycle Process

def

working substance

Carnot engine runs between two heat source w/ temp T_h and T_ℓ

A→B isothermal

$$Q_h = RT_h \ln \frac{V_B}{V_A} \quad (13.2.1)$$

B→C adiabatic

$$\frac{T_h}{T_\ell} = \left(\frac{V_C}{V_B} \right)^{\gamma-1} \quad (13.2.2)$$

C→D isothermal

$$Q_\ell = -RT_\ell \ln \frac{V_D}{V_C} \quad (13.2.3)$$

D→A adiabatic

$$\frac{T_\ell}{T_h} = \left(\frac{V_A}{V_D} \right)^{\gamma-1} \quad (13.2.4)$$

with (13.2.2), (13.2.4)

$$\frac{V_C}{V_B} \frac{V_A}{V_D} = 1 \quad (13.2.5)$$

thus

$$\frac{V_B}{V_A} = \frac{V_C}{V_D} \quad (13.2.6)$$

with (13.2.1), (13.2.3)

$$\frac{Q_h}{Q_\ell} = \frac{T_h}{T_\ell} \quad (13.2.7)$$

$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_\ell}{Q_h} = 1 - \frac{T_\ell}{T_h} \quad (13.2.8)$$

13.3 Carnot's Theorem

13.4

13.5

13.6

13.7 Clausius' Theorem

For Carnot Cycle

$$\frac{Q_h}{Q_\ell} = \frac{T_h}{T_\ell} \quad (13.7.1)$$

thus

$$\sum \frac{Q_{rev}}{T} = \frac{Q_h}{T_h} + \frac{-Q_\ell}{T_\ell} = 0 \quad (13.7.2)$$

i.e.

$$\oint \frac{dQ_{rev}}{T} = 0 \quad (13.7.3)$$

Clausius Inequality

$$\oint \frac{dQ}{T} \leq 0 \quad (13.7.4)$$

14 Entropy

14.1 Definition

Prove $\int_A^B \frac{dQ_R}{T}$ is path-independent
def:

$$dS = \frac{dQ_R}{T} \quad (14.1.1)$$

where "R" means reversible.

$$S_B - S_A = \int_A^B \frac{dQ_R}{T} \quad (14.1.2)$$

For adiabatic process (aka isentropic process, 等熵过程)

$$dS = 0 \quad (14.1.3)$$

14.2 Irreversible Change

$$\oint \frac{dQ_R}{T} = 0 \quad (14.2.1)$$

$$\oint \frac{dQ}{T} \leq 0 \quad (14.2.2)$$

$$\int_A^B \frac{dQ}{T} + \oint_B^A \frac{dQ_R}{T} \leq 0 \quad (14.2.3)$$

$$\oint_A^B \frac{dQ}{T} \leq \int_A^B \frac{dQ_R}{T} \quad (14.2.4)$$

$$dS = \int_A^B \frac{dQ_R}{T} \geq \oint_A^B \frac{dQ}{T} \quad (14.2.5)$$

For isolated system, $dQ = 0$, thus

$$dS \geq 0 \quad (14.2.6)$$

14.3 Revisit First Law

For reversible process

$$dU = TdS - pdV \quad (14.3.1)$$

Attention: Also ok for irreversible process

For irreversible process

$$dQ \leq TdS \quad dW \geq -pdV \quad (14.3.2)$$

thus

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad (14.3.3)$$

$$p = - \left(\frac{\partial U}{\partial V} \right)_S \quad (14.3.4)$$

$$\frac{p}{T} = - \left(\frac{\partial U}{\partial V} \right)_S \left(\frac{\partial S}{\partial U} \right)_V = \left(\frac{\partial S}{\partial V} \right)_U \quad (14.3.5)$$

14.4 Joule Expansion (Irreversible)

isol sys, ideal gas. $V_0 \rightarrow 2V_0$

$$p_i V_0 = RT_i \quad (14.4.1)$$

$$p_f \cdot 2V_0 = RT_f \quad (14.4.2)$$

isol \rightarrow

$$T_i = T_f \quad (14.4.3)$$

thus

$$p_f = \frac{p_i}{2} \quad (14.4.4)$$

Since $dU = 0$, thus

$$TdS = pdV \quad (14.4.5)$$

$$\Delta S = \int_{V_0}^{2V_0} \frac{p}{T} dV = \int_{V_0}^{2V_0} \frac{R}{V} dV = R \ln 2 \quad (14.4.6)$$

14.5 Statistical Basis for Entropy

with (14.3.3), we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V \quad (14.5.1)$$

consider

$$\frac{1}{k_B T} = \frac{d \ln \Omega}{dE} \quad (14.5.2)$$

Def

$$S = k_B \ln \Omega \quad (14.5.3)$$

14.6 Entropy of Mixing

gas1, p, T, xV, xN

gas2, $p, T, (1-x)V, (1-x)N$

\rightarrow gas1,2 p, T, V, N

$$\begin{aligned} \Delta S &= \int_{xV}^V xNk_B \frac{dV}{V} + \int_{(1-x)V}^V (1-x)Nk_B \frac{dV}{V} \\ &= -Nk_B [x \ln x + (1-x) \ln(1-x)] \end{aligned} \quad (14.6.1)$$

14.7

14.8 Entropy and Probability

A sys has N micro-states (等概率), divided into some macro-states, each containing n_i micro-states.

$$\sum_i n_i = N \quad (14.8.1)$$

thus

$$P_i = \frac{n_i}{N} \quad (14.8.2)$$

Entropy

$$S_{tot} = S + S_{micro} \quad (14.8.3)$$

where S is connected to macro-states, which we can measure
 S_{micro} is connected to micro-states

$$S_{micro} = \sum_i P_i S_i = \sum_i P_i k_B \ln n_i \quad (14.8.4)$$

thus

$$\begin{aligned} S &= S_{tot} - S_{micro} = k_B \ln N - \sum_i P_i k_B \ln n_i \\ &= k_B \left(\ln \frac{n_i}{P_i} - \right) \end{aligned} \quad (14.8.5)$$

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16 Thermodynamic Potentials

16.1 Internal Energy

$$dU = TdS - pdV \quad (16.1.1)$$

for isochoric process (等容过程)

$$dU = TdS \quad (16.1.2)$$

for reversible isochoric process

$$dU = dQ = C_V dT \quad (16.1.3)$$

16.2 Enthalpy

$$H \equiv U + pV \quad (16.2.1)$$

thus

$$dH = TdS + Vdp \quad (16.2.2)$$

For isobaric process (等压过程)

$$dH = TdS \quad (16.2.3)$$

for reversible isobaric process

$$dH = dQ_R = C_p dT \quad (16.2.4)$$

16.3 Helmholtz Function

$$F \equiv U - TS \quad (16.3.1)$$

thus

$$dF = -SdT - pdV \quad (16.3.2)$$

16.4 Gibbs Function

$$G \equiv H - TS = U + pV - TS \quad (16.4.1)$$

thus

$$dG = -SdT + Vdp \quad (16.4.2)$$

Gibbs-Helmholtz Equations

$$\begin{aligned} U &= F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V \\ &= T^2 \frac{F - T \left(\frac{\partial F}{\partial T} \right)_V}{T^2} = -T^2 \left(\frac{\partial}{\partial T} \frac{F}{T} \right)_V \end{aligned} \quad (16.4.3)$$

$$H = -T^2 \left(\frac{\partial}{\partial T} \frac{G}{T} \right)_p \quad (16.4.4)$$

16.5

16.6 Maxwell Relations

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V \quad (16.6.1)$$

$$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p \quad (16.6.2)$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad (16.6.3)$$

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \quad (16.6.4)$$

E.g. 16.4

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (16.6.5)$$

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \left(\frac{\partial}{\partial V} T \left(\frac{\partial S}{\partial T} \right)_V \right)_T = \quad (16.6.6)$$