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大学物理笔记

多普勒效应

source:v_s, observer:v_O,distance L

issued at $t=0, x=0$, recieved at $t_1', L+v_O t_1'$

issued at $t=T, x=v_S T$, received at $t_2', L+v_O t_2'$

由运动学:

$$
\begin{aligned}
v_P t_1' &= L + v_O t_1' \\
v_P(t_2' - T) &= L + v_O t_2' - v_S T
\end{aligned}
$$

于是

$$t_1' = \frac{L}{v_P - v_O}$$
$$t_2' = \frac{L}{v_P - v_O} + \frac{v_P - v_S}{v_P - v_O}T$$
$$T' = t_2' - t_1' = \frac{v_P - v_S}{v_P - v_O}T$$
$$\nu' = \frac{v_P - v_O}{v_P - v_S}\nu$$

Discussion:

$v_O > v_S$(including $v_S \leq 0$):separating, $\nu' < \nu$, Doppler redshift

$v_S > v_O$(including $v_O \leq 0$):approaching, $\nu' > \nu$, Doppler blueshift

靠近:频率变高;远离:频率变低

考虑波源的运动与波振面的运动(supersonic speed $v_S > v_p$)

马赫锥:$sin\theta = \frac{v_P}{v_S}$

驻波(stationary wave)

- 推导

由$kx - \omega t - \phi = const$,求导得 $v = \frac{\omega}{k}$

$$\begin{aligned} u_1 &= Acos(kx - \omega t - \phi) \\ u_2 &= Acos(kx + \omega t) \\ &= Acos(k(x + \frac{\omega}{k}t)) \\ \text{从而}u_1 + u_2 &= 2Acos(kx - \frac{\phi}{2})cos(wt + \frac{\phi}{2}) \end{aligned} \tag{1}$$

令 $(u_1 + u_2)_{x=0} = 0$,得 $\phi = \pi$; 令 $(u_1 + u_2)_{x=L} = 0$,得 $L = \frac{n\pi}{k} = \frac{n\lambda}{2}$

注意 $\lambda = T \cdot v_P = \frac{2\pi}{\omega} \cdot \frac{\omega}{k} = \frac{2\pi}{k}$, $k = \frac{2\pi}{\lambda}$, $\omega = vk$,有

$$\begin{aligned} f &= \frac{\omega}{2\pi} = \frac{kv}{2\pi} = n\frac{v}{2L} \\ &= f_n \\ &= nf_1 \end{aligned}$$

波节(node),波腹(antinode)的定义

- 半波损失

fixed hard boundary; from high spped to low speed

由(1)式,令 $(u_1 + u_2)_{x=0} = 0$,得 $\phi = \pi$,即为在固定端的相差

第九章　Relativistic Mechanics 相对论力学

9.1 伽利略变换

- 观测者:一套矫正好的时钟,可记录 x, y, z, t
- 结果 $t'_A - t'_B = t_A - t_B$,$x'_A - x'_B = x_A - x_B - u(t_A - t_B)$

  同时测量:$x'_A - x'_B = x_A - x_B$

  速度直接叠加,加速度不变
- Galileo's relativity: 力学定律在不同惯性参考系中相同
- 电学:不满足麦克斯韦方程组

9.2 洛伦兹变换 Lorentz Transformation

- Two basic principles of Special Theory of Relativity
  - 所有惯性参考系中物理定律相同(力学,电学等)
  - 光速不变
- 推导

假定变换为线性变换(考虑匀速直线运动);

待定系数:

$$
\begin{aligned}
x' &= a_{11}x + a_{12}y + a_{13}z + a_{14}t \\
y' &= y \\
z' &= z
\end{aligned}
$$

For arbitrary y,z if $x' = 0$,$x = ut$;则

$$x' = a_{11}(u)(x - ut), a_{11}(0) = 1 \tag{1.1}$$

By the priciple of relativity, we have

$$
\begin{gathered}
x = a_{11}(-u)(x' + ut'), \text{带入}(1.1), \text{有} \\
t' = f(x, x'(u, t)) = a_{44}t + a_{41}x
\end{gathered}
$$

从而

$$
\begin{aligned}
x' &= a(x - ut) \\
t' &= b(t - ex)
\end{aligned} \tag{1.2}
$$

解得 $x = \frac{1}{\Delta}(bx' + aut')$

与 $x = a_{11}(-u)(x' + ut')$比较,得 $a = b$

考虑光速不变:假设 $t = t' = 0$时在原点发出光信号,有

$$
\begin{gathered}
x^2 + y^2 + z^2 = c^2t^2 \\
x'^2 + y'^2 + z'^2 = c^2t'^2
\end{gathered}
$$

代入 (1.2)式,有

$$
\begin{aligned}
e &= \frac{u}{c^2} \\
a &= \frac{1}{\sqrt{1-\beta^2}} = \gamma = \sqrt{1-\frac{v^2}{c^2}} \\
\text{其中}\beta &= \frac{u}{c}
\end{aligned}
$$

完整的变换关系为

$$
\begin{aligned}
x' &= \gamma(x-ut) \\
y' &= y \\
z' &= z \\
t' &= \gamma(t-\frac{u}{c^2}x)
\end{aligned}
$$

考虑事件对 $(x_1', t_1'), (x_2', t_2')$,洛伦兹变换是

$$
\begin{aligned}
\Delta x' &= \gamma(\Delta x - u\Delta t) \\
\Delta y' &= \Delta y \\
\Delta z' &= \Delta z \\
\Delta t' &= \gamma(\Delta t - \frac{u}{c^2}\Delta x)
\end{aligned}
\tag{1.3}
$$

- 讨论
    - 逆变换: $u \to -u$　直接根据相对性原理
    - Invariance of spacetime interval 时空间隔不变:$(\Delta s)^2 = (c\Delta t)^2 - (\Delta x)^2 - (\Delta y)^2 - (\Delta z)^2 = (\Delta s')^2$
    - 伽利略变换:时间归时间 空间归空间　时间空间分别不变

- 事件对
    - 光信号联系: $(c\Delta t)^2 = (\Delta x)^2, \Delta s = 0$
    - 固有时间间隔与固有空间间隔

- Simultaneous measurement $\Delta x' = \ell_0$ in $S'(\Delta t' = 0)$ 形成一个事件

  the same pair of events in S:

$$
\begin{aligned}
\Delta x &= \gamma(\Delta x' + u\Delta t') = \gamma\Delta x' = \gamma\ell_0 \\
\Delta t &= \gamma(\Delta t + \frac{u}{c^2}\Delta x') = 0
\end{aligned}
$$

同时的相对性

也即 $\ell = \ell_0\sqrt{1-\frac{v^2}{c^2}} = \frac{\ell 0}{\gamma}$

- 用光速不变推出钟慢:

$$
\Delta t' = \frac{2L_0}{c}
$$
$$
(\frac{u\Delta t}{2})^2 + L_0^2 = (\frac{c\Delta t}{2})^2(\text{用到光速不变})
$$
$$
\Delta t = \frac{2L_0}{\sqrt{c^2-u^2}} = \frac{2L_0/c}{\sqrt{1-\beta^2}} = \gamma\Delta t'
$$

- 用光速不变推出尺缩:

$$
c\Delta t_1 = L + u\Delta t_1, c\Delta t_2 = L - u\Delta t_2
$$
$$
\Delta t = \Delta t_1 + \Delta t_2 = \frac{L}{c+u} + \frac{L}{c-u} = \frac{2L}{c}\frac{1}{1-\beta^2}
$$
$$
\Delta t' = \frac{2L_0}{c} = \gamma\Delta t
$$
$$
\frac{2L_0}{c\gamma} = \frac{2L}{c}\frac{1}{1-\beta^2}
$$
$$
\text{于是}L = \frac{L_0}{\gamma}
$$

- 因果律及信号传播(Causality and signal speed)

  - An event $P(x_P, t_P)$ causes an event $Q(x_Q, t_Q)$. 信号传输速度

$$
v_S = \frac{x_Q - x_P}{t_Q - t_P} = \frac{\Delta x}{\Delta t}
$$

在 $S'(u)$系中时间间隔为

$$
\Delta t' = \gamma\Delta t(1 - \frac{uv_S}{c^2})
$$

为保证先后次序,必须有

$$
1 - \frac{uv_S}{c^2} < 0
$$
$$
\text{则}v_S < c
$$

- 光多普勒效应

  - 由$(1.3), \Delta t = \sqrt{\frac{1+\beta}{1-\beta}}\Delta t'$
  - redshift: $\nu_0 = \sqrt{\frac{1-\beta}{1+\beta}}\nu_e$

- 波动方程: 用洛伦兹变换恰好符合(洛伦兹不变)

9.3 时空图和孪生paradox

- Minkowski Space
  - 洛伦兹变换在时空图中的体现
- Twin paradox: 在宇宙飞船加速,减速的过程中经历了非惯性系
- Pole-barn Paradox: 火车进隧道;火车系:隧道收缩;地面系:火车收缩
  - 涉及同时的相对性:看能否在地面系同时关上前门和后门(火车系觉得没有同时)
  - 地面系的观测者觉得能关进去,在火车系的观测者看来后门早就关起来了
- Visual Apperance

- 球不变　立方体转过一个角度

9.4　相对论运动学

- 速度变换公式(求导可得)

$$
\begin{aligned}
v_x' &= \frac{v_x - u}{1 - v_x \dfrac{u}{c^2}} \\
v_y' &= \frac{v_y}{\gamma(1 - v_x \dfrac{u}{c^2})} \\
v_z' &= \frac{v_z}{\gamma(1 - v_x \dfrac{u}{c^2})}
\end{aligned}
$$

9.5　相对论动力学(Relativistic Dynamics)

- 广义相对论: 引力场,非惯性系
- 讨论m, p, F, E_k, a
- Discuss a completely inelastic collision(保持动量守恒)
  - In $S'(-u): u, -u \to 0, 0$
  - In $S: v_x, 0 \to u, u$;　$v_x = \dfrac{u+u}{1+u\frac{u}{c^2}}(9.5.1)$
  - 而 $m\dfrac{u+u}{1+\frac{uu}{c^2}} + m \times \cancel{0} = 2mu$,动量守恒不成立.
  - 假定 $m \equiv m(v), m_0 \equiv m(0)$,有

$$
\begin{aligned}
m(v_x) + m_0 &= m_{total}(u) \\
m(v_x) \cdot v_x + m_0 \cdot 0 &= m_t(u)u \\
&= [m(v_x) + m_0]u \\
\text{求得} m(v_x) &= \frac{m_0}{\frac{v_x}{u} - 1}
\end{aligned}
$$

由 $(9.5.1)$,$\dfrac{v_x}{u} - 1 = \sqrt{1-\beta^2}$,则 $m(v) = \gamma m_0$. 于是

$$
\begin{aligned}
p &= \gamma m_0 v \\
E_k &= \int F \cdot dx = \int \frac{d}{dt}(mv) \cdot dx = \int v \cdot d(mv) \\
\text{而} d(mv) &= vdm + mdv \\
\text{则} E_k &= \int (v^2 dm + mvdv)
\end{aligned}
$$

考虑 $m^2(1-\frac{v^2}{c^2}) = m_0^2, m^2(c^2 - v^2) = m_0^2 c^2$,两边微分得

$$
\begin{gathered}
c^2 2mdm - v^2 2mdm - m^2 2vdv = 0, \\
c^2 dm - v^2 dm - mdv = 0, c^2 dm = v^2 dm + mdv
\end{gathered}
$$

于是

$$
\begin{aligned}
E_k &= \int c^2 dm = mc^2 - m_0c^2 \\
&= m_0c^2\left[\frac{1}{\sqrt{1-\frac{v^2}{c^2}}} - 1\right] \\
&= (\gamma - 1)m_0c^2
\end{aligned}
$$

- 讨论
    - 牛顿力学中

$$E_k = \int v \cdot d(mv) = \int mv \cdot dv = \frac{1}{2}mv^2$$

- - 相对论中,mass-energy $E = mc^2 = E_k + m_0c^2$
- - 已知动能求速度: $\gamma = \frac{E_k}{m_0c^2} + 1$
- 相对论能量-动量关系
    - $E = \sqrt{c^2p^2 + m_0^2c^4}$
    - 若 $m_0 = 0, E = cp, p = \frac{E}{c}$
    - 若 $cp << m_0c^2$,泰勒展开后得到牛顿力学.

期末考试大致内容

- 相对论运动学: 速度的变换
- 理想气体(或给定气体的状态方程) 等温膨胀,绝热等过程, 功和热, 内能等
- 理想气体的性质: 速度,平均动能等
- 过程中温度的变化,熵的变化
- 过程中 **亥姆霍兹自由能变**, 求平衡态(可能有数学上求导等)
- 比热容, 温度.
- 相变 三相点.

Project Proposal

- structure
    - Template
    - Guideline
- how and where
- basics of thesis writing
- deadline

第十章 温度

10.1 Equilibruim state

System	exchange
isolated	×

System	exchange
closed	energy
open	energy&matter

- Thermodynamic Equilibruim state: 宏观状态不随时间改变,除非外界条件发生变化.
- description of equilibruim state: state variables
  - extensive quantity: $F(n\ systems) = nF(1\ system)$
  - intensive quantity: $F(n\ systems) = F(1\ system)$
- relaxation time τ: 恢复平衡所用时间
- Quasi-static process 准静态过程: $t >> \tau$, 每一点都是平衡态, 可以在状态图上画出.
- No-dissipative, quasi-static process is reversible. (无耗散准静态过程是可逆的); All natural process(自发过程) is irreversible.
  - 系统和外界同时恢复初态

10.2 Thermal equilibruim and temperature

- The zeroth law of thermodynamics: 热平衡的传递性(热平衡的系统有共同性质)
- 温度: 衡量热平衡的一种物理性质
- 各种温标

10.4 物态方程

- 微分的常见写法 $(\frac{\partial U}{\partial V})_T$, $(\frac{\partial U}{\partial V})_P$. 保持右下标不变
- P, V, T不独立, $f(P,V,T)=0 \to U(T,P) = U(T, V(P,T)) = U(T,V) = 0$
- 等压线膨胀系数 $a_\ell = \frac{1}{L}\frac{\partial L}{\partial T}_p; \alpha_V = \frac{1}{V}(\frac{\partial V}{\partial T})_P = \frac{1}{L^3}(\frac{\partial L^3}{\partial T})_P = 3\alpha_\ell$
- 等温线膨胀系数 $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}_T$
- 体积变化方程

$$
\begin{aligned}
\frac{dV}{V} &= \frac{1}{V}(\frac{\partial V}{\partial T})_p dT + \frac{1}{V}(\frac{\partial V}{\partial p})_T dp = \alpha_V(T)dT - \kappa_T(p)dp \\
&\text{(全微分)} \\
ln\frac{V}{V_0} &= \alpha_V \Delta T - \kappa_T \Delta p \\
V &= V_0(1 + \alpha_V \Delta T - \kappa_T \Delta p)
\end{aligned}
$$

- Van der Waal's equation

$$
\left[p + a(\frac{n}{V})^2\right](V - nb) = nRT
$$

推导: 对1mol理想气体:

$$
\begin{aligned}
p = \frac{RT}{V_m} &\leftarrow \frac{RT}{V_m - b}(\text{相互作用, 体积减小}) \\
&\leftarrow \frac{RT}{V_m - b} - \frac{a}{V^2}(\text{相互作用, 压强减小, 体积越小作用力越大})
\end{aligned}
$$

第十一章 热力学第一定律

11.1 功,内能和热力学第一定律

- 准静态过程压活塞 $\bar{d}W = -p\bar{d}V$, $W = -\int_{V_i}^{V_f} pdV$ (依赖于 $P-V$图上的路径,不是全微分)
- 绝热功: Internal energy function $\Delta U = U_B - U_A \equiv W_{BA} \equiv -W_{AB}$(用与路径无关的绝热功定义内能变化)
- 非绝热功: $\Delta U = W + Q$外界做的功和外界传给内部的热量; 微分 $dU = \bar{d}Q + \bar{d}W$(功和热不是全微分,与路径有关)

11.3 热容和比热容(Heat capacity and specific heat capacity)

- $C = \lim\limits_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}$; specific: $C_m = \frac{C}{n}$
  - $C = 0$: 绝热(adiabatic)过程, $\Delta Q = 0$
  - $C = \infty$: 等温(isothermal)过程,$\Delta T = 0$
- $C_V = \lim\limits_{\Delta T \to 0} (\frac{\Delta Q}{\Delta T})_V = \lim\limits_{\Delta T \to 0} (\frac{\Delta U}{\Delta T})_V = (\frac{\partial U}{\partial T})_V$
- $C_P = \lim\limits_{\Delta T \to 0} (\frac{\Delta Q}{\Delta T})_p = \lim\limits_{\Delta T \to 0} (\frac{\Delta U + p\Delta V}{\Delta T})_p = (\frac{\partial (U + pV)}{\partial T})_p \equiv (\frac{\partial H}{\partial T})_{p'}$ $H = U + pV$: enthalpy, 焓
- ratio of specific heat: $\gamma = \frac{C_p}{C_V}$
- heat capacity of ideal gases

monatomic ideal gas	$C_V = \frac{3}{2}nR$
双原子 ideal gas	$C_V = \frac{5}{2}nR$
三原子 ideal gas	$C_V = \frac{6}{2}nR$

11.4 Free expansion and internal energy of gas

- Case of free expansion

$$
\begin{aligned}
U &= U(T,V) \\
dU &= (\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV \\
T &= T(U,V) \\
dU &= (\frac{\partial U}{\partial T})_V [(\frac{\partial T}{\partial U})_V dU + (\frac{\partial T}{\partial V})_U dV] + (\frac{\partial U}{\partial V})_T dV \\
&\text{对照左右,得}
\end{aligned}
$$

$$
(\frac{\partial U}{\partial T})_V (\frac{\partial T}{\partial U})_V = 1
$$

$$
\begin{aligned}
(\frac{\partial U}{\partial V})_T &= -(\frac{\partial U}{\partial T})_V (\frac{\partial T}{\partial V})_U = -C_V (\frac{\partial T}{\partial V})_U \to \text{焦耳系数} = 0(\text{理想气体}) \\
\text{故} U &= U(T)
\end{aligned}
$$

- 焦耳的实验非常不严谨
- 理想气体:

$$
\begin{aligned}
dU(T) &= \frac{dU}{dT} dT = C_V dT \\
U &= U_0 + C_V T \\
dQ &= dU - dW = C_V dT + pdV \\
\text{理想气体}: d(pV) &= d(nRT) \\
pdV + Vdp &= nRdT, pdV = nRdT - Vdp \\
dQ &= (C_V + nR)dT - Vdp \\
C_p &= C_V + nR \to C_V = \frac{nR}{\gamma - 1}, C_p = \frac{\gamma nR}{\gamma - 1}
\end{aligned}
$$

11.5 Adiabatic equation

$$
\begin{aligned}
dQ &= dU - dW, \\
&= C_V dT + pdV \\
C_V dT + pdV &= 0 \\
\text{又} Vdp + pdV &= nRdT = (\gamma - 1) C_V dT
\end{aligned}
$$

消去 dT,得

$$
\begin{aligned}
Vdp + \gamma pdV &= 0 \\
\frac{dp}{p} + \gamma \frac{dV}{V} &= 0 \\
lnp + \gamma lnV &= C \\
pV^\gamma &= C
\end{aligned}
$$

由 $\gamma > 1$, 绝热线比等温线陡峭

- adiabatic work

$$
\begin{aligned}
W_S &= -\int_{V_1}^{V_2} pdV = -C\int_{V_1}^{V_2}\frac{dV}{V^\gamma} = \frac{C}{\gamma-1}\left(\frac{V_2}{V_2^\gamma}-\frac{V_1}{V_1^\gamma}\right) \\
&= \frac{1}{\gamma-1}(p_2V_2-p_1V_1) \\
&= \frac{nR}{\gamma-1}(T_2-T_1) \\
&= C_V(T_2-T_1) = \Delta U
\end{aligned}
$$

- 声音的传播: 绝热

11.6 卡诺循环

- 高温热源 T_1等温膨胀→绝热膨胀→低温热源 T_2等温压缩→绝热压缩
- $T_1, U = U(T_1) = const$ 热机吸热,做功
- T_2 热机放热
- 整个循环: $\Delta U = 0, \Delta Q_{12} + \Delta Q_{34} - \Delta W = 0$

$$
\begin{gathered}
\text{效率}\eta = \frac{\Delta W}{\Delta Q_{12}} = \frac{\Delta Q_{12}+\Delta Q_{34}}{\Delta Q_{12}} = \frac{Q_1-Q_2}{Q_1} \\
(\text{考察做功过程中的放热}Q_2\text{，放热越多效率越低})
\end{gathered}
$$

$$
\begin{aligned}
\text{等温过程}: Q_1 = \Delta W_{12} = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2}\frac{nRT_1}{V}dV = nRT_1 ln\frac{V_2}{V_1} \\
Q_2 = -\Delta Q_{34} = nRT_2 ln\frac{V_3}{V_4} \\
\eta = 1-\frac{T_2 ln\frac{V_3}{V_4}}{T_1 ln\frac{V_2}{V_1}} \\
2\to 3: T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1} \\
4\to 1: T_1V_1^{\gamma-1} = T_2V_4^{\gamma-1} \\
\eta = 1-\frac{T_2}{T_1}
\end{aligned}
$$

要学会将此推导推广到其他热机上

- 可逆过程: 外界不可逆
- 逆卡诺循环: 从低温热源吸热 到高温热源被做功,放热

第十二章 热力学第二定律

12.1 内容

- No process is possible whose sole result is the absorption of heat from a reservoir and the conversion of this heat into work.
- No process is possible whose sole result is the transfer of heat from a cooler to a hotter body.
- 自发过程具有方向性

12.2 卡诺定理

- 任何热机效率不超过可逆热机
- 证明: 任意热机做功驱动可逆热机的逆过程, 反证法与热二矛盾

12.3 熵与熵原理

- 熵的引入

假设$Q_2 < 0$为放热:

$$\text{效率不大于卡诺热机}:\eta_A = 1 + \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}$$
$$\sum_{i=1}^{2} \frac{Q_i}{T_i} \leq 0$$
$$\text{一般过程}:\sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0(\text{系统与很多热源接触})$$
$$\oint \frac{dQ}{T} \leq 0$$
$$(\text{取等}:\text{可逆过程}, \text{考虑}Q_i \to -Q_i)$$
$$(\text{环路积分})$$
$$\text{写作全微分}:\frac{\bar{d}Q}{T} \equiv dS$$
$$S_B - S_A = \int_A^B \left(\frac{dQ}{T}\right)_R$$

若环路中包含不可逆过程:

$$\oint \left(\frac{dQ}{T}\right) < 0$$
$$\int_A^B \left(\frac{dQ}{T}\right)_{IR} + \int_A^B \left(\frac{dQ}{T}\right)_R < 0$$
$$\int_A^B \left(\frac{dQ}{T}\right)_{IR} - \int_B^A \left(\frac{dQ}{T}\right)_R < 0$$
$$S_B - S_A > \int_A^B \left(\frac{dQ}{T}\right)_{IR}$$
$$\int_A^B dS > \int_A^B \left(\frac{dQ}{T}\right)_{IR}$$
$$dS > \left(\frac{dQ}{T}\right)_{IR}$$

- 熵原理: 任何过程: $dS \geq \dfrac{dQ}{T}$
  - 绝热过程: $dQ = 0$; 可逆: $dS = 0$, isentropic 等熵过程
  - 孤立系统: $dS \geq 0$; 非平衡趋于平衡: 熵增加; 平衡态: 宏观特征不变,熵最大
- 热二的另一种形式: The entropy of an isolated system never decreases.
  - 从单一热源吸热的熵变: $\Delta S = \dfrac{\Delta Q}{T} = \dfrac{-Q}{T} < 0$,矛盾!

    - 两热源 $T_1 > T_2$, T_1吸热, T_2放热: $\Delta S = \frac{Q}{T_1} - \frac{Q}{T_2} < 0$, 矛盾!

- 克劳修斯不等式的证明: 考虑多热源与单一热源 T_0由多个卡诺机联合:

    - 系统作循环过程,分别与热源 T_i交换 Q_i的热量
    - $T_0 \to T_i$之间加上卡诺热机
    - $T_0 \to Q_{0i}$
    - Carnot engines: $\frac{Q_{0i}}{T_0} = \frac{Q_i}{T_i}$
    - 对整个辅助系统: T_i,系统,热机不变, 热源 T_0 放热,对外做功. 第一定律: $\sum_{n=1}^{n} Q_{0i} = \sum_{n=1}^{n} W_i$
    - 第二定律: 没有真正做功 $\sum_{n=1}^{n} Q_{0i} = T_0 \sum_{n=1}^{n} \frac{Q_i}{T_i} = \sum_{n=1}^{n} W_i \leq 0$

- 求熵变

    - 理想气体

$$
\begin{aligned}
dS &= \frac{1}{T}(dU + pdV)(\text{第一定律}) \\
&= C_V \frac{dT}{T} + nR\frac{dV}{V}(\text{第二类曲线积分}) \\
S_f - S_i &= C_v ln\frac{T_f}{T_i} + nRln\frac{V_f}{V_i} \\
S &= C_v lnT + nRlnV + S_0 \\
\text{状态函数}: S(T, V) &= C_v lnT + nRlnV + S_0
\end{aligned}
$$

-   -   - Free expansion from $V \to 2V(T = const)$:用熵作为状态函数来求: $\Delta S = nRln2 > 0$, irreversible
    - 热库reservior $\Delta S = \int \frac{dQ}{T} = \frac{\Delta Q}{T}$吸热熵增,放热熵减
    - 由准静态过程连接的状态: $\Delta S = \int_i^f \frac{dQ}{T}, dQ = C_p dT \ / \ C_V dT$
    - 由不可逆过程联系的: 找到相应的可逆过程(如不可逆的自由膨胀转化为等温过程) $\Delta S = \frac{1}{T} \int pdV = nRln\frac{V_f}{V_i}$
    - 混合: $\Delta S = \int_{T_1}^{Tf} \frac{m_1 c_1 dT}{T} + \int_{T_2}^{Tf} \frac{m_2 c_2 dT}{T}$
        - 吉布斯佯谬: 相同气体混合

- 再探功与热

    - 做功: 有广义距离: 电热丝,搅拌,微波炉等;
    - 但这些功只能转化为热,熵也就增加了$\Rightarrow$耗散功; 只要有耗散,就不可逆

- 熵的微观解释: $S = k_B lnW, W$: 微观状态数

    - 自由膨胀到两倍体积: N个粒子, $W = 2^N W_0, \ \Delta S = k_B Nln2$
    - 熵: 广延量: 微观状态用乘法原理计算, lnW可加
    - 习题 (12.9):棋盘密度最大:平衡状态

12.4 热力学势

- 内能的计算

$$
\begin{aligned}
&dQ = TdS \\
&dU = TdS - pdV + \mu dn \\
&\quad (fundamental\ equation\ of\ thermodynamics) \\
&\quad (\mu dn\text{代表与外界的物质交换，}\mu\text{指化学势})
\end{aligned}
$$

$$(\frac{\partial U}{\partial S})_{V,n} = T, (\frac{\partial U}{\partial V})_{S,n} = -p, (\frac{\partial U}{\partial n})_{S,V} = \mu$$

U是广延量：

$$U(\lambda S, \lambda V, \lambda n) = \lambda U(S, V, n)$$

两边对λ求导数：

$$(\frac{\partial U}{\partial(\lambda S)})S + (\frac{\partial U}{\partial(\lambda V)}) + (\frac{\partial U}{\partial(\lambda n)})_n = U$$

令$\lambda = 1$：

$$U = TS - pV + \mu n$$

欧拉齐次函数定理:设 $f(x_1, x_2, \cdots, x_n)$是k次函数,

$$f(\lambda x_1, \lambda x_2, \cdots, \lambda x_n) = \lambda^k f(x_1, x_2, \cdots, x_n)$$

$$\sum_{n=1}^{n} \frac{\partial f}{\partial(\lambda x_i)} \frac{\partial(\lambda x_i)}{\partial \lambda} = k\lambda^{k-1} f(x_1, x_2, \cdots, x_n)$$

$$\text{令}\lambda = 1,\text{得}$$

$$\sum_{n=1}^{n} \frac{\partial f}{\partial x_i} x_i = kf(x_1, x_2, \cdots, x_n)$$

- 其他热力学势的引入

$$
\begin{aligned}
dU &= TdS - pdV - Vdp + Vdp + \mu dn \\
d(U + pV) &= TdS + Vdp + \mu dn \equiv dH \\
&\quad (\sim reaction\ heat, enthopy) \\
dU &= TdS - pdV + \mu dn - TdS - SdT \\
d(U - TS) &= -SdT - pdV + \mu dn \equiv dF \\
&\quad (\sim useful\ work,\ Helmholtz\ free\ energy) \\
d(U - TS + pV) &= -SdT + Vdp + \mu dn \equiv dG \\
&\quad (Gibbs\ free\ energy) \\
G &= F + pV = H - TS(free\ enthopy) \\
F &= U - TS
\end{aligned}
$$

Legendre变换:

$$
\begin{aligned}
df &= udx + vdy,\ \text{是}x\text{与}y\text{的函数} \\
g &= f - ux \\
dg &= df - udx - xdu \\
&= udx + vdy - udx - xdu \\
&= -xdu + vdy, \text{是}u\text{与}y\text{的函数}
\end{aligned}
$$

-
  - 化学势的求法: $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p}$,摩尔吉布斯自由能

$$
\begin{aligned}
G &= \left(\frac{\partial G}{\partial n}\right)_{T,p} n = \mu n \\
dG &= nd\mu + \mu dn \\
nd\mu &= -SdT + Vdp \\
d\mu &= -S_m dT + V_m dp \\
&(S_m\text{：摩尔熵}, V_m\text{：摩尔体积})
\end{aligned}
$$

- 麦克斯韦关系

$$
\begin{aligned}
U(S,V,n) &= TS - pV + \mu n \\
\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right) &= \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right) = \frac{\partial^2 G}{\partial T \partial p} \\
-\left(\frac{\partial S}{\partial p}\right)_{T,n} &= \left(\frac{\partial V}{\partial T}\right)_{p,n} \\
&(\text{也可从全微分理解}) \\
dU &= TdS - pdV \\
&= T\Big[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV - pdV\Big] \\
\text{由}dF = -SdT - pdV&, \text{结合麦克斯韦关系：} \\
&= T\Big[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial T}\right)_V dV - pdV\Big] \\
\text{考虑}C_V = T\left(\frac{\partial S}{\partial T}\right)_V&\text{：} \\
&= C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV - pdV \\
\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial p}{\partial T}\right)_V - p
\end{aligned}
$$

- Criteria of thermodynamics equilibrium

$$
\begin{aligned}
\Delta S_t &= \Delta S + \Delta S_0 = \Delta S - \frac{\Delta Q}{T_0} \\
& where\ Q\ is\ released\ to\ the\ system \\
&= \Delta S - \frac{\Delta U - \Delta W - \mu\Delta n}{T_0} \ge 0 \\
\Delta U &\le T_0 \Delta S + \Delta W + \mu \Delta n \\
(\Delta U)_{S,V,n} &\le 0 \\
\Delta F &= \Delta(U - TS) \le -S\Delta T - p\Delta V + \mu\Delta n \\
(\Delta F)_{T,V,n} &\le 0 \\
\Delta G &= \Delta(F = pV) \le -S\Delta T + V\Delta p + \mu\Delta n \\
(\Delta G)_{T,p,n} &\le 0
\end{aligned}
$$

- 热力学势的物理意义
    - $(\Delta H)_p = \Delta U + p\Delta V = \Delta Q$,化学反应中等压过程的反应热. $\Delta H > 0$: endothermic 吸热; $\Delta H < 0$: exothermic 放热
    - 等温最大功与亥姆霍兹自由能 设想系统与reservoir T_0接触,这是等温过程

$$
\begin{aligned}
\Delta S_t &= \Delta S + \Delta S_{reservoir} \\
& (\text{热源损失}\Delta Q\text{的热量}) \\
&= \Delta S - \frac{\Delta Q}{T_0} \ge 0 \\
\text{对系统：} & \\
\Delta Q &= \Delta U - \Delta W_{to\ system} \\
\Delta W_{to\ system} &\ge \Delta U - T_0 \Delta S = \Delta F \\
\Delta W_{by\ system} &= -\Delta W \le -\Delta F
\end{aligned}
$$

-
    - 额外功与吉布斯自由能

等温等压过程/ isothermal isobaric:

$$
\begin{aligned}
\Delta W &= -p\Delta V + \Delta W_{other} (non-expansion\ work) \\
\Delta W &\ge \Delta U - T_0 \Delta S \\
-\Delta W_{other} &\le \Delta(U - TS + pV) \equiv -\Delta G
\end{aligned}
$$

- 平衡条件: 温度,压强,化学势

第十三章 理想气体的微观模型

Microscopic Model for Ideal gas

13.1 理想气体

- Microscopic description
    - It contains of N identical molecules
    - The molecules obey Newton's law
    - The average spacing $>> r$(相互作用不产生内能的改变)
    - Collisions are elastic and are of negligible duration.

- Microscopic meaning of **pressure**

考虑粒子撞壁运动

$$\begin{aligned}\Delta p_x &= p_f - p_i = -2mv_x \\ \Delta t &= \frac{2\ell}{v_x}\text{撞击频率} \\ \bar{F} &= -\frac{\Delta p_x}{\Delta t}(the\ force\ on\ wall) \\ &= \frac{2mv_x}{\frac{2\ell}{v_x}} = \frac{mv_x^2}{\ell}\end{aligned}$$

$$\begin{aligned}p = \frac{1}{\ell^2}\sum_{n=1}^{N}\bar{F}_n &= \frac{m}{\ell^3}(v_{x1}^2 + v_{x2}^2 + \cdots) \\ &= \frac{Nm}{\ell^3}\frac{(v_{x1}^2 + v_{x2}^2 + \cdots)}{N} \\ &= \frac{Nm}{\ell^3}\bar{v_x^2} \\ &= \frac{Nm}{3V}\bar{v^2}(isotropic\text{ 各向同性}) \\ &= \frac{1}{3}\rho\bar{v^2}\end{aligned}$$

定义方均根速率 $v_{rms} = \sqrt{\bar{v^2}} = \sqrt{\frac{3p}{\rho}}$

- Microscopic interpretation of T and U

$$\begin{aligned}pV &= \frac{2}{3}N(\frac{1}{2}m\bar{v^2}) \\ nRT &= \frac{2}{3}N(\frac{1}{2}m\bar{v^2}) \\ \frac{1}{2}m\bar{v^2} &= \frac{3}{2}\frac{nR}{N}T = \frac{3}{2}\frac{R}{N_A}T = \frac{3}{2}k_BT \\ k_B &: \text{玻尔兹曼常数 联系宏观温度与微观速度} \\ LHS &: \text{单个粒子内能}\end{aligned}$$

- 理想气体定体积热容 C_V
    - monatomic: 只有平动自由度 $U = (3 \times \frac{1}{2}k_BT)N = \frac{3}{2}k_BNT = \frac{3}{2}nRT$, 对 T 求导即得 C_V
    - diatomic: 多两个转动自由度
    - ployatomic: 多三个转动自由度

13.2 Equilibrium distributions

$$\begin{aligned}\bar{v^2} &= \frac{n_1v_1'^2 + n_2v_2'^2 + \cdots}{N} \\ &= \int v^2\frac{dn}{N}\end{aligned}$$

在引入的速度空间内 dn is the number of modules in $v_x \to v_x + dv_x, y, z$亦然, i.e. $\frac{dn}{N}$ is the probability that one molecule near v. It's proportional to dv_x. Let us suppose

$$
\begin{aligned}
\frac{dn(v_x, v_y, v_z)}{N} &= f(v_x)dv_x f(v_y)dv_y f(v_z)dv_z \\
\text{速度各向同, 与方向无关}: \\
f(v_x)f(v_y)f(v_z) &= \phi(v^2) = \phi(v_x^2 + v_y^2 + v_z^2) \\
Simplest\ solution: \\
f(v_x) &= Cexp(-\frac{v_x^2}{\alpha^2}) \\
probability\ satisfies\ normalization: \\
1 &= \int \frac{dn}{N} \\
&= \int (f(v_x)dv_x)^3 \\
&= C\int exp(-\frac{v_x^2}{\alpha^2})dv_x \\
C &= \frac{1}{\int_{-\infty}^{\infty} exp(-\frac{v_x^2}{\alpha^2})dv_x} \\
&= \frac{1}{\alpha\int_{-\infty}^{\infty} exp(-\frac{v_x^2}{\alpha^2})d\frac{v_x}{\alpha}} \\
&= \frac{1}{\alpha\sqrt{\pi}}
\end{aligned}
$$

于是

$$
\begin{aligned}
\frac{dn(v_x, v_y, v_z)}{N} &= (\frac{1}{\alpha\sqrt{\pi}})^3 exp\Big[-\frac{v_x^2 + v_y^2 + v_z^2}{\alpha^2}\Big] \\
&= (\frac{1}{\alpha\sqrt{\pi}})e^{-\frac{v_x^2}{\alpha^2}}dv_x(\frac{1}{\alpha\sqrt{\pi}})e^{-\frac{v_y^2}{\alpha^2}}dv_y(\frac{1}{\alpha\sqrt{\pi}})e^{-\frac{v_z^2}{\alpha^2}}dv_z \\
\bar{v^2} &= \int (v_x^2 + v_y^2 + v_z^2)\frac{dn(v_x, v_y, v_z)}{N} \\
&= 3\int_{-\infty}^{\infty} v_x^2(\frac{1}{\alpha\sqrt{\pi}})e^{-\frac{v_x^2}{\alpha^2}}dv_x(v_x\text{对}dv_y\text{积分得}1) \\
&= 3\times\frac{2\alpha^2}{\sqrt{\pi}}\int_0^{\infty} y^2 e^{-y^2}dy \\
&= 3\times\frac{2\alpha^2}{\sqrt{\pi}}\frac{1}{2}\Gamma(\frac{3}{2}) = 3\times\frac{2\alpha^2}{\sqrt{\pi}}\frac{1}{4}\Gamma(\frac{1}{2}) = 3\times\frac{2\alpha^2}{\sqrt{\pi}}\frac{1}{4}\sqrt{\pi} \\
&= \frac{3}{2}\alpha^2 \\
\alpha^2 &= 2k_B T/m
\end{aligned}
$$

从而有Maxwell velocity distribution:

$$\frac{dn(v_x,v_y,v_z)}{N}=(\frac{m}{2\pi k_BT})^{\frac{3}{2}}exp\Big[-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}\Big]dv_xdv_ydv_z$$
$$dn(v_x,v_y,v_z)=n_0(\frac{m}{2\pi k_BT})^{\frac{3}{2}}exp\Big[-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}\Big]dv_xdv_ydv_z$$

Maxwell speed distribution: 将速度空间的体积元换为速率空间的球壳

$$\begin{aligned}dv_xdv_ydv_z &\to 4\pi v^2dv\\ dn(v) &= n_0(\frac{m}{2\pi k_BT})^{\frac{3}{2}}exp\Big[-\frac{\frac{1}{2}mv^2}{k_BT}\Big]4\pi v^2dv\\ &= f(v)dv\\ \frac{d}{dv}f(v) &= 0, 知\\ v_m &= \sqrt{\frac{2k_BT}{m}}\\ Maxwellian\ can\ be\ written\ as\ &:\\ \frac{dn(v)}{N} &= 4\pi(\frac{1}{\pi v_m^2})^{\frac{3}{2}}exp(-\frac{v^2}{v_m^2})v^2dv\end{aligned}$$

The average speed

- Gaussian intergral using Gamma function:

$$\begin{aligned}I &= \int_0^\infty e^{-x^2}dx\\ \Gamma(v) &= \int_0^\infty e^{-t}t^{v-1}dt\\ I &= \int_0^\infty e^{-y}\frac{1}{2\sqrt{y}}dy\\ &= \frac{1}{2}\Gamma(\frac{1}{2})\\ &= \frac{\sqrt{\pi}}{2}\\ I_n &= \int_0^\infty x^ne^{-x^2}dx=\frac{1}{2}\Gamma(\frac{n+1}{2})\end{aligned}$$