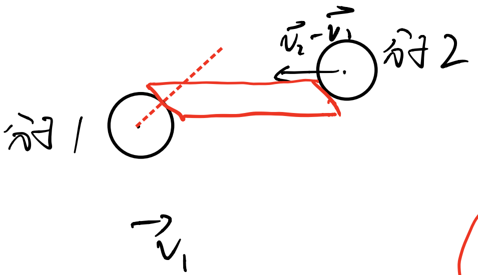
由此可见，近似在一般物理理论中起着重要作用，在从一般规律推导具体规律的过程中其作用也毫不逊色.考虑非重要因素的过于精确的计算不仅会使计算结果毫无价值地复杂化，甚至还会导致存在于现象中的规律被忽视.事实上，不仅规律的具体形式是近似的，而且刻画现象的物理量之间的函数关系也是近似的，超出给定精度极限，这些物理量的关系可能是任意的.

确定所研究现象的近似程度在理论研究中是极端重要的.最严重的错误是，采用非常精确的理论并详细计算所有的细节修正，同时却忽略了比它们大得多的物理量.

л.д.朗道
1940 年

1. 气体分子碰撞频率



$\vec{v}_2 \sim \vec{v}_2+d\vec{v}_2$

$\int$ 体积 · 分子数密度 · 概率

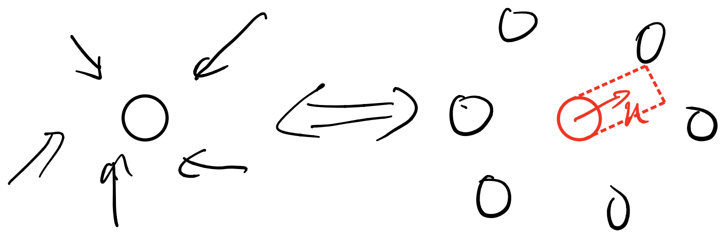
n $\quad$ $f(\vec{v}_2)d\vec{v}_2$

$N(\vec{v}_1)$ 单位时间碰撞到1分子的其他分子数

平均碰撞频率 $\bar{N} = \int N(\vec{v}_1) f(\vec{v}_1) d\vec{v}_1$

$= \sqrt{2}\pi n d^2 \bar{v}$

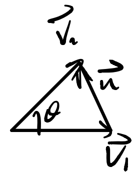
张玉民: 近似



$\bar{N} = \pi d^2 n \bar{u}$

$= \sqrt{2}\bar{v}\pi d^2 n$

巧合



$u^2 = v_1^2+v_2^2+2v_1v_2\cos\theta$

$\overline{u^2} = 2\overline{v^2} + \overline{2v_1v_2\cos\theta} \to 0$

↓近似

$\bar{u} = \sqrt{2}\bar{v}$

平均自由程.

$\lambda = \frac{v}{N(v)}$ 速度为v的分子的自由程.

$\frac{v\,dt \rightarrow \text{走的路程}}{N(v)\,dt \rightarrow \text{碰撞次数}}$

Tait 自由程: $\bar{\lambda}_1 = \int \frac{v}{N(v)} f(v)\,dv = \frac{0.677}{\pi n d^2}$

Maxwell 自由程: $\bar{\lambda} = \frac{\bar{v}}{\bar{N}} = \frac{1}{\sqrt{2}\pi n d^2} \approx \frac{0.707}{\pi n d^2}$

题 1.2: 自由程的概率分布

设过x后还有N个分子未碰撞. 再过 dx.

分子数变化: $dN = -\frac{dx}{\bar{\lambda}} \cdot N$

每个分子在dl被碰的概率.
被碰概率 ∝ 路程.

2. 热力学变量.

状态参量: $p \cdot V \cdot T \cdot A \cdot \nu \ldots$

广延量: $U, V, \nu \cdots$ $\qquad U(V, T \cdots)$

强度量: $p \cdot T \cdots$

把强度量用 $\{x_n\}$ 表示. 广延量用 $\{y_n\}$ 表示.

广延量 → $F(x_1, x_2 \cdots x_n, y_1, y_2 \cdots y_n)$

$$F(x_1, x_2 \cdots x_n, \alpha y_1, \alpha y_2 \cdots \alpha y_n) = \alpha F(x_1 \cdots x_n, y_1 \cdots y_n)$$

强度量 → $G(x_1 \cdots x_n, y_1 \cdots y_n)$

$$G(x_1 \cdots x_n, \alpha y_1 \cdots \alpha y_n) = G(x_1 \cdots x_n, y_1 \cdots y_n)$$

广/广 = 强

eg. Van der Waals 气体内能

$$U = -\frac{\nu^2 a}{V} + \nu c_v T = U(T, V, \nu)$$

$$U(T, \alpha V, \alpha \nu) = -\alpha \frac{\nu^2 a}{V} + \alpha \nu c_v T = \alpha U(T, V, \nu)$$

3. 温度. 温标.

平衡: 热平衡 —— 温度

热平衡时少一个自由度. $f(p,V) = const. = T$

状态方程: $f(p,V,T)=0$

经验温标的确定: 测温物质、定标方程(一般用线性).

eg. 一种物质定容温标与定压温标相等. 证明其状态方程为 $\theta = \alpha(p+a)(V+b)+c$ (α, a, b, c 为常数)

$\theta_p = A(p)V + B(p)$ $\qquad\qquad$ $\theta_V = D(V)p + E(V)$

$\frac{\partial\theta}{\partial V} = A(p)$ $\qquad\qquad$ $\frac{\partial\theta}{\partial p} = D(V)$

$$\frac{\partial^2\theta}{\partial V\partial p} = \frac{dA}{dp} = \frac{\partial^2\theta}{\partial p\partial V} = \frac{dD}{dV} = const = \alpha$$

$$\Rightarrow \begin{cases} A = \alpha(p+a) \\ D = \alpha(V+b) \end{cases}$$

$$d\theta = \frac{\partial\theta}{\partial p}dp + \frac{\partial\theta}{\partial V}dV = \alpha(V+b)dp + \alpha(p+a)dV = d[\alpha(p+a)(V+b)]$$

$$\theta = \alpha(p+a)(V+b) + c$$

热学中的偏导数.

$$df(x,y) = f_1(x,y)dx + f_2(x,y)dy$$

$$\left(\frac{df}{dx}\right)_y = f_1(x,y) \equiv \left(\frac{\partial f}{\partial x}\right)_y$$

$$f(x,y,z)=0 \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

证: $df = f_x dx + f_y dy + f_z dz = 0$

$$\left.\begin{aligned} \left(\frac{\partial x}{\partial y}\right)_z &= -f_y/f_x \\ \left(\frac{\partial y}{\partial z}\right)_x &= -f_z/f_y \\ \left(\frac{\partial z}{\partial x}\right)_y &= -f_x/f_z \end{aligned}\right\} \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

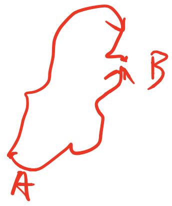
恰当微分（全微分）

$f(x,y)$　　$df(x,y) = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy$

$$df(\vec r) = \underbrace{\nabla f}_{F(\vec r)} \cdot d\vec r$$

$\frac{\partial^2 f}{\partial x_i \partial x_j} \rightleftharpoons \frac{\partial f_i}{\partial x_j} = \frac{\partial f_j}{\partial x_i}$　$\left(f_i = \frac{\partial f}{\partial x_i}\right)$

$\nabla \times \vec F = 0$



$\int_C \vec F \cdot d\vec r = f(\vec B) - f(\vec A)$

$đW = -pdV$　　$đQ = cdT$　不是恰当微分，与路径有关。

eg. $\vec F(\vec r) = xy\,\vec e_x + x^2\vec e_y$　　容易验证 $\frac{\partial F_x}{\partial y} \neq \frac{\partial F_y}{\partial x}$.

积分因子 $g(x,y)\vec F \cdot d\vec r = g(x,y)\,xy\,dx + g(x,y)\,x^2dy$

$$\frac{\partial(gxy)}{\partial y} = \frac{\partial(gx^2)}{\partial x}$$

猜 $g(x,y) = g_1(x)\,g_2(y)$：

$$\frac{y}{g_2}\frac{dg_2}{dy} = 1 + \frac{x}{g_1}\frac{dg_1}{dx} = const = C \Rightarrow \begin{cases} g_1 = k_1 x^{C-1} \\ g_2 = k_2 y^{C} \end{cases}$$

$$\Rightarrow g = k x^{C-1} y^{C}$$

看一些例子.

1. 求物态方程.

eg. $\begin{cases} \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} \\ \left(\frac{\partial p}{\partial T}\right)_V = \frac{p}{T} \end{cases}$　只显含 p, T.

求 $f(p,V,T) = 0$

$$\left(\frac{\partial V}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \Big/ \left(\frac{\partial p}{\partial T}\right)_V = -\frac{RT}{p^2}$$

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT = -\frac{RT}{p^2}dp + \frac{R}{p}dT = d\left(\frac{RT}{p}\right)$$

$$\therefore V = \frac{RT}{p} + C$$

eg. $\begin{cases} \alpha = \frac{1}{T}\left(1+\frac{3a}{VT^2}\right) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \\ \beta = \frac{1}{p}\left(1+\frac{a}{VT^2}\right) = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \end{cases}$ 求 $f(p,V,T)=0$

$$\frac{dV}{V} = \frac{1}{T}\left(1+\frac{3a}{VT^2}\right)dT - \frac{1}{p}\left(1+\frac{a}{VT^2}\right)dp$$

$$\Rightarrow \frac{dp}{p} = \frac{1+\frac{3a}{VT^2}}{T\left(1+\frac{a}{VT^2}\right)}dT - \frac{1}{V\left(1+\frac{a}{VT^2}\right)}dV \rightarrow -\ln\left(V+\frac{a}{T^2}\right)$$

$$\ln p = -\ln\left(V+\frac{a}{T^2}\right) + g(T)$$

$$\Downarrow$$

$$\frac{dp}{p} = -\frac{1}{V\left(1+\frac{a}{VT^2}\right)}dV + \frac{\frac{2a}{T^3}}{V+\frac{a}{T^2}}dT + g'(T)\,dT$$

$$\Longrightarrow g'(T) = \frac{1}{T} \quad \Rightarrow g(T) = \ln T + \ln C$$

$$\Rightarrow \ln p = -\ln\left(V+\frac{a}{T^2}\right) + \ln T + \ln C$$

$$\Rightarrow p = \frac{C\cdot T}{V+\frac{a}{T^2}}$$

2、给内能．$f(p,V,T)=0$．求 c_v、c_p．

$$\begin{cases} U(p,V,T) \\ f(p,V,T)=0 \end{cases}$$

$$dU = \frac{\partial U}{\partial p}dp + \frac{\partial U}{\partial V}dV + \frac{\partial U}{\partial T}dT$$

$dV=0$，两边除 dT ： $\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V + \left(\frac{\partial U}{\partial T}\right)_p = C_V$

$$c_p = \left(\frac{dQ}{dT}\right)_p = \left(\frac{dU+p\,dV}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

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

eg. $\begin{cases} (p+\frac{a}{V^2})(V-b)=RT \\ U = cT-\frac{a}{V} \end{cases}$ 求 c_v, c_p.

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = c$$

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = c + \left(\frac{a}{V^2}+p\right)\left(\frac{\partial V}{\partial T}\right)_p.$$

3. 给过程. 求热容.

$\begin{cases} U(p,V,T) \\ f(p,V,T)=0 \end{cases}$ 过程方程 $g(p,V,T)=0$

$$C = \left(\frac{dU+pdV}{dT}\right)_{g=0} = \frac{\frac{\partial U}{\partial T}dT + \frac{\partial U}{\partial V}dV + \frac{\partial U}{\partial p}dp + pdV}{dT}$$

$$= \frac{\partial U}{\partial T} + \frac{\partial U}{\partial p}\left(\frac{dp}{dT}\right)_g + \left(\frac{\partial U}{\partial V}+p\right)\left(\frac{dV}{dT}\right)_g$$

EOS: $\frac{\partial f}{\partial p}dp + \frac{\partial f}{\partial V}dV + \frac{\partial f}{\partial T}dT = 0$

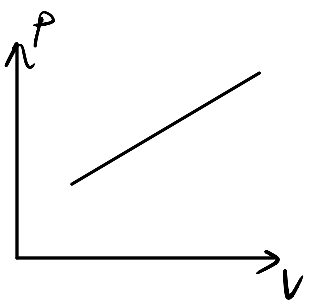
过程: $\frac{\partial g}{\partial p}dp + \frac{\partial g}{\partial V}dV + \frac{\partial g}{\partial T}dT = 0$

$$\Rightarrow \begin{cases} \frac{\partial f}{\partial p}\left(\frac{dp}{dT}\right) + \frac{\partial f}{\partial V}\left(\frac{dV}{dT}\right) + \frac{\partial f}{\partial T} = 0 \\ \frac{\partial g}{\partial p}\left(\frac{dp}{dT}\right) + \frac{\partial g}{\partial V}\left(\frac{dV}{dT}\right) + \frac{\partial g}{\partial T} = 0 \end{cases}$$

$$\Downarrow$$

$$\left(\frac{dp}{dT}\right)_g = ? \qquad \left(\frac{dV}{dT}\right)_g = ?$$

eg. $p = kV+b$



$\begin{cases} pV = \nu RT \\ p = kV+b \end{cases}$

$\Rightarrow (kV+b)V = \nu RT$

$\Rightarrow \frac{dV}{dT} = \frac{\nu R}{2kV+b}$

$$C = \frac{dQ}{dT} = \frac{C_v dT + p dV}{dT}$$

$$= C_v + p\cdot\frac{\nu R}{2kV+b}$$

$$= C_v + \nu R\frac{p}{kV+p}$$

4. 给 C, 求过程方程. (与3差不多)

一些结论：（对简单系统）

在 p-V 图中，

a. 某过程吸放热转换点，必是过程曲线与绝热曲线相切点。

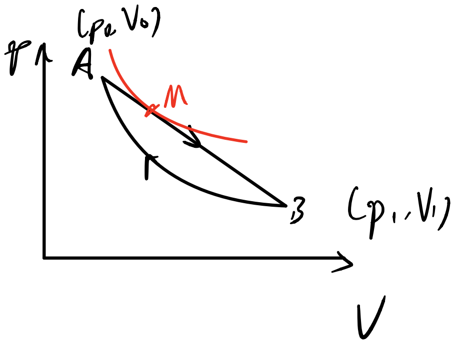
b. 2条不同等温线无交点。

c. 2条不同绝热线无交点。

d. 1条等温与1条绝热线交点不超过1个。

eg. 绝热 + 直线。

求 η.



$$\begin{cases} p = \dfrac{p_0 V_1 - p_1 V_0}{V_1 - V_0} - \dfrac{p_0 - p_1}{V_1 - V_0} V \\ \dfrac{dp}{dV} = -\gamma \dfrac{p}{V} \end{cases}$$

$$\Rightarrow \quad V_M = \frac{\gamma a}{(\gamma + 1) b}$$

能态方程. $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$.

证明：$dU = TdS - pdV$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

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

∵有 $d(U - TS) = -SdT - pdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

#

光子气体

空腔 热平衡时. $u(\nu)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3 d\nu}{e^{h\nu/kT}-1}$ 黑体辐射谱.

$u = \int u(\nu)d\nu = \alpha T^4$ 内能密度.

$n = \int \frac{u(\nu)}{h\nu}d\nu = \beta T^3$ 光子数密度. (粒子数不守恒).

$p = \frac{1}{3}u$ 光子平均能量 $\bar{E} = 2.70kT$.

CMB. (宇宙微波背景辐射). 也是一个黑体谱

现在的 CMB — $T_0 \simeq 2.725 \pm 0.001\,K$. $\Rightarrow u = 4.17\times10^{-14}\,J/m^3$

$n = 4.11\times10^{8}\,m^{-3}$

411个CMB光子 $/cm^3$

$\bar{E} = 6.34\times10^{-4}\,eV$

$\lambda \sim 2mm$

CMB是 Big Bang 的证据.

假设 早期宇宙 $T \gg 10^4 K$. 光子气体主导. 原子全部电离状态.

光子、电子 相互作用.

宇宙膨胀. $T\downarrow$. $\sim 3000K$时. 中性原子形成. 光子开始自由传播.

CMB在此时形成. $\sim T \sim 3000K$.

$3000K \longrightarrow 2.725K$.

一个在膨胀的空腔 $V \propto a(t)^3$ → 宇宙的尺度因子.

$0 = dQ = dU + pdV = d(uV) + \frac{1}{3}u\,dV = \frac{4}{3}u\,dV + V\,du$

$\Rightarrow \frac{4}{3}\cdot\alpha T^4 dV + V\cdot 4\alpha T^3 dT = 0$

$\Rightarrow \frac{dT}{T} = -\frac{1}{3}\frac{dV}{V} = -\frac{1}{3}\cdot\frac{3a^2 da}{a^3} = -\frac{da}{a}$. $T\downarrow$ 1100倍.

$\Rightarrow \frac{d}{dt}(\ln T) = -\frac{d}{dt}(\ln a) \Rightarrow T \propto \frac{1}{a}$. $a\uparrow$ 1100倍.