1. Maxwell 分布

$$\begin{cases} f(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}m(v_x^2+v_y^2+v_z^2)/(kT)} \\ f_1(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{1}{2}mv_x^2/kT} \end{cases}$$

$$(v_x, v_y, v_z) \longrightarrow (v, \theta, \varphi)$$

粒子在 $\vec{v} \sim \vec{v}+d\vec{v}$ 的概率

$$f(v,\theta,\varphi)\, dv\, d\theta\, d\varphi = f(v_x, v_y, v_z)\, dv_x dv_y dv_z = f(v_x, v_y, v_z)\, v^2 \sin\theta\, dv\, d\theta\, d\varphi$$

$$\Rightarrow \quad f(v,\theta,\varphi) = f(v_x, v_y, v_z)\, v^2 \sin\theta$$

$\therefore$ Maxwell 速率分布 $F(v) = \int f(v,\theta,\varphi)\, d\theta\, d\varphi$

$$= \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^{2\pi}\int_0^{\pi} e^{-\frac{1}{2}mv^2/kT}\, v^2 \sin\theta\, d\theta\, d\varphi$$

$$\boxed{F(v) = 4\pi v^2 \cdot \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mv^2/kT}}$$

eg. 有个粒子动能 $\varepsilon = \frac{1}{2}mv^2$，求 $\langle\varepsilon\rangle$, $\langle\varepsilon^2\rangle$, $\sqrt{\langle(\varepsilon-\bar{\varepsilon})^2\rangle}$

$$\langle\varepsilon\rangle = \int_0^\infty \left(\tfrac{1}{2}mv^2\right) F(v)\, dv \qquad \langle\varepsilon^2\rangle = \int_0^\infty \left(\tfrac{1}{2}mv^2\right)^2 F(v)\, dv \quad \cdots$$

另一种方法. 求 Maxwell 动能分布，即粒子动能在 $\varepsilon \sim \varepsilon + d\varepsilon$ 的概率.

$g(\varepsilon)\, d\varepsilon$

$$g(\varepsilon)\, d\varepsilon = F(v)\, dv$$

$$\Rightarrow g(\varepsilon) = F(v) \left|\frac{dv}{d\varepsilon}\right| = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mv^2/kT} \left|\frac{dv}{d\varepsilon}\right|$$

$$\text{代入} \begin{cases} \varepsilon = \frac{1}{2}mv^2 \\ d\varepsilon = mv\,dv = m \cdot \sqrt{\frac{2\varepsilon}{m}}\, dv \end{cases}$$

$$g(\varepsilon) = 4\pi \cdot \frac{2\varepsilon}{m} \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{\varepsilon}{kT}} \frac{1}{\sqrt{2m\varepsilon}}$$

$$\boxed{g(\varepsilon) = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT}\right)^{\frac{3}{2}} \sqrt{\varepsilon}\, e^{-\frac{\varepsilon}{kT}}}$$

$$\langle\varepsilon\rangle = \int_0^\infty \varepsilon\, g(\varepsilon)\, d\varepsilon = \frac{2}{\sqrt{\pi}} \left(\frac{1}{kT}\right)^{\frac{3}{2}} \int_0^\infty \varepsilon^{\frac{3}{2}} e^{-\frac{\varepsilon}{kT}}\, d\varepsilon$$

令 $\varepsilon = kT \cdot x^2$

$$= \frac{4kT}{\sqrt{\pi}} \int_0^\infty x^4 e^{-x^2}\, dx$$

$$\int_0^\infty x^4 e^{-x^2}dx = \int_0^\infty \left(-\frac{1}{2}\right)x^3\, d(e^{-x^2}) = \underbrace{-\frac{1}{2}x^3 e^{-x^2}\Big|_0^\infty}_{0} + \int \frac{1}{2}e^{-x^2}3x^2 dx$$

$$= \frac{3}{2}\int_0^\infty x^2 e^{-x^2}dx$$

$$= \frac{3}{2}\int_0^\infty \left(-\frac{1}{2}\right)x\, d(e^{-x^2})$$

$$= \underbrace{-\frac{3}{4}xe^{-x}\Big|_0^\infty}_{0} + \frac{3}{4}\int_0^\infty e^{-x^2}dx$$

$$= \frac{3}{8}\sqrt{\pi}$$

$$\langle \varepsilon \rangle = \frac{4kT}{\sqrt{\pi}}\cdot\frac{3}{8}\sqrt{\pi} = \frac{3}{2}kT$$

$$\langle \varepsilon^2 \rangle = \frac{15}{4}(kT)^2$$

$$\sqrt{\langle(\varepsilon-\bar\varepsilon)^2\rangle} = \sqrt{\langle \varepsilon^2 - 2\varepsilon\bar\varepsilon + \bar\varepsilon^2\rangle} = \sqrt{\langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2} = \sqrt{\frac{15}{4}(kT)^2 - \frac{9}{4}(kT)^2}$$

$$= \sqrt{\frac{3}{2}kT}$$

eg. 对于任意的速度分布，必定 $\underbrace{\sqrt{\langle v^2\rangle}}_{\text{方均根速率}} \geqslant \overbrace{\langle v\rangle}^{\text{平均速率}} \geqslant \underbrace{|\langle\vec v\rangle|}_{\text{平均速度的大小.}}$

$$\langle v^2\rangle = \int v^2 f(\vec v)\, d^3\vec v$$

$$\langle v\rangle = \int v f(\vec v)\, d^3\vec v$$

$$\langle \vec v\rangle = \int \vec v f(\vec v)\, d^3\vec v$$

$$\langle (v-\bar v)^2\rangle = \langle v^2\rangle - \langle v\rangle^2 \geqslant 0 \Rightarrow \boxed{\sqrt{\langle v^2\rangle} \geqslant \langle v\rangle}$$

$$\langle v\rangle^2 = \left(\int v f(\vec v)\, d^3\vec v\right)^2 = \int v_1 v_2 f(\vec v_1) f(\vec v_2)\, d^3\vec v_1\, d^3\vec v_2$$

$$\geqslant \int \vec v_1\cdot\vec v_2 f(\vec v_1) f(\vec v_2)\, d^3\vec v_1\, d^3\vec v_2$$

$$= \left(\int \vec v_1 f(\vec v_1)\, d^3\vec v_1\right)\cdot\left(\int \vec v_2 f(\vec v_2)\, d^3\vec v_2\right)$$

$$= |\langle\vec v\rangle|^2$$

$$\therefore \langle v\rangle \geqslant |\langle\vec v\rangle|$$

eg. 近独立粒子系统 符合 Maxwell 分布律

求 (1) 以最概然速率为速率单位的速率分布.

(2) 动能的最概然值 ε_p. 是否 $= \frac{1}{2}mv_p^2$?

(3). $\langle \frac{1}{v} \rangle$ 是否 $= \frac{1}{\langle v \rangle}$

(1) 令 $x = \frac{v}{v_p}$ $\quad dx = \frac{dv}{v_p}$ $\quad v_p = \sqrt{\frac{2kT}{m}}$

$$f(x)\,dx = F(v)\,dv$$

$$\Rightarrow f(x) = F(v)\left|\frac{dv}{dx}\right| = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mv^2/kT}\, v_p$$

$$= 4\pi\, x^2 v_p^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}m x^2 v_p^2/kT}$$

$$f(x) = \frac{4}{\sqrt{\pi}}\, x^2 e^{-x^2}$$

(2) 上面已得出, 动能分布 $g(\varepsilon) = \frac{2}{\sqrt{\pi}}\left(\frac{1}{kT}\right)^{\frac{3}{2}} \sqrt{\varepsilon}\, e^{-\frac{\varepsilon}{kT}}$

$$\frac{dg}{d\varepsilon} = 0 \Rightarrow \frac{1}{2}\frac{1}{\sqrt{\varepsilon}} e^{-\frac{\varepsilon}{kT}} - \frac{1}{kT}\sqrt{\varepsilon}\, e^{-\frac{\varepsilon}{kT}} = 0 \Rightarrow \varepsilon_p = \frac{1}{2}kT$$

$$\frac{1}{2}mv_p^2 = kT \neq \varepsilon_p$$

(3) $\langle \frac{1}{v} \rangle = \int_0^\infty \frac{1}{v} F(v)\,dv = \frac{4}{\pi}\frac{1}{\langle v \rangle}$

eg. 某分子体系. 局限在某一平面区域内 作二维运动. 近独立.

(1). 平衡时速度分布, 速率分布 . 分子质量 m, 温度 T.

(2). v_p. $\langle v \rangle$, $\sqrt{\langle v^2 \rangle}$

(3). 用何宏观量 描述 该系统. 状态方程?

(4). 等温过程方程

(5). 绝热过程方程

(准静态)

(1). $f(\vec{v}) = f(v_x) f(v_y) = \frac{m}{2\pi kT} e^{-\frac{1}{2}m(v_x^2+v_y^2)/kT}$

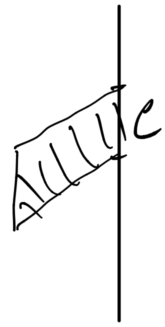
$$F(v) = 2\pi v \cdot \frac{m}{2\pi kT} e^{-\frac{1}{2}mv^2/kT}$$

(2) $\frac{dF}{dv} = 0 \Rightarrow 1 - v^2 \cdot \frac{m}{kT} = 0 \Rightarrow v_p = \sqrt{\frac{kT}{m}}$

$$\langle v \rangle = \int v F(v)\,dv = \sqrt{\frac{\pi kT}{2m}}$$

$$\langle v^2 \rangle = \int v^2 F(v)\,dv = \frac{2kT}{m}, \quad \sqrt{\langle v^2 \rangle} = \sqrt{\frac{2kT}{m}}$$

(3)



$$\int_0^\infty dx \int_{-\infty}^{\infty} dy \quad n v_x \Delta t \; l \cdot f(v_x, v_y) \cdot 2m v_x$$

$$= 2mnl\Delta t \int_0^\infty v_x^2 f_1(v_x)\, dv_x$$

$$= nl\Delta t \int_{-\infty}^{+\infty} m v_x^2 f_1(v_x)\, dv_x$$

$$= nl\Delta t\, kT \qquad \because \langle \tfrac{1}{2} m v_x^2 \rangle = \tfrac{1}{2} kT$$

$\therefore p = nkT$ （与三维相同）

$\langle \varepsilon \rangle = kT$ $\qquad pA = NkT = \nu RT$ （A为面积）

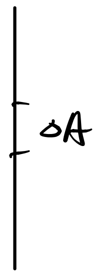
(4) $T = \text{const} \Rightarrow pA = \text{const}$

(5) $đQ = dU + pdV = \nu R dT + p dA = 2p dA + A dp = 0$

$\Rightarrow pA^2 = \text{const}. \qquad (C_{v,m} = R,\ \gamma = 2)$

2. 泻流

碰壁数



Δt

$$\Delta N = \Gamma \Delta A \Delta t$$

$$\Gamma = \frac{1}{4} n \bar{v} = \frac{1}{4} n \sqrt{\frac{8kT}{\pi m}} = \frac{1}{4} \frac{p}{kT} \sqrt{\frac{8kT}{\pi m}} = \frac{p}{\sqrt{2\pi m kT}}$$

泻流中的速度分布. (小孔外真空)

$$\begin{cases} g_2(v_y) = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{1}{2} m v_y^2 / kT} \\ g_3(v_z) = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{1}{2} m v_z^2 / kT} \end{cases}$$

$$g_1(v_x) = \frac{v_x f_1(v_x)}{\int_0^\infty v_x f_1(v_x)\, dv_x} = \frac{m}{kT} v_x\, e^{-\frac{1}{2} m v_x^2 / kT}$$

← (从计算Γ的过程出发可得出)

∴ 速率分布 $G(v) = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \int_0^\pi g(\vec{v})\, v^2 \sin\theta\, d\theta\, d\varphi$

$$= \frac{m}{kT} \frac{m}{2\pi kT} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} d\varphi \int_0^\pi d\theta\, e^{-\frac{1}{2} m v^2 / kT}\, v \sin\theta \cos\varphi \cdot v^2 \sin\theta$$

$$\int_0^\pi \sin^2\theta\, d\theta = \frac{\pi}{2}, \quad \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos\varphi\, d\varphi = 2$$

$$G(v) = \frac{m^2}{2(kT)^2} v^3 e^{-\frac{1}{2} m v^2 / kT} \sim v^3 e^{-\frac{1}{2} m v^2 / kT}$$

泻流中气体分子的:

最概然速率: $\frac{dG}{dv} = 0 \Rightarrow v_p = \sqrt{\frac{3kT}{m}}$

平均速率: $\langle v \rangle = \int_0^\infty v\, G(v)\, dv = \sqrt{\frac{9\pi kT}{8m}}$

方均根速率: $\langle v^2 \rangle = \int_0^\infty v^2 G(v)\, dv = \frac{4kT}{m} \Rightarrow \sqrt{\langle v^2 \rangle} = 2\sqrt{\frac{kT}{m}}$

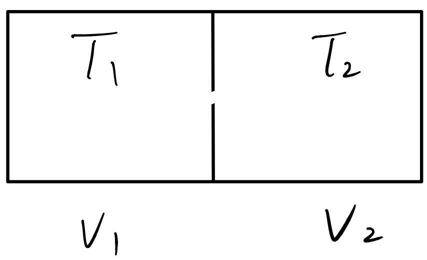
平均动能: $\langle \varepsilon \rangle = \frac{1}{2} m \langle v^2 \rangle = 2kT$ $> \frac{3}{2} kT$ (容器内)

泻流时2种情况:

① 等温

$$\begin{cases} n_1V_1 + n_2V_2 = n_0V_1 \quad \text{(总粒子数)} \\ \dfrac{d(n_1V_1)}{dt} = \left[-\dfrac{1}{4}n_1\sqrt{\dfrac{8kT}{\pi m}} + \dfrac{1}{4}n_2\sqrt{\dfrac{8kT}{\pi m}}\right]A \end{cases}$$

② 绝热



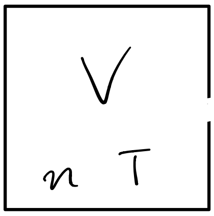
粒子数
$$\begin{cases} n_1V_1 + n_2V_2 = n_0V_1 \\ \dfrac{d(n_1V_1)}{dt} = \left[-\dfrac{1}{4}n_1\sqrt{\dfrac{8kT_1}{\pi m}} + \dfrac{1}{4}n_2\sqrt{\dfrac{8kT_2}{\pi m}}\right]A \end{cases}$$

能量
$$\begin{cases} n_1V_1\cdot\dfrac{3}{2}kT_1 + n_2V_2\cdot\dfrac{3}{2}kT_2 = n_0V_1\cdot\dfrac{3}{2}kT_0 \\ \dfrac{d}{dt}\left(n_1V_1\dfrac{3}{2}kT_1\right) = \left[-\dfrac{1}{4}n_1\bar{v}_1(2kT_1) + \dfrac{1}{4}n_2\bar{v}_2\cdot(2kT_2)\right]\cdot A \end{cases}$$

eg. 真空容器容积 V，初始真空，出现一个面积为 A 的小孔，

大气压 p_0，$T = 300K$ 不变。多长时间后容器内压强变为 $\frac{1}{10}p_0$

假设进入容器的气体弛豫时间很短



n_0，T，p_0 $\qquad$ $\Gamma = \frac{1}{4}n\bar{v} = \frac{1}{4}n\sqrt{\frac{8kT}{\pi m}}$

$$\Rightarrow \frac{d(nV)}{dt} = \left(-\frac{1}{4}n\sqrt{\frac{8kT}{\pi m}} + \frac{1}{4}n_0\sqrt{\frac{8kT}{\pi m}}\right)A = -\frac{1}{4}A\bar{v}(n-n_0)$$

$$\int_0^n \frac{dn}{n-n_0} = -\int_0^t \frac{\bar{v}A}{4V}dt$$

$$\Rightarrow \ln\frac{n_0-n}{n_0} = -\frac{\bar{v}A}{4V}t \quad , \quad n = n_0\left(1-e^{-\frac{\bar{v}A}{4V}t}\right)$$

$$n = \frac{1}{10}n_0 \Rightarrow t = \frac{4V}{\bar{v}A}\ln\frac{10}{9}$$

eg. 绝热容器 V，内有高压 N_2，压强 >> 大气压。 $T_0 = 300K$.

$t=0$ 时向外泻流，面积为 A $\qquad$ 视为向真空泻流.

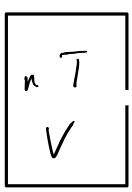
设容器内气体弛豫时间极短.

(1). 容器内气体温度变化如何？定性分析

(2). 定量考查内部 p, T 变化.

(1). $T\downarrow$ $\because$ 泻流出分子平均动能大于内部的.

(2).



$$\frac{d(nV)}{dt} = -\frac{1}{4}n\sqrt{\frac{8kT}{\pi m}}A \quad ①$$

$$\frac{d}{dt}\left[nV\cdot\frac{5}{2}kT\right] = -\frac{1}{4}n\sqrt{\frac{8kT}{\pi m}}A\cdot(\overset{\text{平动}}{2}+\overset{\text{转动}}{1})kT \quad ②$$

$$\Rightarrow \frac{d}{dt}\left[nV\cdot\frac{5}{2}kT\right] = \frac{d(nV)}{dt}\cdot 3kT$$

$$\Rightarrow d\left(\frac{5}{2}nT\right) = 3T\,dn$$

$$\Rightarrow 5\frac{dT}{T} = \frac{dn}{n} \quad \Rightarrow \frac{n}{n_0} = \left(\frac{T}{T_0}\right)^5$$

代入 ①：

$$V\frac{dT}{dt} = -\frac{1}{20}T\sqrt{\frac{8kT}{2m}}\ A$$

$$\Rightarrow \int_{T_0}^{T}\frac{dT}{T^{\frac{3}{2}}} = \int_0^t -\frac{A}{20V}\sqrt{\frac{8k}{2m}}\ dt$$

$$\Rightarrow \quad -2\left[\frac{1}{\sqrt{T}} - \frac{1}{\sqrt{T_0}}\right] = -\frac{A}{20V}\sqrt{\frac{8k}{2m}}\ t$$

$$\Rightarrow \quad T = \left[\frac{1}{\sqrt{T_0}} + \frac{A}{40V}\sqrt{\frac{8k}{2m}}\ t\right]^{-2} = T_0\left[1+\frac{A}{40V}\sqrt{\frac{8kT_0}{2m}}\ t\right]^{-2}$$

$$p = nkT = n_0\left(\frac{T}{T_0}\right)^5 kT = n_0 k T_0\left[1+\frac{A}{40V}\sqrt{\frac{8kT_0}{2m}}\ t\right]^{-12}$$

$$= p_0\left[1+\frac{A}{40V}\sqrt{\frac{8kT_0}{2m}}\ t\right]^{-12}$$