高等热力学与统计物理第九次作业

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1. 一稀薄气体处于外力场内，相应的势能为 $V(\vec{r})$。假设 $V(\vec{r})$ 在分子相互作用力程范围内的变化很小，求出 Boltzmann 方程的近似静态解并用平均数密度平均动能定义的温度表示所得得解。

处于势场 $V(\vec{r})$ 中受力为:

$$\vec{F}(r) = -\vec{\nabla}V(\vec{r}).$$

则 Boltzmann 方程可以写为:

$$\begin{aligned}&\frac{\partial}{\partial t}f(\vec{r},\vec{p};t) + \left(\frac{\vec{p}}{m}\cdot\vec{\nabla}_{\vec{r}} + \vec{F}\cdot\vec{\nabla}_{\vec{p}}\right)f(\vec{r},\vec{p};t)\\ &= \int d^3\vec{p}_2\, d^3\vec{p}_1'\, d^3\vec{p}_2'|T_{fi}|^2\delta^4(P_f - P_i)[f(\vec{r},\vec{p}_1';t)f(\vec{r},\vec{p}_2';t) - f(\vec{r},\vec{p};t)f(\vec{r},\vec{p}_2;t)].\end{aligned}$$

假设 Boltzmann 方程的试探解为:

$$f(\vec{r},\vec{p};t) = C\rho e^{-A(\vec{p}-\vec{p}_0)^2}$$

则坐标空间中粒子数密度为:

$$\rho = \int d^3\vec{p} f(\vec{r},\vec{p};t) = C\rho\int d^3\vec{p} e^{-A(\vec{p}-\vec{p}_0)^2} = C\rho\left(\frac{\pi}{A}\right)^{3/2}.$$

则有系数间关系为:

$$C = \left(\frac{A}{\pi}\right)^{3/2}$$

则考虑动量空间中粒子数密度为: $g(\vec{p};t) = \frac{f(\vec{r},\vec{p};t)}{\rho(\vec{r};t)} = \left(\frac{A}{\pi}\right)^{3/2} e^{-A(\vec{p}-\vec{p}_0)^2}$。则平均动量为:

$$\langle\vec{p}\rangle = \int d^3\vec{p}\vec{p}\left(\frac{A}{\pi}\right)^{3/2} e^{-A(\vec{p}-\vec{p}_0)^2} = \left(\frac{A}{\pi}\right)^{3/2}\int d^3\vec{p}(\vec{p}+\vec{p}_0)e^{-A\vec{p}2} = \vec{p}_0.$$

平均动量为 0 条件即为 $\vec{p}_0 = 0$。此时平均动能为:

$$\epsilon \equiv \langle\frac{\vec{p}^2}{2m}\rangle = \left(\frac{A}{\pi}\right)^{3/2}\frac{1}{2m}\int d^3\vec{p}\,\vec{p}^2 e^{-A\vec{p}2} = \frac{3}{4mA}.$$

若定义平均动能对应的温度为 $T_0 = \frac{2\epsilon}{3k}$，其中 k 为 Boltzmann 常数，则系数可以写为:

$$A = \frac{1}{2mkT_0}.$$

对于该试探解，Boltzmann 方程右侧为 0，则有:

$$\frac{\partial}{\partial t}\rho(\vec{r};t) + \frac{\vec{p}}{m}\cdot\vec{\nabla}_{\vec{r}}\rho(\vec{r};t) - \vec{\nabla}_{\vec{r}}V(\vec{r})\cdot(-2A\vec{p})\rho(\vec{r};t) = 0.$$

通解为:

$$\rho(\vec{r}) = C_1 e^{-2mAV(\vec{r})}.$$

其中 C_1 满足:

$$\int d^3\vec{r}\rho(\vec{r}) = N.$$

N 为气体分子总数。则 Boltzmann 方程近似静态解为:

$$f(\vec{r},\vec{p}) = \frac{C_1}{(2\pi mkT_0)^{3/2}} \exp\left(-\frac{V(\vec{r})}{kT_0} - \frac{\vec{p}^2}{2mkT_0}\right).$$

2. 写下一个均匀且无外力作用的气体的 Boltzmann 方程并证明下列 Boltzmann H-定理:

$$\frac{dH}{dt} \leq 0$$

其中 $H \equiv \int d^3\vec{p} f(\vec{p},t) \ln f(\vec{p},t)$。

对于均匀且无外力作用的气体，有:

$$\vec{\nabla}_{\vec{r}} f = 0,\ \vec{F} = 0.$$

则 Boltzmann 方程可以写为:

$$\frac{\partial}{\partial t} f(\vec{p};t) = \int d^3\vec{p}_2\, d^3\vec{p}_1'\, d^3\vec{p}_2' |T_{fi}|^2 \delta^4(P_f - P_i)[f(\vec{p}_1';t)f(\vec{p}_2';t) - f(\vec{p};t)f(\vec{p}_2;t)].$$

可以计算:

$$\begin{aligned}
\frac{dH}{dt} &= \int d^3\vec{p} \frac{\partial}{\partial t}(f(\vec{p},t)\ln f(\vec{p},t)) \\
&= \int d^3\vec{p} \frac{\partial}{\partial t} f(\vec{p};t) + \int d^3\vec{p} \ln f(\vec{p};t) \frac{\partial}{\partial t} f(\vec{p};t)
\end{aligned}$$

考虑等式右侧第一项则有:

$$\int d^3\vec{p} \frac{\partial}{\partial t} f(\vec{p};t) = \frac{d}{dt}\int d^3\vec{p} f(\vec{p};t) = \frac{d\rho}{dt} = 0.$$

其中 ρ 为实空间中粒子数密度，由于均匀且无外力作用，则有: $\frac{d\rho}{dt} = 0$。将 Boltzmann 方程带入上式可得:

$$\frac{dH}{dt} = \int d^3\vec{p}\, d^3\vec{p}_2\, d^3\vec{p}_1'\, d^3\vec{p}_2' |T_{fi}|^2 \delta^4(P_f - P_i)[f(\vec{p}_1';t)f(\vec{p}_2';t) - f(\vec{p};t)f(\vec{p}_2;t)] \ln f(\vec{p};t).$$

交换 $\vec{p}$ 和 $\vec{p}_2$ 以及 $\vec{p}_1'$ 和 $\vec{p}_2'$ 可得:

$$\frac{dH}{dt} = \int d^3\vec{p}\, d^3\vec{p}_2\, d^3\vec{p}_1'\, d^3\vec{p}_2' |T_{fi}|^2 \delta^4(P_f - P_i)[f(\vec{p}_1';t)f(\vec{p}_2';t) - f(\vec{p};t)f(\vec{p}_2;t)] \ln f(\vec{p}_2;t).$$

对上面两式利用时间反演不变性可得:

$$\frac{dH}{dt} = \int d^3\vec{p}\, d^3\vec{p}_2\, d^3\vec{p}_1'\, d^3\vec{p}_2' |T_{fi}|^2 \delta^4(P_f - P_i)[f(\vec{p};t)f(\vec{p}_2;t) - f(\vec{p}_1';t)f(\vec{p}_2';t)] \ln f(\vec{p}_1';t).$$

$$\frac{dH}{dt} = \int d^3\vec{p}\, d^3\vec{p}_2\, d^3\vec{p}_1'\, d^3\vec{p}_2' |T_{fi}|^2 \delta^4(P_f - P_i)[f(\vec{p};t)f(\vec{p}_2;t) - f(\vec{p}_1';t)f(\vec{p}_2';t)] \ln f(\vec{p}_2';t).$$

则有:

$$\begin{aligned}\frac{dH}{dt} =&\frac{1}{4}\int d^3\vec{p}\, d^3\vec{p}_2\, d^3\vec{p}_1'\, d^3\vec{p}_2' |T_{fi}|^2\delta^4(P_f-P_i)\\ &\times[f(\vec{p}_1';t)f(\vec{p}_2';t)-f(\vec{p};t)f(\vec{p}_2;t)]\ln\frac{f(\vec{p};t)f(\vec{p}_2;t)}{f(\vec{p}_1';t)f(\vec{p}_2';t)}.\end{aligned}$$

注意到如果 $f(\vec{p}_1';t)f(\vec{p}_2';t)-f(\vec{p};t)f(\vec{p}_2;t)>0$，则有：$\ln\frac{f(\vec{p};t)f(\vec{p}_2;t)}{f(\vec{p}_1';t)f(\vec{p}_2';t)}<0$;

如果 $f(\vec{p}_1';t)f(\vec{p}_2';t)-f(\vec{p};t)f(\vec{p}_2;t)<0$，则有：$\ln\frac{f(\vec{p};t)f(\vec{p}_2;t)}{f(\vec{p}_1';t)f(\vec{p}_2';t)}>0$;

如果 $f(\vec{p}_1';t)f(\vec{p}_2';t)-f(\vec{p};t)f(\vec{p}_2;t)=0$，则有：$\ln\frac{f(\vec{p};t)f(\vec{p}_2;t)}{f(\vec{p}_1';t)f(\vec{p}_2';t)}=0$;

综上所述，有

$$\frac{dH}{dt}\leq 0.$$