高等热力学与统计物理第五次作业

董建宇

1 证明体积为 V，温度为 T 的辐射场有以下关系：

$$\begin{aligned}
E &= V\frac{\pi^2(kT)^4}{15(\hbar c)^3} \\
F &= -\frac{1}{3}E \\
S &= \frac{4E}{3T} \\
P &= \frac{1}{3}\frac{E}{V}
\end{aligned}$$

对于辐射场有：化学式 $\mu = 0$，能量动量关系为：$\epsilon = c|\vec{p}| = c\hbar|\vec{k}|$，服从波色分布，简并度为 2。则计算粒子数有：

$$N = 2\sum_{\vec{k}}\frac{1}{e^{\beta\epsilon}-1} = 2\int\frac{V}{(2\pi)^3}4\pi k^2\,dk\frac{1}{e^{\beta\epsilon}-1} = V\int\frac{\epsilon^2}{\pi^2(\hbar c)^3}\frac{1}{e^{\beta\epsilon}-1}\,d\epsilon.$$

即态密度表达式为：

$$D(\epsilon) = \frac{\epsilon^2}{\pi^2(\hbar c)^3}.$$

则内能为：

$$E = V\int_0^\infty D(\epsilon)\frac{\epsilon}{e^{\beta\epsilon}-1}\,d\epsilon = \frac{V}{\pi^2(\hbar c)^3\beta^4}\int_0^\infty\frac{x^3}{e^x-1}\,dx = \frac{V}{\pi^2(\hbar c)^3\beta^4}\frac{\pi^4}{15} = V\frac{\pi^2(kT)^4}{15(\hbar c)^3}.$$

其中 $\beta = \frac{1}{kT}$，$x = \beta\epsilon$。
巨配分函数为：

$$\mathcal{Q} = \prod_{\vec{k}}\frac{1}{1-e^{-\beta\epsilon(\vec{k})}}.$$

则系统压强为：

$$P = \frac{kT}{V}\ln\mathcal{Q} = -\frac{kT}{V}\sum_{\vec{k}}\ln(1-e^{-\beta\epsilon(\vec{k})}) = -\frac{kT}{\pi^2(\hbar c)^3}\int_0^\infty\epsilon^2\ln(1-e^{-\beta\epsilon})\,d\epsilon.$$

计算上述积分：

$$\begin{aligned}
\mathbf{I} &= \int_0^\infty\epsilon^2\ln(1-e^{-\beta\epsilon})\,d\epsilon = \int_0^\infty\ln(1-e^{-\beta\epsilon})\,d(\epsilon^3/3) \\
&= \frac{1}{3}\epsilon^3\ln(1-e^{-\beta\epsilon})\Big|_0^\infty - \frac{\beta}{3}\int_0^\infty\frac{\epsilon^3}{e^{\beta\epsilon}-1}\,d\epsilon
\end{aligned}$$

$$= -\frac{1}{3\beta^3}\int_0^\infty \frac{x^3}{e^x-1}\,dx = -\frac{1}{3\beta^3}\frac{\pi^4}{15}.$$

则压强为:

$$P = \frac{1}{3}\frac{\pi^2(kT)^4}{15(\hbar c)^3} = \frac{1}{3}\frac{E}{V}.$$

熵为:

$$S = \frac{PV+E}{T} = \frac{4}{3}\frac{E}{T}.$$

Helmholtz 自由能为:

$$F = E - TS = -\frac{1}{3}E.$$

2 考虑两维自旋为零的自由 boson 系统

(1) 推导单位面积的态密度公式;

(2) 推导粒子数密度（面密度）用温度和易逸度表达的公式;

(3) 证明此系统无凝聚现象

(1) 计算粒子数密度 N:

$$N = \sum_{\vec{k}} \frac{1}{e^{\beta(\epsilon-\mu)}-1} = \int \frac{S}{(2\pi)^2}\,dk_x\,dk_y \frac{1}{e^{\beta(\epsilon-\mu)}-1} = S\int \frac{m}{2\pi\hbar^2}\frac{1}{e^{\beta(\epsilon-\mu)}-1}\,d\epsilon.$$

则态密度表达式为:

$$D(\epsilon) = \frac{m}{2\pi\hbar^2}.$$

(2) 易逸度为: $z = e^{\beta\mu}$，则粒子数密度为:

$$\frac{N}{S} = \frac{m}{2\pi\hbar^2}\int_0^\infty \frac{ze^{-\beta\epsilon}}{1-ze^{-\beta\epsilon}}\,d\epsilon = \frac{mkT}{2\pi\hbar^2}\int_0^\infty \frac{ze^{-x}}{1-ze^{-x}}\,dx = -\frac{mkT}{2\pi\hbar^2}\ln(1-z).$$

(3) 假设该系统有凝聚现象，临界温度为 T_C，基态能量为 0，则当系统处在临界温度时，有 $\mu \to \epsilon_0- = 0-$ 即 $z \to 1-$:

$$N = \lim_{z\to 1-}\frac{Sm}{2\pi\hbar^2}\int_0^\infty \frac{ze^{-\epsilon'/(kT_C)}}{1-ze^{-\epsilon'/(kT_C)}}\,d\epsilon' = \lim_{z\to 1-} -\frac{SmkT_C}{2\pi\hbar^2}\ln(1-z) \to +\infty$$

即假设不成立，所以该系统无凝聚现象。

3 证明在高温或低密度区域 ($\rho\lambda^3 << 1$)，自旋为 j 的非相对论自由量子气体的状态方程和熵由下列两式给出:

$$PV = NkT\left[1 \pm \frac{\rho\lambda^3}{2^{5/2}(2j+1)} + \cdots\right]$$

$$S = Nk\ln\frac{(2j+1)e^{5/2}}{\rho\lambda^3} \pm Nk\frac{\rho\lambda^3}{2^{7/2}(2j+1)} + \cdots$$

其中上边的符号对应于 fermions，下边的符号对应于 bosons，λ 为热波长，$\cdots$ 代表 $\rho\lambda^3$ 的更高阶项。

对于自旋为 j 的非相对论自由量子气体，简并度为：$\omega = 2j+1$，则状态方程为：

$$\frac{P}{kT} = \frac{2j+1}{\lambda^3}\left(z \mp \frac{z^2}{2^{5/2}} + \cdots\right).$$

其中易逸度满足:

$$\rho = \frac{N}{V} = \frac{2j+1}{\lambda^3}\left(z \mp \frac{z^2}{2^{3/2}} + \cdots\right).$$

级数反演得:

$$z = \frac{\rho\lambda^3}{2j+1} \pm \frac{1}{2^{3/2}}\left(\frac{\rho\lambda^3}{2j+1}\right)^2 + \cdots.$$

则状态方程可以写为:

$$\frac{P}{kT} = \frac{N}{V}\left(1 \pm \frac{1}{2^{5/2}}\frac{\rho\lambda^3}{2j+1} + \cdots\right)$$

理想费米（波色）气体的巨配分函数的对数为:

$$\ln\Xi = \pm\sum_l \omega_l \ln\left(1 \pm e^{-\alpha-\beta\varepsilon_l}\right)$$

即:

$$\ln\Xi = \pm g\frac{2\pi V(2m)^{3/2}}{h^3}\int\sqrt{\varepsilon}\ln\left(1 \pm e^{-\alpha-\beta\varepsilon}\right)\,d\varepsilon.$$

在弱兼并条件下，理想费米（波色）气体的压强为:

$$\begin{aligned}
p &= \frac{1}{\beta}\frac{\partial}{\partial V}\ln\Xi \\
&= \pm\frac{2\pi g(2m)^{3/2}}{h^3\beta}\int\sqrt{\varepsilon}\left(\pm e^{-\alpha-\beta\varepsilon} - \frac{1}{2}e^{-2\alpha-2\beta\varepsilon}\right)\,d\varepsilon \\
&= \frac{g(2\pi m)^{3/2}}{h^3\beta^{5/2}}e^{-\alpha}\left(1 \mp \frac{1}{4\sqrt{2}}e^{-\alpha}\right) \\
&= \frac{NkT}{V}\left(1 \pm \frac{1}{4\sqrt{2}}e^{-\alpha}\right)
\end{aligned}$$

其中，利用玻尔兹曼分布近似有:

$$e^{-\alpha} = \frac{N}{V}\frac{h^3}{(2\pi mkT)^{3/2}}\frac{1}{g}.$$

则理想费米（波色）气体的压强为:

$$p = \frac{NkT}{V}\left(1 \pm \frac{1}{4\sqrt{2}}\frac{N}{V}\frac{h^3}{(2\pi mkT)^{3/2}}\frac{1}{g}\right).$$

弱简并理想费米（波色）气体的内能为:

$$U = \frac{3}{2}NkT\left(1 \pm \frac{1}{4\sqrt{2}}\frac{N}{V}\frac{h^3}{(2\pi mkT)^{3/2}}\frac{1}{g}\right).$$

等容热熔为:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}Nk\left(1 \mp \frac{1}{8\sqrt{2}}\frac{N}{V}\frac{h^3}{(2\pi mkT)^{3/2}}\frac{1}{g}\right)$$

则弱简并理想费米（波色）气体的熵为:

$$\begin{aligned} S &= \int \frac{C_V}{T}\,dT + S_0(V) \\ &= \frac{3}{2}Nk\left(\ln T \pm \frac{1}{12\sqrt{2}}\frac{N}{V}\frac{h^3}{(2\pi mkT)^{3/2}}\frac{1}{g}\right) + S_0(V). \end{aligned}$$

当 $\frac{N}{V}\left(\frac{h}{\sqrt{2\pi mkT}}\right)^3 << 1$ 时，弱简并理想费米（波色）气体趋于经典理想气体，则有:

$$\frac{3}{2}Nk\ln T + S_0(V) = \frac{3}{2}Nk\ln T + Nk\ln\frac{gV}{N} + \frac{3}{2}Nk\left[\frac{5}{3} + \ln\left(\frac{2\pi mk}{h^2}\right)\right]$$

则弱简并理想费米（波色）气体的熵为:

$$S = Nk\left(\frac{5}{2} \pm \frac{1}{8\sqrt{2}}\frac{N}{V}\frac{h^3}{(2\pi mkT)^{3/2}}\frac{1}{g} + \frac{3}{2}\ln\frac{2\pi mkT}{h^2} + \ln\frac{gV}{N}\right).$$

其中 $g = \omega = 2j+1$，则有:

$$S = Nk\ln\frac{(2j+1)e^{5/2}}{\rho\lambda^3} \pm Nk\frac{\rho\lambda^3}{2^{7/2}(2j+1)} + \cdots.$$