热力学统计物理第九次作业

董建宇

2021.11

1

由于两种粒子可以看做近独立粒子且可以分辨，则粒子数为 N 的粒子 1 的微观状态数 Ω_1 和粒子数为 N' 的粒子 2 的微观状态数 Ω_2 分别为:

$$\Omega_1 = \frac{N!}{\prod_l a_l!} \prod_l {\omega_l}^{a_l},\ \Omega_2 = \frac{N'!}{\prod_l a_l'!} \prod_l {\omega_l'}^{a_l'}.$$

则系统的总状态数为:

$$\Omega = \Omega_1 \times \Omega_2 = \left(\frac{N!}{\prod_l a_l!} \prod_l {\omega_l}^{a_l} \right) \times \left(\frac{N'!}{\prod_l a_l'!} \prod_l {\omega_l'}^{a_l'} \right).$$

两侧取对数得:

$$\ln \Omega = \ln N! + \ln N'! - \sum_l \ln a_l! + \sum_l a_l \ln \omega_l - \sum_l \ln a_l'! + \sum_l a_l' \omega_l'.$$

当所有的 a_l, a_l' 都很大时有:

$$\begin{aligned} \ln a_l! &= a_l \left(\ln a_l - 1 \right), \quad & \ln a_l' &= a_l' \left(\ln a_l' - 1 \right), \\ \ln N! &= N \left(\ln N - 1 \right), \quad & \ln N'! &= N' \left(\ln N' - 1 \right) \end{aligned}$$

在平衡条件下有:

$$\begin{aligned} &\delta N = \sum_l \delta a_l = 0, \delta N' = \sum_l \delta a_l' = 0, \\ &\delta E = \sum_l \varepsilon_l a_l + \sum_l \varepsilon_l' a_l' = 0, \\ &\delta \ln \Omega = - \sum_l \ln \left(\frac{a_l}{\omega_l} \right) \delta a_l + \sum_l \ln \left(\frac{a_l'}{\omega_l'} \right) \delta a_l'. \end{aligned}$$

因而对于任意的 α,α' 和 β 都有:

$$
\begin{aligned}
&\delta\ln\Omega-\alpha\delta N-\alpha'\delta N'-\beta\delta E\\
=&-\sum_l\left[\ln\left(\frac{a_l}{\omega_l}\right)+\alpha+\beta\varepsilon_l\right]\delta a_l-\sum_l\left[\ln\left(\frac{a_l'}{\omega_l'}\right)+\alpha'+\beta\varepsilon_l'\right]\delta a_l'=0
\end{aligned}
$$

由于 δa_l 和 $\delta a_l'$ 可以任意取值，则有:

$$\ln\left(\frac{a_l}{\omega_l}\right)+\alpha+\beta\varepsilon_l=0,\ \ln\left(\frac{a_l'}{\omega_l'}\right)+\alpha'+\beta\varepsilon_l'=0.$$

即

$$a_l=\omega_l e^{-\alpha-\beta\varepsilon_l},\ a_l'=\omega_l' e^{-\alpha'-\beta\varepsilon_l'}.$$

此时系统的状态数为:

$$\Omega=\left(\frac{N!}{\prod_l\omega_l e^{-\alpha-\beta\varepsilon_l}!}\prod_l\omega_l^{\omega_l^{-\alpha-\beta\varepsilon_l}}\right)\times\left(\frac{N'!}{\prod_l\omega_l' e^{-\alpha'-\beta\varepsilon_l'}!}\prod_l\omega_l'^{\omega_l'^{-\alpha'-\beta\varepsilon_l'}}\right)$$

如果将一种粒子看作一个子系统，有:

$$a_l=\omega_l e^{-\alpha-\beta\varepsilon_l},\ a_l'=\omega_l' e^{-\alpha'-\beta'\varepsilon_l'}$$

则当两系统处于热平衡时有 $\beta=\beta'$，即具有共同的 β。

2

2.1 粒子是玻色子:

粒子 1 的微观状态数 Ω_1 和粒子 2 的微观状态数 Ω_2 分别为:

$$\Omega_1=\prod_l\frac{(\omega_l+a_l-1)!}{a_l!(\omega_l-1)!},\ \Omega_2=\prod_l\frac{(\omega_l'+a_l'-1)!}{a_l'!(\omega_l'-1)!}.$$

则系统的微观状态数为:

$$\Omega=\Omega_1\times\Omega_2=\left(\prod_l\frac{(\omega_l+a_l-1)!}{a_l!(\omega_l-1)!}\right)\times\left(\prod_l\frac{(\omega_l'+a_l'-1)!}{a_l'!(\omega_l'-1)!}\right).$$

两侧取对数可得:

$$
\begin{aligned}
\ln\Omega=&\sum_l\left(\ln(\omega_l+a_l-1)!-\ln a_l!-\ln(\omega_l-1)!\right)\\
&+\sum_l\left(\ln(\omega_l'+a_l'-1)!-\ln a_l'!-\ln(\omega_l'-1)!\right).
\end{aligned}
$$

当 $a_l >> 1, \omega_l >> 1; a'_l >> 1, \omega'_l >> 1$ 时，有:

$$
\begin{aligned}
\ln\Omega = &\sum_l \left((\omega_l + a_l)\ln(\omega_l + a_l) - a_l\ln a_l - \omega_l\ln\omega_l\right) \\
&+ \sum_l \left((\omega'_l + a'_l)\ln(\omega'_l + a'_l) - a'_l\ln a'_l - \omega'_l\ln\omega'_l\right).
\end{aligned}
$$

则在平衡条件下有:

$$
\begin{aligned}
&\delta N = \sum_l \delta a_l = 0,\ \delta N' = \sum_l \delta a'_l, \\
&\delta E = \sum_l \varepsilon_l a_l + \sum_l \varepsilon'_l a'_l = 0, \\
&\delta\Omega = \sum_l \ln\left(\frac{\omega_l}{a_l} + 1\right)\delta a_l + \sum_l \ln\left(\frac{\omega'_l}{a'_l} + 1\right)\delta a'_l.
\end{aligned}
$$

则对于任意的 α, α' 和 β 都有:

$$
\begin{aligned}
&-\delta\Omega + \alpha\delta N + \alpha'\delta N' + \beta\delta E \\
=&\sum_l \left[-\ln\left(\frac{\omega_l}{a_l} + 1\right) + \alpha + \beta\varepsilon_l\right]\delta a_l + \sum_l \left[-\ln\left(\frac{\omega'_l}{a'_l} + 1\right) + \alpha' + \beta\varepsilon'_l\right]\delta a'_l
\end{aligned}
$$

由于 δa_l 和 $\delta a'_l$ 可以取任意值，则有:

$$
-\ln\left(\frac{\omega_l}{a_l} + 1\right) + \alpha + \beta\varepsilon_l = 0,\ \ -\ln\left(\frac{\omega'_l}{a'_l} + 1\right) + \alpha' + \beta\varepsilon'_l = 0.
$$

即

$$
a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} - 1},\ a'_l = \frac{\omega'_l}{e^{\alpha'+\beta\varepsilon'_l} - 1}.
$$

此时系统微观状态数为:

$$
\Omega = \left(\prod_l \frac{(\omega_l + \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l - 1}} - 1)!}{(\frac{\omega_l}{e^{\alpha+\beta\varepsilon_l - 1}})!(\omega_l - 1)!}\right) \times \left(\prod_l \frac{(\omega'_l + \frac{\omega'_l}{e^{\alpha'+\beta\varepsilon'_l - 1}} - 1)!}{(\frac{\omega'_l}{e^{\alpha'+\beta\varepsilon'_l - 1}})!(\omega'_l - 1)!}\right)
$$

2.2 粒子是费米子:

粒子 1 的微观状态数 Ω_1 和粒子 2 的微观状态数 Ω_2 分别为:

$$
\Omega_1 = \prod_l \frac{\omega_l!}{a_l!(\omega_l - a_l)!},\ \Omega_2 = \prod_l \frac{\omega'_l!}{a'_l!(\omega'_l - a'_l)!}.
$$

则系统的微观状态数为:

$$\Omega = \Omega_1 \times \Omega_2 = \left(\prod_l \frac{\omega_l!}{a_l!(\omega_l - a_l)!} \right) \times \left(\prod_l \frac{\omega_l'!}{a_l'!(\omega_l' - a_l)!} \right).$$

两侧取对数可得:

$$\begin{aligned} \ln \Omega = & \sum_l \left(\ln \omega_l! - \ln a_l! - \ln(\omega_l - a_l)! \right) \\ & + \sum_l \left(\ln \omega_l'! - \ln a_l'! - \ln(\omega_l' - a_l)! \right). \end{aligned}$$

当 $a_l >> 1, \omega_l >> 1, \omega_l - a_l ? >> 1; a_l' >> 1, \omega_l' >> 1, \omega_l' - a_l >> 1$ 时，有:

$$\begin{aligned} \ln \Omega = & \sum_l \left(\omega_l \ln \omega_l - a_l \ln a_l - (\omega_l - a_l) \ln(\omega_l - a_l) \right) \\ & + \sum_l \left(\omega_l' \ln \omega_l' - a_l' \ln a_l' - (\omega_l' - a_l') \ln(\omega_l' - a_l) \right). \end{aligned}$$

则在平衡条件下有:

$$\begin{aligned} \delta N &= \sum_l \delta a_l = 0,\ \delta N' = \sum_l \delta a_l', \\ \delta E &= \sum_l \varepsilon_l a_l + \sum_l \varepsilon_l' a_l' = 0, \\ \delta \Omega &= \sum_l \ln \left(\frac{\omega_l}{a_l} - 1 \right) \delta a_l + \sum_l \ln \left(\frac{\omega_l'}{a_l'} - 1 \right) \delta a_l'. \end{aligned}$$

则对于任意的 α, α' 和 β 都有:

$$\begin{aligned} & -\delta\Omega + \alpha \delta N + \alpha' \delta N' + \beta \delta E \\ = & \sum_l \left[-\ln \left(\frac{\omega_l}{a_l} - 1 \right) + \alpha + \beta \varepsilon_l \right] \delta a_l + \sum_l \left[-\ln \left(\frac{\omega_l'}{a_l'} - 1 \right) + \alpha' + \beta \varepsilon_l' \right] \delta a_l' \end{aligned}$$

由于 δa_l 和 $\delta a_l'$ 可以取任意值，则有:

$$-\ln \left(\frac{\omega_l}{a_l} - 1 \right) + \alpha + \beta \varepsilon_l = 0,\ -\ln \left(\frac{\omega_l'}{a_l'} - 1 \right) + \alpha' + \beta \varepsilon_l' = 0.$$

即

$$a_l = \frac{\omega_l}{e^{\alpha + \beta \varepsilon_l} + 1},\ a_l' = \frac{\omega_l'}{e^{\alpha' + \beta \varepsilon_l'} + 1}.$$

此时系统的微观状态数为:

$$\Omega = \left(\prod_l \frac{\omega_l!}{(\frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}+1})!(\omega_l - \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}+1})!} \right) \times \left(\prod_l \frac{\omega_l'!}{(\frac{\omega_l'}{e^{\alpha'+\beta\varepsilon_l'}+1})!(\omega_l' - \frac{\omega_l'}{e^{\alpha'+\beta\varepsilon_l'}+1})!} \right)$$

3

不妨设粒子 1 为玻色子，粒子 2 为费米子，则两种粒子的微观状态数分别为:

$$\Omega_1 = \prod_l \frac{(\omega_l + a_l - 1)!}{a_l!(\omega_l - 1)!},\ \Omega_2 = \prod_l \frac{\omega_l'!}{a_l!(\omega_l' - a_l')!}.$$

则系统的微观状态数为:

$$\Omega = \Omega_1 \times \Omega_2 = \left(\prod_l \frac{(\omega_l + a_l - 1)!}{a_l!(\omega_l - 1)!}\right) \times \left(\prod_l \frac{\omega_l'!}{a_l!(\omega_l' - a_l')!}\right)$$

两侧取对数可得:

$$\begin{aligned}\ln \Omega = &\sum_l \ln(\omega_l + a_l - 1)! - \ln a_l! - \ln(\omega - 1)! \\ &+ \sum_l \ln \omega_l'! - \ln a_l'! - \ln(\omega_l' - a_l')!.\end{aligned}$$

当 $a_l >> 1, \omega_l >> 1; a_l' >> 1, \omega_l' >> 1, \omega_l' - a_l' >> 1$ 时，有:

$$\begin{aligned}\ln \Omega = &\sum_l \left((\omega_l + a_l)\ln(\omega_l + a_l) - a_l \ln a_l - \omega_l \ln \omega_l\right) \\ &+ \sum_l \left(\omega_l' \ln \omega_l' - a_l' \ln a_l' - (\omega_l' - a_l')\ln(\omega_l' - a_l')\right).\end{aligned}$$

在平衡条件下有:

$$\begin{aligned}&\delta N = \sum_l \delta a_l = 0,\ \delta N' = \sum_l \delta a_l' = 0, \\ &\delta E = \sum_l \varepsilon_l \delta a_l + \sum_l \varepsilon_l' \delta a_l' = 0, \\ &\delta \ln \Omega = \sum_l \ln\left(\frac{\omega_l}{a_l} + 1\right)\delta a_l + \sum_l \ln\left(\frac{\omega_l'}{a_l'} - 1\right)\delta a_l'.\end{aligned}$$

则对于任意的 α, α', β 都有:

$$\begin{aligned}&-\delta\Omega + \alpha\delta N + \alpha'\delta N' + \beta\delta E \\ =&\sum_l \left[-\ln\left(\frac{\omega_l}{a_l} + 1\right) + \alpha + \beta\varepsilon_l\right]\delta a_l + \sum_l \left[-\ln\left(\frac{\omega_l'}{a_l'} - 1\right) + \alpha' + \beta\varepsilon_l'\right]\delta a_l'\end{aligned}$$

由于 δa_l 和 $\delta a_l'$ 可以取任意值，则有:

$$-\ln\left(\frac{\omega_l}{a_l} + 1\right) + \alpha + \beta\varepsilon_l = 0,\ \ -\ln\left(\frac{\omega_l'}{a_l'} - 1\right) + \alpha' + \beta\varepsilon_l' = 0.$$

即

$$a_l=\frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}-1},\ a_l'=\frac{\omega_l'}{e^{\alpha'+\beta\varepsilon_l'}+1}.$$

此时系统的微观状态数为:

$$\Omega=\left(\prod_l\frac{(\omega_l+\frac{\omega_l}{e^{\alpha+\beta\varepsilon_l-1}}-1)!}{(\frac{\omega_l}{e^{\alpha+\beta\varepsilon_l-1}})!(\omega_l-1)!}\right)\times\left(\prod_l\frac{(\omega_l'+\frac{\omega_l'}{e^{\alpha'+\beta\varepsilon_l'-1}}-1)!}{(\frac{\omega_l'}{e^{\alpha'+\beta\varepsilon_l'-1}})!(\omega_l'-1)!}\right)$$

4

当两能级的简并度均为 1 时，假设粒子可分辨，系统的熵为:

$$\Omega=\frac{N!}{N_1!N_2!}$$

则系统的熵为:

$$S=k\ln\Omega=k\ln\left(\frac{N!}{N_1!N_2!}\right).$$

当 $N>>1,N_1>>1,N_2>>1$ 时，近似可得:

$$S=k\left(N\ln N-N_1\ln N_1-N_2\ln N_2\right).$$

5

粒子总数等于等于自旋向上的粒子数加自旋向下粒子数:

$$N=N_\uparrow+N_\downarrow.$$

由提示可知:

$$M_z=\frac{1}{2}(N_\uparrow-N_\downarrow).$$

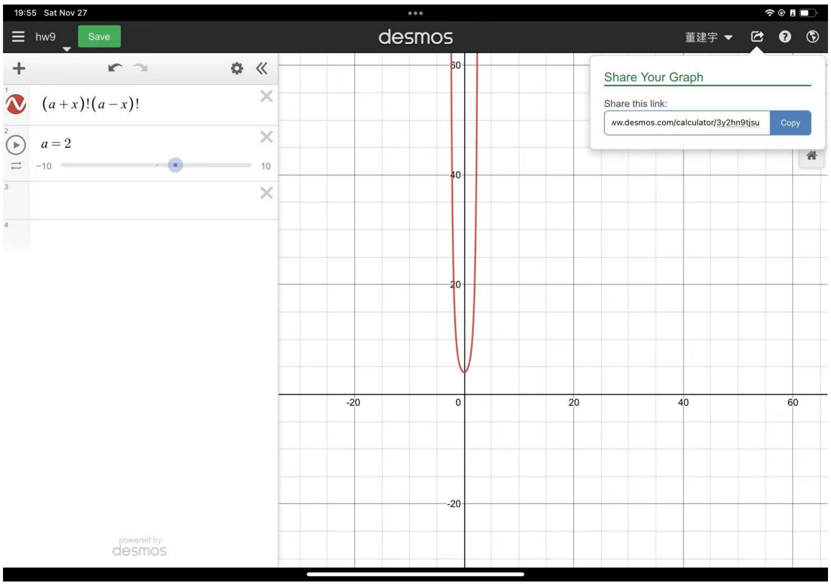
所以可以解得:

$$N_\uparrow=\frac{N}{2}+M_z,\ N_\downarrow=\frac{N}{2}-M_z.$$

当简并度均为 1 时，体系状态数为:

$$\Omega=\binom{N}{N_\uparrow}=\frac{N!}{\left(\frac{N}{2}+M_z\right)!\left(\frac{N}{2}-M_z\right)!}.$$

要使体系状态数最大，则要 $\left(\frac{N}{2}+M_z\right)!\left(\frac{N}{2}-M_z\right)!$ 最小。绘图可知



对于任意的 N 当 $M_z=0$ 时 $(\frac{N}{2}+M_z)!\,(\frac{N}{2}-M_z)!$ 最小。即使体系状态数最大的 M_z 的值为 0。
当 $\frac{N}{2}+M_z$ 和 $\frac{N}{2}-M_z$ 远大于 1 时有

$$\ln\left(\frac{N}{2}+M_z\right)! \approx \left(\frac{N}{2}+M_z\right)\left(\ln\left(\frac{N}{2}+M_z\right)-1\right)$$
$$\ln\left(\frac{N}{2}-M_z\right)! \approx \left(\frac{N}{2}-M_z\right)\left(\ln\left(\frac{N}{2}-M_z\right)-1\right)$$

则有:

$$\begin{aligned}\ln\Omega &= \ln N! - \ln\left(\frac{N}{2}+M_z\right)! - \ln\left(\frac{N}{2}-M_z\right)! \\ &\approx N\ln N - \left(\frac{N}{2}+M_z\right)\ln\left(\frac{N}{2}+M_z\right) - \left(\frac{N}{2}-M_z\right)\ln\left(\frac{N}{2}-M_z\right)\end{aligned}$$

对 M_z 求导可得:

$$\frac{d\ln\Omega}{dM_z} = \ln\left(\frac{N-2M_z}{N+2M_z}\right) = 0.$$

得 $M_z=0$，此时 $\ln\Omega$ 取极值，此时有

$$\frac{d^2\Omega}{dM_z^2} = -\frac{4}{N} < 0.$$

即 $M_z=0$ 为 $\ln\Omega$ 的极大值，即体系最状态数最大时 $M_z=0$，此时系统的微观状态数为:

$$\Omega_{max} = \frac{N!}{(\frac{N}{2})!\,(\frac{N}{2})!}$$