热力学统计物理第九次作业

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1

对于极端相对论粒子有:

$$\varepsilon_l = c\frac{2\pi\hbar}{L}\left(n_x^2+n_y^2+n_z^2\right)^{1/2} = \frac{2\pi\hbar c}{V^{1/3}}\left(n_x^2+n_y^2+n_z^2\right)^{1/2}.$$

计算偏微分可得:

$$\frac{\partial\varepsilon_l}{\partial V} = -\frac{1}{3}\frac{2\pi\hbar c}{V^{4/3}}\left(n_x^2+n_y^2+n_z^2\right)^{1/2} = -\frac{1}{3}\frac{\varepsilon_l}{V}.$$

由题目给出的公式可得:

$$p = -\sum_l a_l\frac{\partial\varepsilon_l}{\partial V} = \frac{1}{3}\frac{\sum_l a_l\varepsilon_l}{V}.$$

其中 $\sum_l a_l\varepsilon_l$ 为粒子体系的内能 U。则有:

$$p = \frac{1}{3}\frac{U}{V}.$$

2

当气体以恒定的速度 v_0 沿 z 方向做整体运动时，分子相对质心运动的能量为:

$$\varepsilon = \frac{1}{2m}\left(p_x^2+p_y^2+(p_z-p_0)^2\right).$$

满足经典极限条件的气体分子有:

$$e^{\alpha} = \frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$

在 $dxdydzdp_xdp_ydp_z$ 范围内分子可能的微观状态数为:

$$\omega = \frac{dxdydzdp_xdp_ydp_z}{h^3}.$$

则质心动量在 $dp_xdp_ydp_z$ 范围内的分子数为:

$$N\left(\frac{1}{2\pi mkT}\right)^{3/2} e^{-\frac{1}{2mkT}\left(p_x^2+p_y^2+(p_z-p_0)^2\right)} dp_xdp_ydp_z.$$

则速度对应的概率密度函数为:

$$f_{\vec{V}}(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}\left(v_x^2+v_y^2+(v_z-v_0)^2\right)}.$$

则方均速率为

$$\begin{aligned}
\overline{v^2} &= \iiint v^2 f_{\vec{V}}(v_x, v_y, v_z) dv_xdv_ydv_z \\
&= \left(\frac{m}{2\pi kT}\right)^{1/2} \left(\int v_x^2 e^{-\frac{m}{2kT}v_x^2} dv_x + \int v_y^2 e^{-\frac{m}{2kT}v_y^2} dv_y + \int v_z^2 e^{-\frac{m}{2kT}(v_z-v_0)^2} dv_z\right) \\
&= \left(\frac{m}{2\pi kT}\right)^{1/2} \times \left[2\sqrt{\frac{2\pi k^3T^3}{m^3}} + \left(\sqrt{\frac{2\pi k^3T^3}{m^3}} + v_0^2\sqrt{\frac{2\pi kT}{m}}\right)\right] \\
&= \frac{3kT}{m} + v_0^2
\end{aligned}$$

则分子的平均平动能量为:

$$\overline{E} = \frac{m}{2}\overline{v^2} = \frac{3}{2}kT + \frac{1}{2}mv_0^2.$$

3

对于一个二维气体，能量表达式为:

$$\varepsilon = \frac{1}{2m}\left(p_x^2 + p_y^2\right).$$

在 $dxdydp_xdp_y$ 区域内，粒子的状态数为:

$$\omega_l = \frac{dxdydp_xdp_y}{h^2}.$$

则该气体的配分函数为:

$$\begin{aligned}
Z_1 &= \sum_l \omega_l e^{-\beta\varepsilon} \\
&= \frac{1}{h^2}\iint dxdy \iint e^{-\frac{\beta}{2m}\left(p_x^2+p_y^2\right)} dp_x dp_y \\
&= \frac{A}{h^2}\int e^{-\frac{\beta}{2m}p_x^2} dp_x \int e^{-\frac{\beta}{2m}p_y^2} dp_y \\
&= \frac{A}{h^2}\frac{2\pi m}{\beta} \\
&= A\left(\frac{h}{\sqrt{2\pi m k_B T}}\right)^{-2}.
\end{aligned}$$

令 $\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}$，则上式可写为:

$$Z_1 = \frac{A}{\lambda_{th}^2}.$$

其中 $\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}$。

4

选取基态能量为 $\varepsilon_1 = 0$，则激发态能量为 $\varepsilon_2 = \Delta$，则配分函数为:

$$Z_{atom} = \sum_l g_l e^{-\beta\varepsilon_l} = g_1 + g_2 e^{-\beta\Delta}.$$

内能为:

$$U = -\frac{\partial}{\partial\beta}\ln Z_{atom} = \frac{g_2\Delta e^{-\beta\Delta}}{g_1 + g_2 e^{-\beta\Delta}}.$$

则原子的热熔为:

$$C = \frac{dQ}{dT} = \frac{dU}{d\beta}\frac{d\beta}{dT} = \frac{-g_1 g_2 \Delta^2 e^{-\beta\Delta}}{\left(g_1 + g_2 e^{-\beta\Delta}\right)^2} \times \frac{-1}{k_B T^2} = \frac{g_1 g_2 \Delta^2 e^{-\beta\Delta}}{k_B T^2 \left(g_1 + g_2 e^{-\beta\Delta}\right)^2}$$

由题意，新的配分函数为:

$$Z = Z_{atom} Z_N = \frac{g_1 + g_2 e^{-\beta\Delta}}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N$$

其中 $\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}}$。
取对数可得:

$$\ln Z = \ln\left(g_1 + g_2 e^{-\beta\Delta}\right) - \ln N! + N\ln V - 3N\ln\left(\frac{h}{\sqrt{2\pi m}}\right) - \frac{3N}{2}\ln\beta.$$

此时内能为:

$$U_1 = -N\frac{\partial}{\partial\beta}\ln Z = \frac{g_2 N\Delta e^{-\beta\Delta}}{g_1 + g_2 e^{-\beta\Delta}} + \frac{3N^2}{2\beta}.$$

则等容热熔为:

$$C = \frac{dU}{dT} = \frac{3k_B N^2}{2} + \frac{g_1 g_2 N\Delta^2 e^{-\beta\Delta}}{k_B T^2\left(g_1 + g_2 e^{-\beta\Delta}\right)^2} = N\left[\frac{3k_B N}{2} + \frac{g_1 g_2 \Delta^2 e^{-\beta\Delta}}{k_B T^2\left(g_1 + g_2 e^{-\beta\Delta}\right)^2}\right].$$