统计力学第九次作业

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10.2

根据式 (10.1.12)

$$\overline{\Delta T \cdot \Delta V} = 0$$

$$\overline{(\Delta T)^2} = \frac{kT^2}{C_V}$$

$$\overline{(\Delta V)^2} = -kT\left(\frac{\partial V}{\partial p}\right)_V$$

展开 ΔS

$$\begin{aligned}
\Delta S &= \left(\frac{\partial S}{\partial T}\right)_v \Delta T + \left(\frac{\partial S}{\partial V}\right)_r \Delta V \\
&= \frac{C_v}{T}\Delta T + \left(\frac{\partial p}{\partial T}\right)_V \Delta V \\
\overline{\Delta T \Delta S} &= \frac{C_v}{T}(\Delta T)^2 + \left(\frac{\partial p}{\partial T}\right)\overline{\Delta T \Delta V} \\
&= \frac{C_v}{T}\frac{kT^2}{C_v} \\
&= kT
\end{aligned}$$

同理

$$\begin{aligned}
\overline{\Delta S \Delta V} &= \frac{C_v}{T}\overline{\Delta T \Delta V} + \left(\frac{\partial p}{\partial T}\right)_v \overline{(\Delta V)} \\
&= \left(\frac{\partial p}{\partial T}\right)_v (-kT)\left(\frac{\partial V}{\partial p}\right)_T \\
&= kT\left(\frac{\partial V}{\partial T}\right)_p
\end{aligned}$$

展开 Δp

$$\Delta p = \left(\frac{\partial p}{\partial T}\right)_v \Delta T + \left(\frac{\partial p}{\partial V}\right)_r \Delta V$$

$$
\begin{aligned}
\overline{\Delta p \Delta V} &= \left(\frac{\partial p}{\partial T}\right) \overline{\Delta T \Delta V} + \left(\frac{\partial p}{\partial V}\right)_r \overline{(\Delta V)^2} \\
&= \left(\frac{\partial p}{\partial V}\right)_r (-kT) \left(\frac{\partial V}{\partial p}\right)_r \\
&= -kT
\end{aligned}
$$

同理

$$
\begin{aligned}
\overline{\Delta p \Delta T} &= \left(\frac{\partial p}{\partial T}\right)_v \overline{(\Delta T)^2} + \left(\frac{\partial p}{\partial V}\right) \frac{\overline{\Delta V \Delta T}}{\Delta V \Delta T} \\
&= \frac{kT^2}{C_V} \left(\frac{\partial p}{\partial T}\right)_V
\end{aligned}
$$

10.3

由于

$$W \propto \mathrm{e}^{\frac{\Delta s(0)}{k}}$$

且可设

$$\Delta S^{(0)} = \Delta S + \Delta S_r$$

在开系中有

$$\Delta S_{\mathrm{r}} = \frac{1}{T} \left(\Delta E_r + p \Delta V_r - \mu \Delta N_{\mathrm{r}}\right)$$

在孤立系统中

$$\Delta E_r = -\Delta E$$

$$\Delta V_r = -\Delta V$$

$$\Delta N_r = -\Delta N$$

即

$$\Delta S_r = -\frac{\Delta E + p \Delta V - \mu \Delta N}{T}$$

代回原式即证

$$W \propto e^{-\frac{\Delta E + p \Delta V - T \Delta S - \mu \Delta N}{kT}}$$

展开 E

$$
\begin{aligned}
E =& \overline{E} + \left(\frac{\partial E}{\partial S}\right)_0 \Delta S + \left(\frac{\partial E}{\partial V}\right)_0 \Delta V + \left(\frac{\partial E}{\partial N}\right)_0 \Delta N + \\
& \frac{1}{2} \left[\left(\frac{\partial^2 E}{\partial S^2}\right)_0 (\Delta S)^2 + \left(\frac{\partial^2 E}{\partial V^2}\right)_0 (\Delta V)^2 + \left(\frac{\partial^2 E}{\partial N^2}\right)_0 (\Delta N)^2 + \right. \\
& \left. 2 \left(\frac{\partial^2 E}{\partial S \partial V}\right)_0 \Delta S \Delta V + 2 \left(\frac{\partial^2 E}{\partial S \partial N}\right)_0 \Delta S \Delta N + 2 \left(\frac{\partial^2 E}{\partial V \partial N}\right)_0 \Delta V \Delta N \right]
\end{aligned}
$$

$$\left(\frac{\partial E}{\partial S}\right)_0 = T$$
$$\left(\frac{\partial E}{\partial V}\right)_0 = -p$$
$$\left(\frac{\partial E}{\partial N}\right)_0 = \mu$$

可得

$$\begin{aligned}
&\Delta E - T\Delta S + p\Delta V - \mu\Delta N \\
=&\frac{1}{2}\Delta S\left[\frac{\partial}{\partial S}\left(\frac{\partial E}{\partial S}\right)_0\Delta S + \frac{\partial}{\partial V}\left(\frac{\partial E}{\partial S}\right)_0\Delta V + \frac{\partial}{\partial N}\left(\frac{\partial E}{\partial S}\right)_0\Delta N\right] + \\
&\frac{1}{2}\Delta V\left[\frac{\partial}{\partial S}\left(\frac{\partial E}{\partial V}\right)_0\Delta S + \frac{\partial}{\partial V}\left(\frac{\partial E}{\partial V}\right)_0\Delta V + \frac{\partial}{\partial N}\left(\frac{\partial E}{\partial V}\right)_0\Delta N\right] + \\
&\frac{1}{2}\Delta N\left[\frac{\partial}{\partial S}\left(\frac{\partial E}{\partial N}\right)_0\Delta S + \frac{\partial}{\partial V}\left(\frac{\partial E}{\partial N}\right)_0\Delta V + \frac{\partial}{\partial N}\left(\frac{\partial E}{\partial N}\right)_0\Delta N\right] \\
=&\frac{1}{2}(\Delta S\Delta T - \Delta p\Delta V + \Delta N\Delta\mu)
\end{aligned}$$

与高斯分布标准形式比较可得

$$\overline{(\Delta N)^2} = kT\left(\frac{\partial N}{\partial\mu}\right)_{T,V}$$

同理有

$$\begin{aligned}
\overline{\Delta\mu\Delta N} &= \left(\frac{\partial\mu}{\partial N}\right)_{T,v}\overline{(\Delta N)^2} \\
&= \left(\frac{\partial\mu}{\partial N}\right)_{r,v}\cdot kT\left(\frac{\partial N}{\partial\mu}\right)_{T,v} \\
&= kT
\end{aligned}$$

当 T, V 不变,

$$\Delta N = \left(\frac{\partial N}{\partial\mu}\right)_{r,V}\Delta\mu$$

因此

$$\overline{(\Delta\mu)^2} = kT\left(\frac{\partial\mu}{\partial N}\right)_{T,V}$$

10.8

一维布朗运动中

$$\overline{[x_i - x_i(0)]^2} = \frac{2kT}{m\gamma}t$$

根据题中所给条件, 三个方向互不相关, 因此对于三维情况

$$\overline{[\boldsymbol{x} - \boldsymbol{x}(0)]^2} = \sum_{i=1}^{3}\overline{[x_i - x_i(0)]^2} = \frac{6kT}{m\gamma}t$$

10.9

此时朗之万方程为

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = -\alpha v + qE + F(t)$$

取平均, 注意到

$$\frac{\mathrm{d}\overline{v}}{\mathrm{d}t} = 0$$

$$\overline{F}(t) = 0$$

$$\overline{v} = \frac{qE}{\alpha}$$

令 $\mu = \frac{\overline{v}}{E}$,

$$\mu = \frac{q}{\alpha}$$

$$D = \frac{kT}{\alpha}$$

比较可得

$$\frac{\mu}{D} = \frac{q}{kT}$$