第九章　涨落

9.1　涨落的广义系综理论

9.2　涨落的准热力学理论

9.1 涨落的广义系综理论

- 广延量：$X_1, X_2, \cdots$；对应的强度量 $y_1, y_2, \cdots$

$$S = S(X_1, X_2, \cdots) \qquad dS = y_1 dX_1 + y_2 dX_2 + \cdots$$

- 微正则系综：系统 + 环境
  系统和环境的广延量总量守恒，强度量相同

$$|T\rangle = |s \otimes R\rangle \qquad \hat{X}_i|T\rangle = \hat{X}_i|s \otimes R\rangle = [X_i(s) + X_i^R(R)]|s \otimes R\rangle$$

$$S_T(\{X_i + X_i^R\}) = k_B \ln \Omega_T(\{X_i + X_i^R\})$$

$$p_s = \sum_{|R\rangle} \frac{1}{\Omega_T} = \frac{\Omega_R(\{X_i^R\})}{\Omega_T(\{X_i^T\})} = \frac{1}{\Omega_T} e^{S_R(\{X_i^T - X_i(s)\})/k_B}$$

$$= \frac{1}{\Omega_T} e^{S_R[\{\overline{X}_i^R - (X_i(s) - \overline{X}_i)]/k_B} = \frac{1}{\Omega_T} \exp\left\{\frac{\overline{S}_R}{k_B} - \frac{X_i(s) - \overline{X}_i}{k_B}\left(\frac{\partial \overline{S}_R}{\partial \overline{X}_i^R}\right) + \cdots\right.$$

$$= \frac{1}{\Omega_T} e^{\overline{S}_R/k_B - \sum_i y_i (X_i - \overline{X}_i)/k_B} = \frac{1}{\Xi} e^{-\sum_i y_i X_i(s)/k_B}$$

$$\Xi(y_1, y_2, \cdots) = \sum_s e^{-\sum_i y_i X_i(s)/k_B}$$

广义配分函数

广延量的平均值和涨落

$$\overline{X_l} = \sum_s X_l(s) p_s = \frac{1}{\Xi} \sum_s X_l(s) e^{-\sum_i y_i X_i(s)/k_B}$$

$$= \frac{1}{\Xi} \sum_s (-k_B) \frac{\partial}{\partial y_l} e^{-\sum_i y_i X_i(s)/k_B} = \frac{1}{\Xi} (-k_B) \frac{\partial}{\partial y_l} \sum_s e^{-\sum_i y_i X_i(s)/k_B}$$

$$= -k_B \frac{1}{\Xi} \frac{\partial \Xi}{\partial y_l} = -k_B \left(\frac{\partial \ln \Xi}{\partial y_l} \right)_{\{y_{i \neq l}\}}$$

$$\overline{X_l X_m} = \frac{1}{\Xi} \sum_s X_l(s) X_m(s) e^{\sum_i y_i X_i(s)/k_B} = k_B^2 \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial y_l \partial y_m}$$

$$= k_B^2 \frac{\partial^2 \ln \Xi}{\partial y_l \partial y_m} + k_B^2 \left(\frac{\partial \ln \Xi}{\partial y_l} \right) \left(\frac{\partial \ln \Xi}{\partial y_m} \right) = k_B^2 \frac{\partial^2 \ln \Xi}{\partial y_l \partial y_m} + \overline{X_l}\, \overline{X_m}$$

$$\overline{\Delta X_l \Delta X_m} = \overline{(X_l - \overline{X_l})(X_m - \overline{X_m})} = \overline{X_l X_m} - \overline{X_l}\, \overline{X_m} = k_B^2 \frac{\partial^2 \ln \Xi}{\partial y_l \partial y_m}$$

$$= -k_B \left(\frac{\partial \overline{X_l}}{\partial y_m} \right)_{\{y_i \neq m\}} = -k_B \left(\frac{\partial \overline{X_m}}{\partial y_l} \right)_{\{y_i \neq l\}}$$

强度量的涨落

- ☞ 按照定义，广义系综的强度量不发生任何变化，无涨落
- ☞ 实际中，强度量的测量依赖于（局部的）广延量

$$y_i = y_i(X_1, X_2, \cdots)$$

- 从这个意义上，当 $\{X_i\}$ 发生涨落时，$\{y_i\}$ 也有涨落

$$\Delta y_i = y_i(\{X_l\}) - y_i(\{\overline{X_l}\}) = y_i(\{\overline{X_l} + \Delta X_l\}) - y_i(\{\overline{X_l}\})$$
$$= \sum_l \left(\frac{\partial y_i}{\partial X_l}\right) \Delta X_l$$

$$\overline{\Delta y_i \Delta X_j} = \overline{\sum_l \left(\frac{\partial y_i}{\partial X_l}\right) \Delta X_l \Delta X_j} = \sum_l \left(\frac{\partial y_i}{\partial X_l}\right) \overline{\Delta X_l \Delta X_j}$$
$$= -\sum_l \left(\frac{\partial y_i}{\partial X_l}\right)_{\{X_{m\neq l}\}} k_B \left(\frac{\partial X_l}{\partial y_j}\right)_{\{y_{k\neq j}\}} = -k_B \left(\frac{\partial y_i}{\partial y_j}\right)_{\{y_{k\neq j}\}} = -k_B \delta_{ij}$$

强度量的涨落

- 强度量的涨落

$$\overline{\Delta y_i \Delta y_j} = \overline{\Delta y_i \sum_m \left(\frac{\partial y_j}{\partial X_m}\right) \Delta X_m} = \sum_m \left(\frac{\partial y_j}{\partial X_m}\right) \overline{\Delta y_i \Delta X_m}$$

$$= -k_B \sum_m \left(\frac{\partial y_j}{\partial X_m}\right) \delta_{im} = -k_B \left(\frac{\partial y_j}{\partial X_i}\right)_{X_{k \neq i}} = -k_B \left(\frac{\partial y_i}{\partial X_j}\right)_{X_{k \neq j}}$$

其它物理量的涨落和关联

$$f = f(\{X_l\}) \qquad \overline{f} = f(\{\overline{X_l}\}) = f(\{\overline{y_l}\})$$

$$\Delta f = f(\{X_l\}) - \overline{f} = f(\{\overline{X}_l + \Delta X_l\}) - \overline{f}$$

$$= \sum_l \left(\frac{\partial f}{\partial X_l}\right) \Delta X_l$$

$$= \sum_l \left(\frac{\partial f}{\partial X_l}\right) \sum_m \left(\frac{\partial X_l}{\partial y_m}\right) \Delta y_m = \sum_m \left[\sum_l \left(\frac{\partial f}{\partial X_l}\right)\left(\frac{\partial X_l}{\partial y_m}\right)\right] \Delta y_m$$

$$= \sum_m \left(\frac{\partial f}{\partial y_m}\right) \Delta y_m$$

$$\Delta g = \sum_l \left(\frac{\partial g}{\partial X_l}\right) \Delta X_l = \sum_m \left(\frac{\partial g}{\partial y_m}\right) \Delta y_m$$

其它物理量的涨落和关联

$$\overline{\Delta f \Delta g} = \sum_{lm} \left(\frac{\partial f}{\partial X_l}\right)\left(\frac{\partial g}{\partial y_m}\right)\overline{\Delta X_l \Delta y_m} = -\sum_{lm} \left(\frac{\partial f}{\partial X_l}\right)\left(\frac{\partial g}{\partial y_m}\right) k_B \delta_{lm}$$

$$= -k_B \sum_{l} \left(\frac{\partial f}{\partial X_l}\right)\left(\frac{\partial g}{\partial y_l}\right) = -k_B \sum_{l} \left(\frac{\partial f}{\partial y_l}\right)\left(\frac{\partial g}{\partial X_l}\right)$$

$$= -k_B \sum_{l} \sum_{m} \left(\frac{\partial f}{\partial X_l}\right)\left(\frac{\partial g}{\partial X_m}\right)\left(\frac{\partial X_l}{\partial y_l}\right)$$

$$= -k_B \sum_{l} \sum_{m} \left(\frac{\partial f}{\partial y_l}\right)\left(\frac{\partial g}{\partial y_m}\right)\left(\frac{\partial y_m}{\partial X_l}\right)$$

例子

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

- 保持 T, N, V 不变；正则系综结果

$$\overline{\Delta E^2} = -k_B \left(\frac{\partial U}{\partial[1/T]}\right)_{NV} = k_B T^2 C_V$$

- 保持 $T, \mu/T, V$ 不变；巨正则系综结果

$$\overline{\Delta N^2} = -k_B \left(\frac{\partial N}{\partial[-\mu/T]}\right)_{T,V} = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{TV} = \frac{k_B T N^2 \kappa_T}{V}$$

$$\overline{\Delta E^2} = -k_B \left(\frac{\partial U}{\partial[1/T]}\right)_{\mu/T,V} = k_B T^2 C_V + \left(\frac{\partial U}{\partial N}\right)_{TV}^2 \overline{\Delta N^2}$$

$$\overline{\Delta E \Delta N} = -k_B \left(\frac{\partial U}{\partial[-\mu/T]}\right)_{TV} = k_B T \left(\frac{\partial U}{\partial \mu}\right)_{TV}$$

$$= k_B T \left(\frac{\partial U}{\partial N}\right)_{TV} \left(\frac{\partial N}{\partial \mu}\right)_{TV} = \left(\frac{\partial U}{\partial N}\right)_{TV} \overline{\Delta N^2}$$

例子

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

- 保持 $T, p/T, N$ 不变：广义系综

$$\overline{\Delta V^2} = -k_B\left(\frac{\partial V}{\partial [p/T]}\right)_{1/T,N} = -k_B T\left(\frac{\partial V}{\partial p}\right)_{TN} = k_B T V \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_{TN}$$

$$= k_B T V \kappa_T$$

和巨正则系综里的 ΔN^2 有关：$V = Nv$，$v = V/N$ 为摩尔体积

$$\overline{\Delta V^2} = \overline{\Delta N^2 v^2} = \overline{\Delta N^2} v^2 = \frac{k_B T N^2}{V}\kappa_T \frac{V^2}{N^2} = k_B T V \kappa_T$$

$$\overline{\Delta U \Delta V} = -k_B\left(\frac{\partial U}{\partial p/T}\right)_{T,N} = -k_B T\left(\frac{\partial U}{\partial p}\right)_T = -k_B T\left(\frac{\partial (G + TS - pV)}{\partial p}\right)$$

$$= k_B T\left[T\left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial p}\right)_T\right]$$

温度涨落

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

$$\overline{\Delta(\frac{1}{T})^2} = \overline{\left(-\frac{\Delta T}{T^2}\right)^2} = -k_B\frac{\partial 1/T}{\partial U} = \frac{k_B}{T^2}\frac{\partial T}{\partial U} = \frac{k_B}{T^2}/\frac{\partial U}{\partial T}$$

$$\overline{\Delta T^2} = \frac{k_B T^2}{C_V}$$

$$-k_B = \overline{\Delta(1/T)\Delta U} = \overline{(-\Delta T/T^2)\Delta U}$$

$$\overline{\Delta T \Delta U} = k_B T^2$$

$$0 = \overline{\Delta(1/T)\Delta V} = -\overline{\Delta T \Delta V/T^2}$$

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

9.2 涨落的准热力学理论

$$p(\{X_i\}) = \sum_{\{s|X_i(s)=X_i\}} p_s = \sum_{\{s|X_i(s)=X_i\}} \frac{1}{\Xi} e^{-\sum_i y_i X_i(s)/k_B}$$

$$= \frac{\Omega(\{X_i\})}{\Xi} e^{-\sum_i y_i X_i/k_B} = \frac{1}{\Xi} e^{[S(\{X_i\})-\sum_i y_i X_i]/k_B}$$

$$= \frac{1}{\Xi} \exp\{S(\{\overline{X_i} + \Delta X_i\})/k_B - \sum_i y_i(\overline{X_i} + \Delta X_i)/k_B\}$$

$$= e^{(-k_B \ln \Xi + \overline{S} - \sum_i y_i \overline{X}_i)/k_B} \exp\left\{\frac{1}{2k_B} \sum_{ij} \frac{\partial^2 S}{\partial X_i \partial X_j} \Delta X_i \Delta X_j + \cdots\right\}$$

$$p(\{\Delta X_i\}) = \frac{1}{C} \exp\left\{\frac{1}{2k_B} \sum_{ij} \frac{\partial^2 S}{\partial X_i \partial X_j} \Delta X_i \Delta X_j\right\}$$

高斯分布

$$= \frac{1}{C} \exp\left\{\frac{1}{2k_B} \left(\frac{\partial y_j}{\partial X_i}\right) \Delta X_i \Delta X_j\right\} = \frac{1}{C} \exp\{\Delta X^T \mathcal{A} \Delta X\}$$

关联

$$p(\{\Delta X_i\}) = \frac{1}{C}\exp\{-\Delta X^T \mathcal{A} \Delta X\}$$

$$\Delta X = \begin{pmatrix} \Delta X_1 \\ \Delta X_2 \\ \vdots \end{pmatrix} \qquad \mathcal{A} = \frac{-1}{2k_B}\begin{pmatrix} \left(\frac{\partial y_1}{\partial X_1}\right) & \left(\frac{\partial y_2}{\partial X_1}\right) & \cdots \\ \left(\frac{\partial y_1}{\partial X_2}\right) & \left(\frac{\partial y_2}{\partial X_2}\right) & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \qquad \mathcal{A}_{ij} = \frac{-1}{2k_B}\left(\frac{\partial y_j}{\partial X_i}\right)$$

$$\overline{\Delta X_i \Delta X_j} = \frac{\int_{-\infty}^{\infty} \Delta X_i \Delta X_j p(\{\Delta X_l\}) d\Delta X}{\int_{-\infty}^{\infty} p(\{\Delta X_l\}) d\Delta X} = \frac{\int_{-\infty}^{\infty} \Delta X_i \Delta X_j e^{-\Delta X^T \mathcal{A} \Delta X} d\Delta X}{\int_{-\infty}^{\infty} e^{-\Delta X^T \mathcal{A} \Delta X} d\Delta X} =?$$

$$\mathcal{A}_{ij} = -k_B\left(\frac{\partial y_j}{\partial X_i}\right) = -k_B\left(\frac{\partial y_i}{\partial X_j}\right) = \mathcal{A}_{ji} \qquad dS = \sum_i y_i dX_i$$

$$U\mathcal{A}U^T = A = diag\{A_1, A_2, \cdots, A_i, \cdots\} \qquad \boxed{UU^T = U^T U = I}$$

$$\Delta X' = U\Delta X \qquad \Delta X_i' = U_{ij}\Delta X_j$$

$$\Delta X = U^T \Delta X' \qquad \Delta X_i = (U^T)_{ij}\Delta X_j' = U_{ji}\Delta X_j'$$

$$d\Delta X = |U^T| d\Delta X' = d\Delta X'$$

关联

$$\overline{\Delta X_i'\Delta X_j'} = \frac{\int_{-\infty}^{\infty} \Delta X_i'\Delta X_j' e^{\sum_l A_l \Delta X_l'^2} \boxed{= e^{-\sum_l \frac{\Delta X_l'^2}{2(2A_l)^{-1}}}} d\Delta X'}{\int_{-\infty}^{\infty} e^{-\sum_l A_l \Delta X_l'^2} d\Delta X'} = \frac{-1}{2A_i}\delta_{ij}$$

$$\overline{\Delta X_i \Delta X_j} = \overline{\sum_{lm} U_{li} U_{mj} \Delta X_l' \Delta X_m'} = -\frac{1}{2}\sum_{lm} U_{li} U_{mj} \frac{1}{A_l}\delta_{lm}$$

$$= -\frac{1}{2}\sum_l (U^T)_{il} A_l^{-1} U_{lj} = -\frac{1}{2}(U^T A U)_{ij}^{-1} = -\frac{1}{2}(\mathcal{A}^{-1})_{ij} = -k_B\left(\frac{\partial X_i}{\partial y_j}\right)$$

$$\mathcal{A} = \frac{-1}{2k_B}\begin{pmatrix} \left(\frac{\partial y_1}{\partial X_1}\right) & \left(\frac{\partial y_2}{\partial X_1}\right) & \cdots \\ \left(\frac{\partial y_1}{\partial X_2}\right) & \left(\frac{\partial y_2}{\partial X_2}\right) & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \qquad \mathcal{A}_{ij} = \frac{-1}{2k_B}\left(\frac{\partial y_j}{\partial X_i}\right)$$

$$\mathcal{A}^{-1} = -2k_B\begin{pmatrix} \left(\frac{\partial X_1}{\partial y_1}\right) & \left(\frac{\partial X_2}{\partial y_1}\right) & \cdots \\ \left(\frac{\partial X_1}{\partial y_2}\right) & \left(\frac{\partial X_2}{\partial y_2}\right) & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \qquad \mathcal{A}_{ij}^{-1} = -2k_B\left(\frac{\partial X_i}{\partial y_j}\right) = -2k_B\left(\frac{\partial X_j}{\partial y_i}\right)$$

Einstein 方法

$$p(\{\Delta X\}) = \frac{1}{C}\exp\left\{\frac{1}{2k_B}\sum_{ij}\left(\frac{\partial y_i}{\partial X_j}\right)\Delta X_i \Delta X_j\right\}$$

$$= \frac{1}{C}\exp\left\{\frac{1}{2k_B}\sum_i \Delta X_i \sum_j \left(\frac{\partial y_i}{\partial X_j}\right)\Delta X_j\right\} = \frac{1}{C}\exp\left\{\frac{1}{2k_B}\sum_i \Delta X_i \Delta y_i\right\}$$

$$dU = đQ - đW = TdS - \sum_i \tilde{y}_i dX_i \Rightarrow dS = \frac{dU}{T} + \sum_i \frac{\tilde{y}_i}{T} dX_i$$

$$p \propto \exp\left\{\frac{1}{2k_B}\left[\Delta U \Delta\left(\frac{1}{T}\right) + \sum_i \Delta X_i \Delta\left(\frac{\tilde{y}_i}{T}\right)\right]\right\}$$

$$\propto \exp\left\{\frac{1}{2k_B}\left[-\frac{\Delta U \Delta T}{T^2} - \sum_i \frac{\tilde{y}_i \Delta X_i \Delta T}{T^2} + \sum_i \frac{\Delta X_i \Delta \tilde{y}_i}{T}\right]\right\}$$

$$\propto \exp\left\{\frac{1}{2k_B}\left[-\frac{\Delta U + \sum_i \tilde{y}_i \Delta X_i}{T}\frac{\Delta T}{T} + \sum_i \frac{\Delta X_i \Delta \tilde{y}_i}{T}\right]\right\}$$

$$\propto \exp\left\{\frac{1}{2k_B}\left[-\frac{\Delta S \Delta T}{T} + \sum_i \frac{\Delta X_i \Delta \tilde{y}_i}{T}\right]\right\} \propto \exp\left\{\frac{-\Delta S \Delta T + \sum_i \Delta X_i \Delta \tilde{y}_i}{2k_B T}\right\}$$

Einstein 方法

$$p \propto \exp\left\{\frac{-\Delta S\Delta T + \sum_i \Delta X_i \Delta\tilde{y}_i}{2k_BT}\right\}$$

- 把上面计算出来的几率当成是一般的表达式
- 计算任意变量组合的涨落或者关联的时候，取其为自变量，得到相应的几率分布，从而得到涨落或关联

例如：保持 N 不变，求 T, V 的涨落和关联

$$p(\Delta T, \Delta V) \propto e^{\frac{-\Delta S\Delta T + \Delta p\Delta V}{2k_BT}}$$

$$\boxed{dF = -SdT - pdV}$$

$$\propto \exp\left\{\frac{1}{2k_BT}\left[-\left(\frac{\partial S}{\partial T}\right)_V \Delta T^2 - \left(\frac{\partial S}{\partial V}\right)_T \Delta T\Delta V + \left(\frac{\partial p}{\partial T}\right)_V \Delta T\Delta V + \left(\frac{\partial p}{\partial V}\right)_T \Delta V^2\right]\right.$$

$$\propto \exp\left\{\frac{1}{2k_BT}\left[-\frac{C_V}{T}\Delta T^2 - \frac{1}{V\frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T}\Delta V^2\right]\right\}$$

$$\propto \exp\left\{-\frac{\Delta T^2}{2k_BT^2/C_V} - \frac{\Delta V^2}{2k_BT\kappa_TV}\right\}$$

Einstein 方法

例如：保持 N 不变，求 T,V 的涨落和关联

$$p(\Delta T,\Delta V)\propto \exp\left\{-\frac{\Delta T^2}{2k_BT^2/C_V}-\frac{\Delta V^2}{2k_BT\kappa_T V}\right\}$$

$$\Rightarrow \overline{\Delta T^2}=\frac{k_BT^2}{C_V}\propto\frac{1}{N}$$

$$\Rightarrow \overline{\Delta V^2}=k_BTV\propto N$$

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

涨落的应用：Rayleigh 散射强度

光强为 I_0 的入射光被体积为 V 的介质散射之后的总散射光强

$$\frac{\epsilon-1}{\epsilon+2}=A\rho$$

Clausius-Mossotti 关系，A 为常数，$\rho=N/V$

$$\frac{I_{scatter}}{I_0}\propto\frac{V^2(\Delta\epsilon)^2}{\lambda^4}$$

$$\frac{3\Delta\epsilon}{(\epsilon+2)^2}=A\Delta\rho\Rightarrow(\Delta\epsilon)=\frac{(\epsilon+2)^2}{3}A(\Delta\rho)$$

$$(\Delta\epsilon)^2=\frac{(\epsilon+2)^4}{9}A^2(\Delta\rho)^2$$

$$(\Delta\rho)^2=\frac{\Delta N^2}{V^2}=\frac{k_BT\kappa_TN^2}{V}\frac{1}{V^2}=\frac{k_BT\kappa_T\rho^2}{V}$$

$$(\Delta\rho)^2=(-\frac{N}{V^2}\Delta V)^2=\frac{N^2}{V^4}(\Delta V)^2=\frac{N^2}{V^4}k_BT\kappa_TV=\frac{k_BT\kappa_T\rho^2}{V}$$

$$\frac{I_{scatter}}{I_0}\propto\frac{V^2(\Delta\epsilon)^2}{\lambda^4}=\frac{k_BT\kappa_TV}{9\lambda^4}(\epsilon+2)^4A^2\rho^2=\frac{k_BT\kappa_TV}{9\lambda^4}(\epsilon+2)^4\frac{(\epsilon-1)^2}{(\epsilon+2)^2}$$

$$=k_BT\kappa_TV(\epsilon-1)^2(\epsilon+2)^2/(9\lambda^4)$$

气体/流体密度涨落导致光散射。1910 年 Einstein 得到此结果，解释了临界乳光现象。在临界点附近 $\kappa_T\Rightarrow\infty$，导致光受到极大的散射。