

7.C. Einstein Fluctuation Theory

7.C.1. General Discussion

Consider a closed and isolated system with energy E . If the system is ergodic, every microstate of the same energy E will be equally probable. Let $\Gamma(E)$ be the total number of microstates with energy E . The entropy of the system is then given by (7.8) as

$$S = k_B \ln \Gamma(E) \quad (7.17)$$

Usually, the system is described by a set of thermodynamic variables such as U, P, T, \dots , etc. They will be denoted as

$$\mathbf{A} = \{A_p\} = \{A_1, \dots, A_m\} \quad p = 1, \dots, m \quad (7.17a)$$

If we are interested in spatially dependent fluctuations, we can divide the system into n cells and label the thermodynamic variables in the i^{th} cell as

$$\mathbf{A}_i = \{A_{pi}\} = \{A_{1i}, \dots, A_{mi}\} \quad i = 1, \dots, n \quad p = 1, \dots, m \quad (7.17b)$$

Since the set of $\{\mathbf{A}_i; i = 1, \dots, n\}$ can always be relabeled as

$$\mathbf{A} = \{A_j\} = \{A_1, \dots, A_M\} \quad j = 1, \dots, M \quad M = mn \quad (7.17c)$$

there is no need to consider (7.17b) separately.

Let $\Gamma(E, \mathbf{A})$ be the number of microstates satisfying the parameters $\{E, \mathbf{A}\}$. Since the system is ergodic, the probability that it is in one of these microstates is

$$P(E, \mathbf{A}) = \frac{\Gamma(E, \mathbf{A})}{\Gamma(E)} \quad (7.18)$$

Meanwhile, the analog of (7.17) gives

$$S(E, \mathbf{A}) = k_B \ln \Gamma(E, \mathbf{A}) \quad (7.19)$$

Combining (7.18 & 9) gives

$$P(E, \mathbf{A}) = \frac{1}{\Gamma(E)} \exp \left[\frac{1}{k_B} S(E, \mathbf{A}) \right] \quad (7.20)$$

Let the equilibrium values of the parameters be denoted by a superscript 0. Fluctuations of \mathbf{A} are defined as

$$\boldsymbol{\alpha} = \mathbf{A} - \mathbf{A}^0 \quad (7.21)$$

Since S is a maximum when the system is in equilibrium,

$$\left(\frac{\partial S}{\partial \mathbf{A}} \right)^0 = 0$$

and

$$\mathbf{g} = \{g_{ij}\} = \left\{ - \left(\frac{\partial^2 S}{\partial A_i \partial A_j} \right)^0 \right\} \text{ is a positive definite matrix} \quad (7.23)$$

Taylor expansion of S about the equilibrium takes the form

$$S(E, \mathbf{A}) = S(E, \mathbf{A}^0) - \frac{1}{2} \boldsymbol{\alpha}^T \cdot \mathbf{g} \cdot \boldsymbol{\alpha} + O(\boldsymbol{\alpha}^3) \quad (7.22)$$

The Einstein theory deals only with fluctuations so small that all terms of $O(\boldsymbol{\alpha}^3)$ can be neglected.

Putting (7.22) into (7.20) then gives

$$P(\boldsymbol{\alpha}) = \frac{1}{\Gamma(E)} \exp \left[\frac{1}{k_B} S(E, \mathbf{A}^0) \right] \times \exp \left[- \frac{1}{2k_B} \boldsymbol{\alpha}^T \cdot \mathbf{g} \cdot \boldsymbol{\alpha} \right] \quad (7.22a)$$

The prefactor can be treated as a constant and determined by the normalization condition

$$\int_{-\infty}^{\infty} d\alpha_1 \dots \int_{-\infty}^{\infty} d\alpha_M P(\boldsymbol{\alpha}) = 1 \quad (7.25)$$

Using the results of Ex.4.9 of §4.D.4, we have

$$\begin{aligned} P(\boldsymbol{\alpha}) &= \sqrt{\frac{\det \mathbf{g}}{(2\pi k_B)^M}} \exp\left(-\frac{1}{2k_B} \boldsymbol{\alpha}^T \cdot \mathbf{g} \cdot \boldsymbol{\alpha}\right) \\ &= \sqrt{\frac{\det \mathbf{g}}{(2\pi k_B)^M}} \exp\left(-\frac{1}{2k_B} \sum_{i,j=1}^M \alpha_i g_{ij} \alpha_j\right) \end{aligned} \quad (7.24)$$

In order to avoid dealing with complex quantities, we define a “characteristic function” by

$$\begin{aligned} l(\mathbf{h}) &= \int_{-\infty}^{\infty} d\alpha_1 \dots \int_{-\infty}^{\infty} d\alpha_M e^{\mathbf{h}^T \cdot \boldsymbol{\alpha}} P(\boldsymbol{\alpha}) \quad [l(\mathbf{h}) = f(\mathbf{k}) |_{\mathbf{k} \rightarrow -i\mathbf{h}}] \\ &= \exp\left(\frac{1}{2} k_B \mathbf{h}^T \cdot \mathbf{g}^{-1} \cdot \mathbf{h}\right) \quad [\text{See Ex.4.9.}] \end{aligned} \quad (7.26)$$

$$= \exp\left(\frac{1}{2} k_B \sum_{ij} h_i g_{ij}^{-1} h_j\right) \quad (7.26a)$$

Note that $l(\mathbf{h})$ is not a Laplace transform of $P(\boldsymbol{\alpha})$ since every integral covers the entire real line, instead of just the negative half. This is possible because the Gaussian decays much faster than the rising exponential.

Using the modified version of (4.17), we have

$$\begin{aligned} \langle \alpha_i \rangle &= \left. \frac{\partial l(\mathbf{h})}{\partial h_i} \right|_{\mathbf{h}=0} \\ &= \left. \frac{\partial}{\partial h_i} \exp\left(\frac{1}{2} k_B \sum_{mn} h_m g_{mn}^{-1} h_n\right) \right|_{\mathbf{h}=0} \\ &= \left. \frac{1}{2} k_B \sum_{mn} (g_{in}^{-1} h_n + h_m g_{mi}^{-1}) l(\mathbf{h}) \right|_{\mathbf{h}=0} \\ &= k_B \sum_n g_{in}^{-1} h_n l(\mathbf{h}) \Big|_{\mathbf{h}=0} \quad [g_{mn}^{-1} = g_{nm}^{-1} \text{ See (7.23). }] \\ &= 0 \end{aligned}$$

Similarly,

$$\begin{aligned} \langle \alpha_i \alpha_j \rangle &= \left. \frac{\partial^2 l(\mathbf{h})}{\partial h_i \partial h_j} \right|_{\mathbf{h}=0} \\ &= \left. \frac{\partial^2}{\partial h_i \partial h_j} \exp\left(\frac{1}{2} k_B \sum_{mn} h_m g_{mn}^{-1} h_n\right) \right|_{\mathbf{h}=0} \\ &= \left. \frac{\partial}{\partial h_i} \left[k_B \sum_n g_{jn}^{-1} h_n l(\mathbf{h}) \right] \right|_{\mathbf{h}=0} \\ &= k_B \left[g_{ji}^{-1} + k_B \sum_n g_{jn}^{-1} h_n k_B \sum_m g_{im}^{-1} h_m \right] l(\mathbf{h}) \Big|_{\mathbf{h}=0} \\ &= k_B g_{ij}^{-1} \end{aligned} \quad (7.27)$$

In matrix form,

$$\langle \boldsymbol{\alpha} \rangle = 0 \quad (7.27a)$$

$$\langle \boldsymbol{\alpha} \boldsymbol{\alpha}^T \rangle = k_B \mathbf{g}^{-1} \quad (7.27b)$$

As shown in Ex.4.9, all moments of odd order vanish, while moments of even order can be expressed as a combination of products of $\langle \boldsymbol{\alpha} \boldsymbol{\alpha}^T \rangle$, as described by the Wick’s theorem.

7.C.2. Fluid Systems

Consider now a closed and isolated fluid of extensive parameters $\{V_T, S_T, N_T, M_T; E_T\}$, where the subscript T is used to denote quantities belonging to the entire system. [M_T is the total mass.]

In the study of spatial correlations of fluctuations, we divide the system into ν cells that are of equal size $V_0 = \frac{V_T}{\nu}$ at equilibrium. As usual, the subscript 0 is used to describe equilibrium values.

The i^{th} cell is described by the extensive parameters

$$\{V_i, S_i, N_i, M_i; E_i\} \quad i = 1, \dots, \nu.$$

and the intensive parameters conjugate to (some of) them

$$\{P_i, T_i, \mu_i', \tilde{\mu}_i\}$$

where μ' & $\tilde{\mu}$ are the chemical potential per particle and per unit mass, respectively. Obviously, only one pair among (μ', N) & $(\tilde{\mu}, M)$ is sufficient to describe the system.

Let the partitions to be flexible, heat conducting, and porous so that work, heat, and particle can be freely exchanged between cells, respectively. The equilibrium state is then characterized by

$$\{P_i, T_i, \mu_i', \tilde{\mu}_i; V_i\} = \{P_0, T_0, \mu_0', \tilde{\mu}_0; V_0\} \quad \forall i$$

According to (2.171) of §2.H.2,

$$\Delta S_T = -\frac{1}{2T_0} \sum_{i=1}^{\nu} (\Delta T_i \Delta S_i - \Delta P_i \Delta V_i + \Delta \tilde{\mu}_i \Delta M_i) \quad (7.28)$$

$$= -\frac{1}{2} \boldsymbol{\alpha}^T \cdot \mathbf{g} \cdot \boldsymbol{\alpha} \quad [(7.22) \text{ used.}] \quad (7.28a)$$

where $\boldsymbol{\alpha}$ can be any three (one from each conjugate pair) of the fluctuations in (7.28).

Putting this into (7.24) gives,

$$P(\boldsymbol{\alpha}) = \sqrt{\frac{\det \mathbf{g}}{(2\pi k_B)^{n\nu}}} \exp\left[-\frac{1}{2k_B T_0} \sum_{i=1}^{\nu} (\Delta T_i \Delta S_i - \Delta P_i \Delta V_i + \Delta \tilde{\mu}_i \Delta M_i)\right] \quad (7.29)$$

where n is the number of independent fluctuations in each cell, i.e., \mathbf{g} is a $(n\nu) \times (n\nu)$ matrix.

Owing to the special status of V_i , it is common practice to remove it by replacing every extensive variable X with the corresponding density $x = \frac{X}{V}$. In particular, $\rho = \frac{M}{V}$ is the mass density. The Gibbs-

Duhem equation [see (2.62) of §2.E]

$$S dT - V dP + M d\tilde{\mu} = 0$$

becomes

$$s dT - dP + \rho d\tilde{\mu} = 0 \quad (7.29a)$$

The Helmholtz energy

$$dA = -S dT - P dV + \tilde{\mu} dM$$

gives

$$\begin{aligned} d(Va) &= V da + a dV \\ &= -Vs dT - PdV + \tilde{\mu}(Vd\rho + \rho dV) \end{aligned}$$

$$\rightarrow V(da + s dT - \tilde{\mu} d\rho) + (a + P - \rho \tilde{\mu}) dV = 0$$

$$\therefore da = -s dT + \tilde{\mu} d\rho \quad [(2.95) \text{ of } \S 2.F.3 \text{ used.}]$$

$$\rightarrow -\left(\frac{\partial s}{\partial \rho}\right)_T = \left(\frac{\partial \tilde{\mu}}{\partial T}\right)_\rho = \frac{\partial^2 a}{\partial \rho \partial T} \quad (7.29b)$$

Choosing T & ρ as the independent variables, we have

$$\begin{aligned}
 \Delta T \Delta S - \Delta P \Delta V + \Delta \tilde{\mu} \Delta M &= \Delta T \Delta (s V) - \Delta P \Delta V + \Delta \tilde{\mu} \Delta (\rho V) \\
 &= V \Delta T \Delta s + s \Delta T \Delta V - \Delta P \Delta V + V \Delta \tilde{\mu} \Delta \rho + \rho \Delta \tilde{\mu} \Delta V \\
 &= V(\Delta T \Delta s + \Delta \tilde{\mu} \Delta \rho) + (s \Delta T - \Delta P + \rho \Delta \tilde{\mu}) \Delta V \\
 &= V(\Delta T \Delta s + \Delta \tilde{\mu} \Delta \rho) \quad [(7.29a) \text{ used.}] \quad (7.30a)
 \end{aligned}$$

Using

$$\begin{aligned}
 \Delta s &= \left(\frac{\partial s}{\partial T} \right)_\rho \Delta T + \left(\frac{\partial s}{\partial \rho} \right)_T \Delta \rho \\
 &= \frac{c_\rho}{T} \Delta T - \left(\frac{\partial \tilde{\mu}}{\partial T} \right)_\rho \Delta \rho \quad [(7.29b) \text{ used.}]
 \end{aligned}$$

where

$$c_\rho = T \left(\frac{\partial s}{\partial T} \right)_\rho = \text{heat capacity per unit volume at constant mass density}$$

and

$$\begin{aligned}
 \Delta \tilde{\mu} &= \left(\frac{\partial \tilde{\mu}}{\partial T} \right)_\rho \Delta T + \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T \Delta \rho \\
 &= \left(\frac{\partial \tilde{\mu}}{\partial T} \right)_\rho \Delta T + \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T \Delta \rho
 \end{aligned}$$

(7.30a) becomes

$$\Delta T \Delta S - \Delta P \Delta V + \Delta \tilde{\mu} \Delta M = V \left[\frac{c_\rho}{T} (\Delta T)^2 + \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T (\Delta \rho)^2 \right] \quad (7.30)$$

Choosing

$$\boldsymbol{\alpha}^T = (\Delta T_1, \Delta \rho_1, \dots, \Delta T_\nu, \Delta \rho_\nu)$$

we have [see (7.23) & (7.28-a)]

$$g_{ij} = \frac{V_0}{T_0} \begin{cases} \frac{c_\rho^0}{T_0} & \text{if } i = j = \text{odd} \\ \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T^0 & \text{if } i = j = \text{even} \\ 0 & \text{if } i \neq j \end{cases} \quad (7.31)$$

Since \mathbf{g} is diagonal,

$$\begin{aligned}
 \det \mathbf{g} &= \left(\frac{V_0}{T_0} \right)^{2\nu} \left(\frac{c_\rho^0}{T_0} \right)^\nu \left[\left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T^0 \right]^\nu \\
 &= \left(\frac{V_0 c_\rho^0}{T_0^2} \right)^\nu \left[\frac{V_0}{T_0} \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T^0 \right]^\nu \quad (7.31a)
 \end{aligned}$$

and (7.29) becomes

$$P(\boldsymbol{\alpha}) = \sqrt{\frac{\left(\frac{V_0 c_\rho^0}{T_0^2} \right)^\nu \left[\frac{V_0}{T_0} \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T^0 \right]^\nu}{(2\pi k_B)^{2\nu}}} \exp \left\{ -\frac{V_0}{2k_B T_0} \sum_{i=1}^{\nu} \left[\frac{c_\rho^0}{T_0} (\Delta T_i)^2 + \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T^0 (\Delta \rho_i)^2 \right] \right\} \quad (7.32)$$

Since (7.32) is a product of 2ν Gaussians, we have, for all $i, j = 1, \dots, \nu$,

$$\langle \Delta T_i \rangle = \langle \Delta V_i \rangle = 0 \quad (7.36)$$

$$\langle \Delta T_i \Delta V_j \rangle = 0 \quad (7.33)$$

$$\langle (\Delta V_i)^2 \rangle = \frac{k_B T_0}{V_0 \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_T} \quad [(7.27) \text{ used. }] \quad (7.34)$$

$$\langle (\Delta T_i)^2 \rangle = \frac{k_B T_0^2}{V_0 c_p^0} \quad (7.35)$$

Caution: In general, \mathbf{g} is not necessarily diagonal for a pair of fluctuations $(\Delta X, \Delta Y)$.
 In which case, $\langle \Delta X_i \Delta Y_i \rangle \neq 0$ or even $\langle \Delta X_i \Delta Y_j \rangle \neq 0$.
 The latter indicates spatial correlations between fluctuations in different cells.