# Lecture-16: The thermodynamic limit

## 1 Fluctuation-dissipation relations

Until now, we have considered systems in which the energy function is purely a function of the state. Now, we consider systems in which the energy function is parametrized by a real scalar $\lambda$ and hence is of the form $E_\lambda(x)$, for any configuration $x \in \mathcal{X}$.

**Definition 1.1.** We denote the partition function for parametrized energy function $E_\lambda : \mathcal{X} \to \mathbb{R}$ by $Z_\lambda : \mathbb{R}_+ \to \mathbb{R}_+$ defined for all $\beta \in \mathbb{R}_+$ as

$$Z_\lambda(\beta) \triangleq \sum_{x\in\mathcal{X}} e^{-\beta E_\lambda(x)}.$$

Boltzmann distribution for state $x$ with parameter $\lambda$ is denoted as

$$\mu_{\beta,\lambda}(x) \triangleq \frac{e^{\beta E_\lambda(x)}}{Z_\lambda(\beta)},$$

and expected value of an observable $\mathcal{O} : \mathcal{X} \to \mathbb{R}$ under Boltzmann distribution $\mu_{\beta,\lambda}$ as $\langle \mathcal{O} \rangle_\lambda$. For two observables $\mathcal{O}, \mathcal{P} : \mathcal{X} \to \mathbb{R}$, we denote the covariance of $\mathcal{O}, \mathcal{P}$ under the Boltzmann distribution for parameter $\lambda$ as

$$\langle \mathcal{O}; \mathcal{P} \rangle_\lambda \triangleq \langle \mathcal{O}\mathcal{P} \rangle_\lambda - \langle \mathcal{O} \rangle_\lambda \langle \mathcal{P} \rangle_\lambda .$$

**Lemma 1.2.** *Consider an interacting particle system with configuration space $\mathcal{X}$ and parametrized energy function $E_\lambda : \mathcal{X} \to \mathbb{R}$ being a smooth function of parameter $\lambda \in \mathbb{R}$. Then, the following statements are true for a fixed parameter $\lambda_0 \in \mathbb{R}$.*

1. *The energy $E_\lambda(x)$ can be expressed in terms of $E_{\lambda_0}(x)$ as*

$$E_\lambda(x) = E_{\lambda_0}(x) + (\lambda - \lambda_0) \left.\frac{\partial E_\lambda(x)}{\partial \lambda}\right|_{\lambda_0} + \Theta((\lambda - \lambda_0)^2). \tag{1}$$

2. *The partition function $Z_\lambda(\beta)$ can be expressed in terms of partition function $Z_{\lambda_0}(\beta)$ as*

$$Z_\lambda(\beta) = Z_{\lambda_0}(\beta)\Big[1 - \beta(\lambda - \lambda_0) \left\langle \left.\frac{\partial E_\lambda(x)}{\partial \lambda}\right|_{\lambda_0} \right\rangle_{\lambda_0} + \Theta((\lambda - \lambda_0)^2)\Big], \tag{2}$$

3. *Partial derivatives of partition function $Z_\lambda(\beta)$ and free entropy $\Phi_\lambda(\beta)$ evaluated at $\lambda_0$ are*

$$\left.\frac{\partial}{\partial \lambda} Z_\lambda(\beta)\right|_{\lambda_0} = -\beta Z_{\lambda_0}(\beta) \left\langle \left.\frac{\partial E_\lambda}{\partial \lambda}\right|_{\lambda_0} \right\rangle_{\lambda_0}, \qquad \left.\frac{\partial \Phi_\lambda(\beta)}{\partial \lambda}\right|_{\lambda_0} = -\beta \left\langle \left.\frac{\partial E_\lambda}{\partial \lambda}\right|_{\lambda_0} \right\rangle_{\lambda_0}. \tag{3}$$

*Proof.* From the hypothesis, the energy function $E_\lambda$ is a smooth function of parameter $\lambda$.

1. The energy function can be expanded into a Taylor series about a value $\lambda_0$ to obtain (1).
2. Taking exponential on both sides of equation (1), we can expand the following ratio of partition functions as

$$\frac{Z_\lambda(\beta)}{Z_{\lambda_0}(\beta)} = \frac{1}{Z_{\lambda_0}(\beta)} \sum_{x\in\mathcal{X}} \exp\left(-\beta E_{\lambda_0}(x) - \beta(\lambda - \lambda_0) \left.\frac{\partial E_\lambda(x)}{\partial \lambda}\right|_{\lambda_0} + \Theta((\lambda - \lambda_0)^2)\right). \tag{4}$$

Using the Taylor's expansion for the exponential $e^x = 1 + x + \Theta(x^2)$, we obtain

$$e^{-\beta(\lambda-\lambda_0)\left.\frac{\partial E_\lambda(x)}{\partial\lambda}\right|_{\lambda_0}} = 1 - \beta(\lambda-\lambda_0)\left.\frac{\partial E_\lambda(x)}{\partial\lambda}\right|_{\lambda_0} + \Theta((\lambda-\lambda_0)^2). \tag{5}$$

Substituting equation (5) in equation (4), we obtain the result.

3. Taking partial derivative of partition function $Z_\lambda(\beta)$ with respect to parameter $\lambda$ in (2) and evaluating it at $\lambda_0$, we get the first result. We can find the partial derivative of free entropy $\Phi_\lambda(\beta) = \log Z_\lambda(\beta)$ with respect to the parameter $\lambda$ evaluated at the value $\lambda_0$ as $\left.\frac{\partial\Phi_\lambda(\beta)}{\partial\lambda}\right|_{\lambda_0} = \frac{1}{Z_\lambda(\beta)}\frac{\partial}{\partial\lambda}Z_\lambda(\beta)\Big|_{\lambda_0}$. □

**Theorem 1.3 (Fluctuation-dissipation theorem).** *For any observable* $\mathcal{O} : \mathcal{X} \to \mathbb{R}$,

$$\langle\mathcal{O}\rangle_\lambda = \langle\mathcal{O}\rangle_{\lambda_0} - \beta(\lambda-\lambda_0)\left\langle \mathcal{O}; \left.\frac{\partial E_\lambda}{\partial\lambda}\right|_{\lambda_0}\right\rangle_{\lambda_0} + \Theta((\lambda-\lambda_0)^2).$$

*Proof.* Using equation (1) for expansion of $e^{-\beta E_\lambda(x)}$ in terms of $e^{-\beta E_{\lambda_0}(x)}$ and equation (2) for expansion of the partition function $Z_\lambda(x)$ in terms of $Z_{\lambda_0}(x)$, we can write the expectation of observable $\mathcal{O}$ for system parameter $\lambda$ in the neighborhood of $\lambda_0$ as

$$\langle\mathcal{O}\rangle_\lambda = \sum_{x\in\mathcal{X}}\frac{\mathcal{O}(x)e^{-\beta E_\lambda(x)}}{Z_\lambda(x)} = \sum_{x\in\mathcal{X}}\frac{\mathcal{O}(x)e^{-\beta E_{\lambda_0}(x)}\left(1-\beta(\lambda-\lambda_0)\left.\frac{\partial E_\lambda(x)}{\partial\lambda}\right|_{\lambda_0}+\Theta((\lambda-\lambda_0)^2)\right)}{Z_{\lambda_0}(\beta)\left[1-\beta(\lambda-\lambda_0)\left\langle\left.\frac{\partial E_\lambda}{\partial\lambda}\right|_{\lambda_0}\right\rangle_{\lambda_0}+\Theta((\lambda-\lambda_0)^2)\right]}.$$

Using the expansion $\frac{1}{1-y} = 1 + y + y^2 + ...$, the denominator can be brought to the numerator, to obtain

$$\begin{aligned}
\langle\mathcal{O}\rangle_\lambda &= \sum_{x\in\mathcal{X}}\mu_{\beta,\lambda_0}(x)\mathcal{O}(x)\left[1-\beta(\lambda-\lambda_0)\left.\frac{\partial E_\lambda(x)}{\partial\lambda}\right|_{\lambda_0}+\Theta((\lambda-\lambda_0)^2)\right]\times\left[1+\beta(\lambda-\lambda_0)\left\langle\left.\frac{\partial E_\lambda}{\partial\lambda}\right|_{\lambda_0}\right\rangle_{\lambda_0}+\Theta((\lambda-\lambda_0)^2)\right]\\
&= \sum_{x\in\mathcal{X}}\mu_{\beta,\lambda_0}(x)\left[\mathcal{O}(x)-\beta(\lambda-\lambda_0)\left(\mathcal{O}(x)\left.\frac{\partial E_\lambda(x)}{\partial\lambda}\right|_{\lambda_0}-\mathcal{O}(x)\left\langle\left.\frac{\partial E_\lambda}{\partial\lambda}\right|_{\lambda_0}\right\rangle_{\lambda_0}+\Theta((\lambda-\lambda_0)^2)\right)\right]\\
&= \langle\mathcal{O}\rangle_{\lambda_0}-\beta(\lambda-\lambda_0)\left[\left\langle\mathcal{O}\left.\frac{\partial E_\lambda}{\partial\lambda}\right|_{\lambda_0}\right\rangle_{\lambda_0}-\langle\mathcal{O}\rangle_{\lambda_0}\left\langle\left.\frac{\partial E_\lambda}{\partial\lambda}\right|_{\lambda_0}\right\rangle_{\lambda_0}\right]+\Theta((\lambda-\lambda_0)^2).
\end{aligned}$$

Result follows from the definition of covariance under the Boltzmann distribution. □

# 2 The thermodynamic limit

The main purpose of statistical physics is to understand the macroscopic behavior of a large number, $N \gg 1$, of microscopic components (atoms, molecules, etc.) under simple local interactions. For example, in the case of water in a bottle, the number $N$ of $H_2O$ molecules is typically of order $10^{23}$, since $18g$ of water contains approximately $6\times 10^{23}$ molecules, and this huge number leads physicists to focus on the $N\to\infty$ limit, also called **the thermodynamic limit**.

## 2.1 The intensive thermodynamic potentials

For large $N$, the thermodynamic potentials are proportional to $N$. The **intensive thermodynamic potentials** $f(\beta)$, $u(\beta)$, $s(\beta)$ are defined as follows.

**Definition 2.1 (Intensive thermodynamic potentials).** Denoting the thermodynamic potentials for $N$ particle system as $F_N(\beta), U_N(\beta), S_N(\beta)$ for the free energy, the internal energy, and the canonical entropy respectively, we can define the **free energy density**, the **energy density**, and the **entropy density** as

$$f(\beta) = \lim_{N\to\infty}\frac{F_N(\beta)}{N}, \qquad u(\beta) = \lim_{N\to\infty}\frac{U_N(\beta)}{N}, \qquad s(\beta) = \lim_{N\to\infty}\frac{S_N(\beta)}{N}. \tag{6}$$

*Remark* 1. The partition function $Z_N(\beta)$ for $N$ particles is a sum of exponentials, and hence is smooth and analytic. It follows that the free energy $F_N(\beta) = -\frac{1}{\beta}\ln Z_N(\beta)$ is also analytic.

**Definition 2.2 (Phase transition).** We say that a **phase transition** occurs, whenever the free energy density $f(\beta)$ is non-analytic.

*Remark* 2. Since the free entropy $\Phi_N(\beta)$ is convex, then so is the free entripy density $\phi(\beta)$, and therefore the free energy density $f(\beta) = -\frac{1}{\beta}\phi(\beta)$ is necessarily continuous whenever it exists. The phase transitions correspond to qualitative changes in the underlying physical system.

**Definition 2.3 (Types of singularities).** Often, the non-analyticities occur at isolated points say $\beta_c$.

**First-order phase transition.** The free energy density is continuous, but its derivative with respect to $\beta$ is discontinuous at $\beta_c$.

**Second-order phase transition.** The free energy and its first derivative are continuous, but the second derivative is discontinuous at $\beta_c$.

## 2.2 Energy spectrum and Micro-canonincal entropy density

When the number of particles $N$ grows, the volume of the configuration space increases exponentially, i.e. $\left|\mathcal{Z}^N\right| = |\mathcal{Z}|^N$. We have seen before that the system is likely to be found in lowest-energy configurations with high probability at low temperatures. From the definition of Boltzmann distribution, it is easy to check that conditioned on the system to be at certain energy level, it is equally likely to be in any configuration with equal energy. Therefore, one of the important factor of interest is the number of configurations for any given energy level. This information is given by the energy spectrum of the system.

**Definition 2.4.** The set of states with energy in the interval $[E, E+\Delta)$ is called the **energy spectrum** of the $N$ particle system, and denoted by $\Omega_\Delta(E) \triangleq \left\{x \in \mathcal{Z}^N : E \leqslant E(x) < E + \Delta\right\}$. The number of states in $\Omega_\Delta(E)$ is given by $\mathcal{N}_\Delta(E) \triangleq |\Omega_\Delta(E)|$.

*Remark* 3. The energy spectrum diverges exponentially in many systems as $N \to \infty$, if the energy is scaled linearly with $N$.

**Definition 2.5.** More precisely, there exists a function $s : \mathbb{R} \to \mathbb{R}$ called the **micro-canonical entropy density**, such that given two numbers $e$ and $\delta > 0$,

$$\sup_{e' \in [e, e+\delta]} s(e') = \lim_{N\to\infty} \frac{1}{N} \log \mathcal{N}_{N\delta}(Ne). \tag{7}$$

**Definition 2.6.** We say that two exponential quantities $A_N$ and $B_N$ are equal **to leading exponential order** and denote this equality by $A_N \doteq_N B_N$, if $\lim_{N\to\infty} \frac{1}{N}\log\frac{A_N}{B_N} = 0$.

*Remark* 4. Using this notation, we can write the following equality for micro-canonical entropy density

$$\mathcal{N}_\Delta(E) \doteq_N e^{Ns(E/N)}. \tag{8}$$

The micro-canonical entropy density $s(e)$ conveys a great amount of information about the system, and is directly related to the intensive thermodynamic potentials through a fundamental relation.

*Remark* 5. Recall that energy function $E : \mathcal{Z}^N \to \mathbb{R}$, and hence we can divide the energy levels into $N\Delta$ intervals. Then, we can partition the configuration space into configurations with energy level in one of these durations. Specifically, we can define $\Omega_{N\Delta}(Nk\Delta) \triangleq \left\{x \in \mathcal{Z}^N : k\Delta \leqslant \frac{E(x)}{N} < (k+1)\Delta\right\}$. Clearly, $(\Omega_{N\Delta}(Nk\Delta) : k \in \mathbb{Z})$ partition the configuration space $\mathcal{Z}^N$, and each of these partitions have cardinality $|\Omega_{N\Delta}(Nk\Delta)| = \mathcal{N}_{N\Delta}(Nk\Delta)$. Therefore, we can write the partition function as

$$Z_N(\beta) = \sum_{x\in\mathcal{Z}^N} e^{-\beta E(x)} = \sum_{k=-\infty}^{\infty} e^{-\beta Nk\Delta} \mathcal{N}_{N\Delta}(Nk\Delta) \left( \frac{1}{\mathcal{N}_{N\Delta}(Nk\Delta)} \sum_{x\in\Omega_{N\Delta}(Nk\Delta)} e^{-\beta N(\frac{E(x)}{N} - k\Delta)} \right).$$

From equation (8), we get the following equality in leading exponential order $\mathcal{N}_{N\Delta}(Nk\Delta) \doteq_N e^{Ns(k\Delta)}$. If $\mathcal{Z}$ is discrete and $\Delta$ is small enough so that the energy levels are exactly at $N\Delta$ intervals, then we can write the partition function as

$$Z(\beta) \doteq_N \sum_{k=-\infty}^{\infty} e^{N(s(k\Delta)-\beta k\Delta)}.$$

For continuous energy levels, we can show that $Z_N(\beta) \doteq_N \int e^{N(s(e)-\beta e)}de$, by taking limit of $\Delta \to 0$.

**Proposition 2.7.** *If the micro-canonical entropy density* (7) *exists for any* $e$ *and if the limit in equation* (7) *is uniform in* $e$*, then the free entropy density* (6) *exists and is given by*

$$\phi(\beta) = \max_e (s(e) - \beta e).$$

*If the maximum of* $s(e) - \beta e$ *is unique, then the internal-energy density equals* $\arg\max(s(e) - \beta e)$.

*Proof.* From the definition, the free entropy density $\phi(\beta)$ can be written as $\phi(\beta) = \lim_{N\to\infty} \frac{1}{N} \ln Z_N(\beta)$. From the computation of $N$-particle partition function in Remark 5, we can evaluate this limit for discrete configuration space as

$$\phi(\beta) = \lim_{N\to\infty} \frac{1}{N} \sum_{k=-\infty}^{\infty} e^{N(s(k\Delta)-\beta k\Delta)} = \sup_k [s(k\Delta) - \beta k\Delta] = \max_e [s(e) - \beta e].$$

Recall that $\phi(\beta) = \lim_{N\to\infty} \frac{1}{N} \ln Z_N(\beta)$. If $e^* \triangleq \arg\max(s(e) - \beta e)$ is unique, then $Z_N(\beta) \doteq_N e^{N(s(e^*)-\beta e^*)}$. It follows that

$$\lim_{N\to\infty} \mu_{N,\beta}(x) = \lim_{N\to\infty} \frac{1}{\mathcal{N}_{N\Delta}(Nk\Delta)} \mathbb{1}_{\{x\in\Omega_{N\Delta}(Nk\Delta)\}} = e^{-Ns(e^*)} \mathbb{1}_{\{E(x)=Ne^*\}}.$$

It follows that $u(\beta) = \lim_{N\to\infty} \frac{1}{N} \langle E \rangle_N = e^*$. ∎

**Example 2.8 ($N$ identical two-level systems).** We consider an $N$ particle system, where the configuration space $\mathcal{X} = \mathcal{Z}^N$ of $N$ particles with identical two-level sets $\mathcal{Z} = \{0, 1\}$. For any configuration $x \in \mathcal{X}^N$, we let $x_i \in \mathcal{Z}$ denote the configuration of particle $i \in [N]$. As in the previous two-level system example, for each particle $i \in [N]$

$$E_i(x_i) = E_{\text{single}}(x_i) \triangleq \epsilon_0(1 - x_i) + \epsilon_1 x_i.$$

Without any loss of generality, we assume $\epsilon_1 > \epsilon_0$, and define the energy gap as $\Delta \triangleq \epsilon_1 - \epsilon_0$. We take the energy of the $N$ particle system to be the sum of the single-particle energies, i.e.

$$E(x) \triangleq \sum_{i=1}^{N} E_i(x_i) = \sum_{i=1}^{N} E_{\text{single}}(x_i) = N\epsilon_0 + \Delta \sum_{i=1}^{N} x_i.$$

We can next study the energy spectrum for this model. For any configuration $x \in \mathcal{Z}^N$, we can define the set of particles in state $k \in \{0, 1\}$ as $S_k \triangleq \{i \in [N] : x_i = k\}$. Clearly, $(S_0, S_1)$ partitions the set of particles $[N]$, and the system energy is given by $E(x) = N\epsilon_0 + |S_1|\Delta$. The number of possible subsets $S_1 \subseteq [N]$ such that $|S_1| = n$ is equal to the binomial coefficient $\binom{N}{n}$. Therefore, we conclude that $E(x) \in \{N\epsilon_0 + n\Delta : n = 0, \dots, N\}$ and for any energy $E = N\epsilon_0 + n\Delta$, there are $\binom{N}{n}$ configurations $x \in \mathcal{Z}^N$ such that $E(x) = E$. This is one of the rare examples, where we can completely specify the number of configurations at each energy level, which is

$$\mathcal{N}_\Delta(E) = \binom{N}{n} \approx 2^{NH(\frac{n}{N})} = 2^{NH\left(\frac{E-N\epsilon_0}{N\Delta}\right)} = 2^{NH\left(\frac{\frac{E}{N}-\epsilon_0}{\Delta}\right)}.$$

Using the definition of micro-canonical entropy density (7), we get $s(e) = H\left(\frac{e-\epsilon_0}{\Delta}\right)$. We can write the free energy density in terms of micro-canonical entropy density as

$$f(\beta) = -\frac{1}{\beta}\phi(\beta) = -\frac{1}{\beta}\sup_e (s(e) - \beta e) = -\frac{1}{\beta}\sup_e \left(H\left(\frac{e-\epsilon_0}{\Delta}\right) - \beta e\right).$$

To evaluate the supremum in the above equation, we take the first derivative of $H\left(\frac{e-\epsilon_0}{\Delta}\right) - \beta e$ with respect to energy density $e$ and equate it to zero, to get $\frac{\partial H\left(\frac{e-\epsilon_0}{\Delta}\right)}{\partial e}\Big|_{e=e^*} - \beta = 0$. Recall that $\frac{\partial H(p)}{\partial p} = \ln(\frac{1}{p} - 1)$ to obtain the stationary point

$$e^* = \epsilon_0 + \Delta \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}.$$

Since $H : [0, 1] \to \mathbb{R}_+$ is a concave function, it follows that $e^*$ corresponds to the unique maxima. Substituting this back into the expression for the free energy, we get

$$f(\beta) = -\frac{1}{\beta}\left(H\left(\frac{e^* - \epsilon_0}{\Delta}\right) - \beta e^*\right) = \epsilon_0 - \frac{1}{\beta}\ln(1 + e^{-\beta\Delta}).$$

This expression is identical to the free energy for a single particle as expected, since summation of energy functions amounts to no interaction system. The free energy of non-interacting $N$ particle system, is the aggregate free energy of $N$ independent single particle systems.