[Readings] Topics in Non-Equilibrium Statistical Mechanics

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0 Preface

Here is the reading assignment of the course *Non-Equilibrium Statistical Mechanics*. Apart from the course textbook by Pottier, I have referred to several other books in preparing these notes:

- Pottier, *Nonequilibrium Statistical Mechanics: Linear Irreversible Processes*, Oxford University Press 2010.

- Kardar, *Statistical Physics of Particles*, Cambridge University Press 2007.

- Peliti, *Statistical Mechanics in a Nutshell*, Princeton University Press 2011.

- Weinberg, *The Quantum Theory of Fields, Vol.1*, Cambridge University Press 1995.

Regarding the division into formalism and application, I choose to lean towards the former. Therefore, among the many examples and applications in the textbook, I have included only the particularly enlightening (and interesting) ones. On the other hand, in a few places where the discussion in the book is not detailed enough, I have tried to borrow examples from or build toy models inspired by the other books.

I find my (re)organization of materials very helpful in clarifying the ideas for myself. I hope it should also help whoever comes across these notes as well.

1 Probability and Random Processes

1.1 Random Variables

A random variable X takes values in the sample space Ω with probability density function (PDF) $p(x)$. The characteristic function $\tilde{p}(k) := \langle e^{ikx} \rangle$ generates the moments. Its logarithm generates the cumulants.

$$\tilde{p}(k) = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle, \quad \ln \tilde{p}(k) = \sum_{n=1}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle_c. \tag{1.1}$$

The moments and cumulants satisfy a graphical relation:

$$
\begin{aligned}
\langle x \rangle &= \langle x \rangle_c & \langle x^3 \rangle &= \langle x^3 \rangle_c + 3\langle x^2 \rangle_c \langle x \rangle_c + \langle x \rangle_c^3 \\
&= (.), & &= (...) + 3(..)(.) + (.)(.)(.), \\
\langle x^2 \rangle &= \langle x^2 \rangle_c + \langle x \rangle_c^2 & \langle x^4 \rangle &= \langle x^4 \rangle_c + 4\langle x^3 \rangle_c \langle x \rangle_c + 3\langle x^2 \rangle_c \langle x^2 \rangle_c + 6\langle x^2 \rangle_c \langle x \rangle_c^2 + \langle x \rangle_c^4 \\
&= (..) + (.)(.), & &= (....) + 4(...)(.) + 3(..)(..) + 6(..)(.)(.) + (.)(.)(.)(.),
\end{aligned}
\tag{1.2}
$$

$$\cdots \tag{1.3}$$

$$
\begin{aligned}
p(k) &= \exp \ln \tilde{p}(k), \\
[\text{diagrams}] &= \exp[\text{connected diagrams}].
\end{aligned}
\tag{1.4}
$$

In the multi-variate case, each dot is dressed with a label indicating which variable it represents.

If the distribution $p(x)$ has a long tail, some of the moments may not converge.

Example: Cauchy distribution.

$$p(x) = \frac{a}{\pi} \frac{1}{(x-\mu)^2 + a^2} \implies \langle x^n \rangle \sim \int^{\infty} x^{n-2} \mathrm{d}x = \infty. \tag{1.5}$$

In fact, with proper regularization to justify the translation $x \mapsto x + \mu$, it's possible to define $\langle (x - \mu)^{2n-1} \rangle = 0$.

The characteristic function is well-defined, but is not differentiable at $k = 0$. To see this, close the contour from above if $k > 0$ and from below if $k < 0$:

$$\tilde{p}(k) = \frac{a}{\pi} \int_{-\infty}^{+\infty} \frac{e^{ikx}}{(x-\mu)^2 + a^2} \mathrm{d}x = 2ai \, \mathrm{sgn}(k) \operatorname*{res}_{x=\mu+ia\,\mathrm{sgn}(k)} \frac{e^{ikx}}{(x-\mu)^2 + a^2} = e^{-a|k|+ik\mu}. \tag{1.6}$$

1.2 Gaussian Distribution and the Central Limit Theorem

In the most general form with n variables,

$$p(\mathbf{x}) = \frac{1}{\mathcal{N}} \exp\left(-\frac{1}{2}\mathbf{x}^T \mathsf{A}\mathbf{x} + \mathbf{x}^T \mathbf{J}\right), \quad \mathcal{N} = \sqrt{\frac{(2\pi)^n}{\det \mathsf{A}}} \exp\left(\frac{1}{2}\mathbf{J}^T \mathsf{A}^{-1}\mathbf{J}\right). \tag{1.7}$$

The characteristic function is also of Gaussian form:

$$\tilde{p}(\mathbf{k}) = \exp\left(-\frac{1}{2}\mathbf{k}^T \mathsf{A}^{-1}\mathbf{k} + i\mathbf{k}^T \mathsf{A}^{-1}\mathbf{J}\right), \tag{1.8}$$

$$\langle x_i \rangle_c = (A^{-1})_{ij} J_j, \quad \langle x_i x_j \rangle_c = (A^{-1})_{ij}, \quad \langle x_i x_j x_k \cdots \rangle_c = 0. \tag{1.9}$$

For the centered distribution ($\mathbf{J} = 0$ so that $\langle x_i x_j \rangle_c = \langle x_i x_j \rangle$), we obtain Wick's theorem by applying the graphical relation, e.g.,

$$\langle x_i x_j x_k x_l \rangle = \langle x_i x_j \rangle \langle x_k x_l \rangle + \langle x_i x_k \rangle \langle x_j x_l \rangle + \langle x_i x_l \rangle \langle x_j x_k \rangle. \tag{1.10}$$

$$* \; * \; * \; * \; *$$

Consider the normalized deviation $Y = \sum_{i=1}^{N}(X_i - \mu)/\sqrt{N}$ of N independently and identically distributed (IID) variables taken from the distribution $p(x)$, with $\langle x \rangle_c = \mu$ and $\langle x^2 \rangle_c = \sigma^2$.

$$\tilde{p}_Y(k) = \prod_{i=1}^{N} \left\langle \exp\left(i\frac{k}{\sqrt{N}}(X_i - \mu)\right) \right\rangle = \left(e^{-ik\mu}\tilde{p}(k/\sqrt{N})\right)^N \tag{1.11}$$

$$\ln \tilde{p}_Y(k) = N\ln(e^{-ik\mu}\tilde{p}(k/\sqrt{N})) = N \times \left(-\frac{1}{2}\sigma^2\frac{k^2}{N} + O\left(\frac{k^3}{N^{3/2}}\right)\right) \xrightarrow{N\to\infty} -\frac{1}{2}\sigma^2 k^2. \tag{1.12}$$

Therefore, $p_Y(y)$ converges to a centered Gaussian distribution of variance σ^2.

- Independence is not necessary for convergence.

    A special case with finite cumulants. Suppose all cumulants $\langle x \cdots x \rangle_c$ are finite. Consider the sum $S = \sum_{i=1}^{N} X_i$ of variables taken from the joint distribution $p(\mathbf{x})$.

$$\tilde{p}_S(k) = \langle e^{ikS} \rangle = \sum_{n=1}^{\infty} \frac{(ik)^n}{n!} \sum_{i_1,\cdots,i_n} \langle x_{i_1} \cdots x_{i_n} \rangle_c \implies \langle s^n \rangle_c = \sum_{i_1,\cdots,i_n} \langle x_{i_1} \cdots x_{i_n} \rangle_c. \tag{1.13}$$

    The variable $Y = (S - \langle s \rangle_c)/\sqrt{N}$ satisfies $\langle y \rangle_c = 0$, and $\langle y^n \rangle_c = \langle s^n \rangle_c N^{-n/2}$ for $n \geq 2$. Now, if $\langle s^n \rangle_c = o(N^{n/2})$ for all $n > 2$ and $\langle s^2 \rangle_c = O(N)$, only $\langle y^2 \rangle_c$ survives in the large-N limit.

$$\lim_{N\to\infty} p_Y(y) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{y^2}{2\sigma^2}\right), \quad \sigma^2 = \lim_{N\to\infty} \frac{\langle s^2 \rangle_c}{N}. \tag{1.14}$$

    From $\sum_{ij} \langle x_i x_j \rangle_c = O(N)$ we see that there cannot be any long-range correlation, i.e., the number of j such that $\langle x_i x_j \rangle_c = O(1)$ for any fixed i must remain finite as $N \to \infty$.

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- Finiteness of variance σ^2 is not necessary for convergence. If $\langle x^2 \rangle_c = \infty$, the attraction domain of the Gaussian distribution is characterized by the following condition:

$$\lim_{y \to \infty} y^2 \frac{\int_{|x|>y} p(x)\mathrm{d}x}{\int_{|x|<y} x^2 p(x)\mathrm{d}x} = 0. \tag{1.15}$$

The above condition is satisfied if $p(x)$ decreases as $|x|^{-3}$ or faster as $|x| \to \infty$, since

$$0 < y^2 \frac{\int_{|x|>y} p(x)\mathrm{d}x}{\int_{|x|<y} x^2 p(x)\mathrm{d}x} < \mathcal{C}y^2 \frac{\int_{|x|>y} |x|^{-3}\mathrm{d}x}{\int_{|x|<y} x^2 p(x)\mathrm{d}x} = \mathcal{C}y^2 \frac{1/y^2}{\int_{|x|<y} x^2 p(x)\mathrm{d}x} \xrightarrow{y \to \infty} 0.$$

- Distributions $p(x)$ that decreases as $1/|x|^{1+\alpha}$ have infinite variance for $0 < \alpha \le 2$. Simple power counting suggests $\tilde{p}(k)$ is singular at $k = 0$ with leading order $|k|^\alpha$. ????? The normalized deviation is now $Y = \sum_{i=1}^{N}(X_i - \mu)/N^{1/\alpha}$.

$$\ln \tilde{p}_Y(k) = N \ln \tilde{p}(k/N^{1/\alpha}) = N \times \left(-\mathcal{C}\frac{|k|^\alpha}{N} + O\left(\frac{|k|^{1+\alpha}}{N^{1+1/\alpha}}\right) \right) \xrightarrow{N \to \infty} -\mathcal{C}|k|^\alpha. \tag{1.16}$$

It's been proved that $p_Y(y)$ converges to a stable distribution. A distribution is stable if any linear combination of two independent variables taken from the distribution has the same distribution.

1.3 Random Processes

This is simply the continuous version of the multi-variate random distributions. Instead of $\{X_i\}_{i=1}^{N}$, we now have a continuum of random variables $\{X(t)\}$. Each realization is a function $x(t)$.

The n-time densities $p_n(x_1, t_1; \cdots; x_n, t_n)$ are hierarchically marginalized:

$$\int p_n(x_1, t_1; \cdots; x_n, t_n)\mathrm{d}x_{s+1} \cdots \mathrm{d}x_n = p_s(x_1, t_1; \cdots; x_s, t_s). \tag{1.17}$$

The n-time averages are the continuous analogs of moments. We are often interested in the autocorrelation function $\kappa(t_1, t_2)$, the continuous analog of variance:

$$\kappa(t_1, t_2) = \langle X(t_1)X(t_2) \rangle - \langle X(t_1) \rangle \langle X(t_2) \rangle = \int x_1 x_2 [p_2(x_1, t_1; x_2, t_2) - p_1(x_1, t_1)p_1(x_2, t_2)]\mathrm{d}x_1\mathrm{d}x_2. \tag{1.18}$$

In the above expression, we have assumed that $X(t)$ is a real-valued signal. If it is complex-valued, $\kappa(t_1, t_2) = \langle X(t_1)^* X(t_2) \rangle - \langle X(t_1)^* \rangle \langle X(t_2) \rangle$.

- A stationary process is one with time-translation invariance, in which case $\kappa(t_1, t_2) = \kappa(t_2 - t_1)$.

- An ergodic process is one where statistical properties can be deduced from a single sample that's sufficiently long.

- Fact: If a stationary process has absolutely integrable $\kappa(\tau)$, it is ergodic in the mean: $\langle X \rangle = \bar{X}$.

From now on, we focus on stationary and mean-ergodic processes. It's often useful to consider the frequency spectrum of a process. However, any particular realization may not be periodic or square-integrable, so that "IR regularization" is needed.

Given a particular realization $x(t)$, there are two ways to regularize it:

- Fourier transform. Define the cut-off signal $x_T^{\text{cut}}(t)$ that vanishes outside $[0, T]$.

$$\tilde{x}_T(\omega) = \int_0^T x_T^{\text{cut}}(t)e^{i\omega t}\mathrm{d}t, \quad x_T^{\text{cut}}(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \tilde{x}_T(\omega)e^{-i\omega t}\mathrm{d}\omega. \tag{1.19}$$

- Fourier series. Extend the $[0, T]$ segment periodically to obtain $x_T^{\text{per}}(t)$.

$$a_n = \frac{1}{T}\int_0^T x_T^{\text{per}}(t)e^{i\omega_n t}\mathrm{d}t, \quad x_T^{\text{per}}(t) = \sum_{n=-\infty}^{+\infty} a_n e^{-i\omega_n t}. \tag{1.20}$$

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Written symbolically,

$$X(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{X}(\omega)e^{-i\omega t}\mathrm{d}\omega = \sum_{n=-\infty}^{+\infty} A_n e^{-i\omega_n t}, \quad \omega_n = \frac{2\pi n}{T}, \tag{1.21}$$

$$\tilde{X}(\omega) = \int_0^T X(t)e^{i\omega t}\mathrm{d}t, \quad A_n = \frac{1}{T}\int_0^T X(t)e^{i\omega_n t}\mathrm{d}t, \quad A_n = \frac{1}{T}\tilde{X}(\omega_n). \tag{1.22}$$

We would take the $T \to \infty$ limit at the end of a calculation.

The mean of A_n is determined by:

$$\langle A_n \rangle = \frac{1}{T}\int_0^T \langle X \rangle e^{i\omega_n t}\mathrm{d}t = \langle X \rangle \delta_{0n}. \tag{1.23}$$

Notice that $A_0 \sim \tilde{X}(0)$ is not a random variable. Any particular realization a_0 is the temporal average of $x(t)$ over $[0, T]$, which (in the limit $T \to \infty$) is equal to $\langle X \rangle$ because of ergodicity.

In the vicinity of frequency ω_n, each mode carries energy proportional to $|A_n|^2$ and the density of modes are $\frac{T}{2\pi}$. Define the spectral density at that point to be $S(\omega_n) = T|A_n|^2$. In the continuous limit,

$$S(\omega) = \lim_{T\to\infty} \frac{1}{T}\langle |\tilde{X}(\omega)|^2 \rangle. \tag{1.24}$$

Since $X(t)$ is stationary, $\langle X(t) \rangle \equiv \langle X \rangle$, hence different frequencies are uncorrelated.

$$\langle \tilde{X}(\omega)\tilde{X}(\omega')^* \rangle = 2\pi\delta(\omega - \omega')S(\omega). \tag{1.25}$$

On the other hand, for a centered process where $\langle X \rangle = 0$,

$$\kappa(\tau) = \langle X^*(t)X(t+\tau) \rangle = \lim_{T\to\infty} \int \langle \tilde{X}^*(\omega_1)\tilde{X}(\omega_2) \rangle e^{i\omega_1 t - i\omega_2(t+\tau)} \frac{\mathrm{d}\omega_1}{2\pi}\frac{\mathrm{d}\omega_2}{2\pi}. \tag{1.26}$$

Therefore, we obtain the Wiener-Khinchin theorem:

$$\kappa(\tau) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} S(\omega)e^{-i\omega\tau}\mathrm{d}\omega, \quad S(\omega) = \int_{-\infty}^{+\infty} \kappa(\tau)e^{i\omega\tau}\mathrm{d}\tau. \tag{1.27}$$

Example: Lorentzian spectral density.

$$\kappa(\tau) = \frac{1}{2\tau_0}e^{-|\tau|/\tau_0}, \quad S(\omega) = \frac{\omega_0^2}{\omega^2 + \omega_0^2}, \quad \omega_0\tau_0 = 1. \tag{1.28}$$

The limit $\tau_0 \to 0$ is the white noise limit, since $\kappa(\tau) \to \delta(\tau)$ and $S(\omega) \to 1$.

If the process is not centered, the spectral density is the sum of $S(\omega)$ for the centered process and $2\pi|\langle X \rangle|^2\delta(\omega)$, and the autocorrelation is the sum of $\kappa(\tau)$ for the centered process and $|\langle X \rangle|^2$.

2 Linear Thermodynamics of Irreversible Processes

2.1 Review of Equilibrium Thermodynamics

[Kardar] builds equilibrium thermodynamics from the bottom up by considering the consequences of the four laws one by one, introducing the concepts of temperature, energy, entropy difference, and absolute entropy. Here, we take the top-down approach by assuming the existence of an extensive state function $S = S(X_i)$, where $\{X_i\}$ are the extensive coordinates (energy, volume, particle numbers, etc.) subject to conservation laws. The intensive variables $\{F_i\}$ are defined such that $\mathrm{d}S = \sum_i F_i \mathrm{d}X_i$ along the equilibrium hypersurface.

Case study: Discontinuous phase transition. Legendre transform vs. convexity?

2.2 Description of Systems in Local Equilibrium

If the system has two characteristic time/length scales, the microscopic degrees of freedom decouple from the macroscopic, thermodynamic desciption:

- If microscopic variables relax much faster than macroscopic variables, we may define instantaneous quantities.

- If the system is composed of a large number of microscopically large pieces, we may define local quantities.

Consider a system satisfying the local equilibrium hypothesis: the local, instantaneous entropy has the same functional form as the global equilibrium entropy. This is equivalent to the statement that the local instantaneous entropy is extensive, ruling out systems where long-range interactions are not negligible, such as the rarefied gas or any strong-coupling system. In mathematical terms, we consider systems where every thermodynamic variable Π satisfies:

$$\frac{\Delta \Pi}{\Pi} \ll \frac{\delta \Pi}{\Pi} \ll 1. \tag{2.1}$$

Here, $\delta\Pi/\Pi$ is the thermodynamic fluctuation over a short time/length, so that $\delta\Pi/\Pi \ll 1$ justifies the local, instantaneous description; $\Delta\Pi/\Pi$ is the variation over the entire time/length scale of the system, so that $\delta\Pi/\Pi \gg \Delta\Pi/\Pi$ justifies the neglection of long-range interactions.

Under the above assumptions, any extensive thermodynamic quantity in a continuum is described by a density field:

$$A(t) = \int_V a(\mathbf{r}, t)\mathrm{d}V, \quad \frac{\mathrm{d}A}{\mathrm{d}t} = \int_V \sigma_A \mathrm{d}V - \int_{\partial V} \mathbf{J}_A \cdot \mathrm{d}\mathbf{\Sigma}, \quad \frac{\partial a}{\partial t} = \sigma_A - \nabla \cdot \mathbf{J}_A. \tag{2.2}$$

Here, $a(\mathbf{r}, t)$ is the density per unit volume, $\mathbf{J}_A$ is the current density, and σ_A is the source density. On the other hand, if the system is composed of a finite number of subsystems, there is no distinction between a flux and a source (since topologically the subsystems are vertices of a graph). In that case, we define $I_A = \mathrm{d}A/\mathrm{d}t$ for each subsystem.

The claim is that local entropy production is always a bilinear form of affinities and fluxes, as long as the system is embracive enough that all extensive quantities are "transferred" across the system instead of being "generated" by external sources. We illustrate this with an example.

Example: Rod between two temperatures. Choose the system to include the rod and the two heat reservoirs. It is described by entropy (density) functions $S_H(t)$, $S_C(t)$, $s(\mathbf{r}, t)$.

During the time interval $[t, t + \mathrm{d}t]$, a particular cell located at $\mathbf{r}$ changes from one equilibrium to another: $\partial s/\partial t = \sum_i F_i \partial x_i/\partial t$. However, nothing is said about the relation of equilibrium states between different cells, so that $\nabla \cdot \mathbf{J}_S = \nabla \cdot \sum_i F_i \mathbf{J}_i$.

$$\sigma_S = \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_S = \sum_i \left(F_i \frac{\partial x_i}{\partial t} + F_i \nabla \cdot \mathbf{J}_i + (\nabla F_i) \cdot \mathbf{J}_i \right) = \sum_i \left(F_i \sigma_{X_i} + (\nabla F_i) \cdot \mathbf{J}_i \right). \tag{2.3}$$

In the middle, the extensive quantities are locally conserved ($\sigma_i = 0$) so that $\sigma_S = \sum_i (\nabla F_i) \cdot \mathbf{J}_i$.

At one end of the rod (say, the hot one), one might be tempted to say that $\sigma_E \neq 0$ due to the energy source that is the reservoir. However, since our system includes the reservoir, the heat is not "generated" by an external source, but is "transferred" from the reservoir. Therefore, the correct interpretation is that $\sigma_E = 0$ but we should include another term $-I_E^{(H)}\delta(\mathbf{r} - \mathbf{r}_H)$ in the equation to obtain $\sigma_S = -F_E^{(H)} I_E^{(H)} \delta(\mathbf{r} - \mathbf{r}_H) + \sum_i (\nabla F_i) \cdot \mathbf{J}_i$. For the reservoir itself, $\mathrm{d}S_H/\mathrm{d}t = F_E^{(H)} I_E^{(H)}$. The total energy is conserved:

$$0 = \frac{\mathrm{d}}{\mathrm{d}t}\left(E^{(H)} + E^{(C)} + \int e(\mathbf{r})\mathrm{d}V \right) = I_E^{(H)} + I_E^{(C)} - \int (\nabla \cdot \mathbf{J}_E)\mathrm{d}V \tag{2.4}$$

All heat emitted from the rod, $\int (\nabla \cdot \mathbf{J}_E)\mathrm{d}V$, is absorbed by the reservoirs.

2.3 Interlude: Thermal Fluctuations at Equilibrium

Consider the thermal fluctuations δX_i in the extensive coordinates. For now, we don't assume local equilibrium, but simply require the decoupling of microscopic degrees of freedom so that the extensive coordinates $\{X_i\}$ fully characterize the (out-of-equilibrium) macrostate.

What is the probability distribution of fluctuations? The Einstein formula answers this question ingeniously by inverting the Boltzmann entropy formula. For an isolated system, since $S = k_B \ln \Omega$, the number of microstates corresponding to the fluctuated macrostate is $\exp((S + \delta S)/k_B)$. The probability is proportional to the number of microstates, as all of them are assumed to be equally likely: $w \propto \exp(\delta S/k_B)$.

If the system is not isolated, the environment states are marginalized, and the probability is proportional to

$$\Omega(\{X\}) := \Omega_{\text{sys}}(\{X\})\Omega_{\text{env}}(\{X^{\text{tot}} - X\}) = \exp\left(\frac{S_{\text{sys}}(\{X\}) + S_{\text{env}}(\{X^{\text{tot}} - X\})}{k_B}\right). \tag{2.5}$$

Since the environment is huge, $X \ll X^{\text{tot}}$. To the lowest order,

$$\begin{aligned}
\Omega(\{X\}) &\approx \exp\left(\frac{S_{\text{sys}}(\{X\}) + S_{\text{env}}(\{X^{\text{tot}}\}) - \sum_i F_{i,\text{env}}(\{X^{\text{tot}}\})X_i}{k_B}\right) \\
&\propto \exp\left(\frac{S_{\text{sys}}(\{X\}) - \sum_i F_{i,\text{env}}(\{X^{\text{tot}}\})X_i}{k_B}\right) \\
&\approx \exp\left(\frac{S_{\text{sys}}(\{X\}) - \sum_i F_{i,\text{env}}(\{X^{\text{tot}} - X\})X_i}{k_B}\right) \\
&= \exp\left(\frac{S_{\text{sys}} - \sum_i F_{i,\text{env}}X_i}{k_B}\right).
\end{aligned} \tag{2.6}$$

The environment value $F_{i,\text{env}}$ does not fluctuate, so the probability of fluctuation

$$w \propto \exp\left(\frac{\delta S - \sum_i F_{i,\text{env}}\delta X_i}{k_B}\right) = \left(\frac{\sum_i (F_{i,\text{sys}} - F_{i,\text{env}})\delta X_i}{k_B}\right) = \left(\frac{\sum_i \delta F_i \delta X_i}{k_B}\right). \tag{2.7}$$

We may interpret the second term as the entropy flow from the environment to the system.

From this, we prove the claim $\langle \delta X_i \delta F_j \rangle = -k_B \delta_{ij}$.

$$\langle \delta X_i \delta F_j \rangle = k_B \int \delta X_i \frac{\partial w}{\partial \delta X_j} \prod_k \mathrm{d}(\delta X_k) = -k_B \int w \frac{\partial \delta X_i}{\partial \delta X_j} \prod_k \mathrm{d}(\delta X_k) = -k_B \delta_{ij}. \tag{2.8}$$

The first term vanishes because $\langle \delta F_j \rangle = 0$ by definition.

What about $\langle (\delta X_i)^2 \rangle$ and $\langle (\delta F_i)^2 \rangle$?

2.4 Kinetic Coefficients

The affinities $\mathcal{F}_i$ indicate the deviation/fluctuation from equilibrium, while the fluxes $\mathcal{J}_i$ record the flow/relaxation as a result. Here, we have flattened all indices such as the vector indices of ∇F and $\mathbf{J}$. As long as the local equilibrium hypothesis is valid, $\mathcal{J}_i(\mathbf{r}, t)$ only depends on the affinities at that place and time. To the lowest order,

$$\mathcal{J}_i(\mathbf{r}, t) = \mathcal{J}_i[\mathcal{F}] = 0 + \sum_k L_{ik}\mathcal{F}_k + O(\mathcal{F}^2), \quad L_{ik} := \frac{\partial \mathcal{J}_i}{\partial \mathcal{F}_k}. \tag{2.9}$$

Since $\sigma_S = \sum_{ik} L_{ik}\mathcal{F}_i\mathcal{F}_k = \sum_{ik} L_{(ik)}\mathcal{F}_i\mathcal{F}_k$ is non-negative-definite, the symmetric part satisfies:

$$L_{ii} \geq 0, \quad L_{ii}L_{kk} \geq L_{(ik)}L_{(ki)} = \frac{1}{4}(L_{ik} + L_{ik})^2. \tag{2.10}$$

Examples.

- Electrical conductivity (isotropic case): $\mathbf{J} = \sigma \mathbf{E}$.

$$\mathbf{J} = q\mathbf{J}_N = qL_{NN}\nabla\left(-\frac{\bar{\mu}}{T}\right) \overset{(*)}{=\!=\!=} \frac{q^2}{T}L_{NN}\mathbf{E}. \tag{2.11}$$

Here, the step $(*)$ is valid as long as the temperature and the carrier density (and hence μ) is uniform, so that $\nabla\bar{\mu} = \nabla(\mu + q\varphi) = -q\mathbf{E}$.

- Diffusion (isotropic case): $\mathbf{J}_N = -D\nabla n$.

$$\mathbf{J}_N = L_{NN}\nabla\left(-\frac{\bar{\mu}}{T}\right) \overset{(*)}{=\!=\!=} -\frac{1}{T}\left.\frac{\partial\mu}{\partial n}\right|_T \nabla n. \tag{2.12}$$

Here, the step $(*)$ is valid as long as the temperature is uniform.

- Thermal conductivity (isotropic case): $\mathbf{J}_E = -\kappa\nabla T$.

$$\mathbf{J}_E = L_{EE}\nabla\left(-\frac{1}{T}\right) = \frac{1}{T^2}L_{EE}\nabla T. \tag{2.13}$$

Due to time-reversal invariance at the microscopic level, the kinetic coefficients satisfy the Onsager reciprocity relations:

$$L_{ik} = (-)^{\mathsf{T}_i + \mathsf{T}_k}L_{ki}, \quad \text{where } \mathsf{T}_{i,k} \text{ are time-reversal parities of } \mathcal{J}_{i,k}. \tag{2.14}$$

Since they reflect the microscopic aspects of the system, the Onsager relations cannot be proved within the framework of thermodynamics. Here, we merely attempt a justification of the statement.

For simplicity, consider a time-reversal parity-even system without magnetic fields or angular momenta. By time-reversal invariance and stationarity,

$$\langle\delta X_i(0)\delta X_k(t)\rangle = \langle\delta X_i(t)\delta X_k\rangle \implies \langle\delta X_i\delta\dot{X}_k\rangle = \langle\delta\dot{X}_i\delta X_k\rangle. \tag{2.15}$$

By Onsager's regression hypothesis (a consequence of the fluctuation-dissipation theorem unprovable in thermodynamics), fluctuations relax by following the same lows as fluxes:

$$\delta\dot{X}_i = \sum_j L_{ij}\delta F_j \implies \sum_j L_{kj}\langle\delta X_i\delta F_j\rangle = \sum_j L_{ij}\langle\delta F_j\delta X_k\rangle \implies L_{ki} = L_{ik}. \tag{2.16}$$

An important consequence is the minimum entropy production theorem, which holds for systems that are time-reversal parity-even ($L_{ik} = L_{ki}$) in the linear regime. Consider the time derivative of the total entropy production $P_S = \int\sigma_S\mathrm{d}V$ of a system kept out of equilibrium by time-independent constraints:

$$\begin{aligned}
\frac{\mathrm{d}P_S}{\mathrm{d}t} &= \int\frac{\partial\sigma_S}{\partial t}\mathrm{d}V \\
&= 2\int\sum_{ik}L_{ik}(\nabla F_i)\cdot\nabla\left(\frac{\partial F_k}{\partial t}\right)\mathrm{d}V \\
&= 2\int\sum_k \mathbf{J}_k\cdot\nabla\left(\frac{\delta\dot{S}}{\delta x_k}\right)\mathrm{d}V \\
&= -2\int\sum_k(\nabla\cdot\mathbf{J}_k)\frac{\delta\dot{S}}{\delta x_k}\mathrm{d}V \\
&= 2\int\sum_{jk}\frac{\partial x_k}{\partial t}\frac{\delta^2 S}{\delta x_k\delta x_j}\frac{\partial x_j}{\partial t}\mathrm{d}V,
\end{aligned} \tag{2.17}$$

where the second equality holds due to the crucial symmetry $L_{ik} = L_{ik}$.

From thermodynamics, we know that the entropy function is convex, i.e., $\delta^2 S/\delta x_k\delta x_j$ is non-positive definite. Hence, $\mathrm{d}P_S/\mathrm{d}t \leq 0$. On the other hand, P_S itself is non-negative. The time-evolution of P_S is therefore towards a stationary limit, where the entropy production P_S reaches a minimum.

3 Kinetic Theory

From now on, we switch gear from the macroscopic description to the microscopic description. As [Kardar] pointed out, our goal is to answer the following questions using the microscopic equations of motion:

- How can we define "equilibrium" for a system of moving particles?

- Do all systems naturally evolve towards an equilibrium state?

- What is the time evolution of a system that is not quite in equilibrium?

3.1 The Microscopic Description

Recall that in thermodynamics, we consider the macrostates of our system, parametrized by a few thermodynamic variables. Similarly, a microscopic description relies crucially on the concept of a microstate.

- Classically, a microstate is a point in phase space, and an observable is a function on phase space.

- In QM, a microstate is a pure state in Hilbert space, and an observable is an operator on Hilbert space.

However, in the thermodynamic limit, we could not obtain precise knowledge of our system. Necessarily, we need to consider ensembles of microstates.

- Classically, an evolving ensemble is a time-dependent distribution $\rho(\mathbf{q}, \mathbf{p}, t)$ that follows Liouville's equation:

$$\lim_{\delta t \to 0} \frac{\rho(\mathbf{q}, \mathbf{p}, t + \delta t) - \rho(\mathbf{q}, \mathbf{p}, t)}{\delta t} = \lim_{\delta t \to 0} \frac{\rho(\mathbf{q}, \mathbf{p}, t + \delta t) - \rho(\mathbf{q} - \{H, \mathbf{q}\}\delta t, \mathbf{p} - \{H, \mathbf{p}\}\delta t, t + \delta t)}{\delta t}$$

$$= \{H, \mathbf{q}\} \cdot \frac{\partial \rho(\mathbf{q}, \mathbf{p}, t)}{\partial \mathbf{q}} + \{H, \mathbf{p}\} \cdot \frac{\partial \rho(\mathbf{q}, \mathbf{p}, t)}{\partial \mathbf{p}}$$

$$= \{H, \rho(\mathbf{q}, \mathbf{p}, t)\} = i\mathcal{L}\rho(\mathbf{q}, \mathbf{p}, t). \tag{3.1}$$

Here, the Liouville operator $\mathcal{L} := -i\{H, \cdot\}$ is Hermitian, as seen by integration by parts, justified by the finiteness of our system:

$$\int f^*(\mathcal{L}g)\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p} = \int (\mathcal{L}f)^* g\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p}. \tag{3.2}$$

The observable $A(\mathbf{q}, \mathbf{p})$ has no time dependence.

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A \rangle = \lim_{\delta t \to 0} \int \frac{\rho(\mathbf{q}, \mathbf{p}, t + \delta t) - \rho(\mathbf{q}, \mathbf{p}, t)}{\delta t} A\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p} \tag{3.3}$$

$$= \int (i\mathcal{L}\rho(\mathbf{q}, \mathbf{p}, t))A\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p} = i \int \rho(\mathbf{q}, \mathbf{p}, t)(\mathcal{L}A)^*\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p} \tag{3.4}$$

$$= -i \int \rho(\mathbf{q}, \mathbf{p}, t)(\mathcal{L}A)\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{p} = \langle -i\mathcal{L}A \rangle. \tag{3.5}$$

In summary,

$$\rho(\mathbf{q}, \mathbf{p}, t) = e^{i\mathcal{L}t}\rho(\mathbf{q}, \mathbf{p}, 0), \quad \frac{\mathrm{d}}{\mathrm{d}t}\langle A \rangle = \langle -i\mathcal{L}A \rangle. \tag{3.6}$$

- In QM, an evolving ensemble is a mixed state $\hat{\rho}(t) = \sum_i |\psi_i(t)\rangle p_i \langle \psi_i(t)|$ that follows von Neumann's equation:

$$\lim_{\delta t \to 0} \frac{\hat{\rho}(t + \delta t) - \hat{\rho}(t)}{\delta t} = \lim_{\delta t \to 0} \sum_i \frac{|\psi_i(t + \delta t)\rangle p_i \langle \psi_i(t)| + |\psi_i(t)\rangle p_i \langle \psi_i(t + \delta t)|}{\delta t}$$

$$= \sum_i -iH|\psi_i(t)\rangle p_i \langle \psi_i(t)| + \sum_i |\psi_i(t)\rangle p_i \langle \psi_i(t)|iH$$

$$= -i[H, \hat{\rho}(t)] = i\mathcal{L}\hat{\rho}(t). \tag{3.7}$$

Here, the Liouville operator $\mathcal{L} := -[H, \cdot]$ is Hermitian, as can be directly verified:

$$\text{tr}(f^\dagger(\mathcal{L}g)) = \text{tr}((\mathcal{L}f)^\dagger g). \tag{3.8}$$

The observable $\hat{A}$ has no time dependence.

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A \rangle = \lim_{\delta t \to 0} \text{tr}\left(\frac{\hat{\rho}(t + \delta t) - \hat{\rho}(t)}{\delta t} A\right) \tag{3.9}$$

$$= \text{tr}((i\mathcal{L}\hat{\rho}(t))A) = i\,\text{tr}(\hat{\rho}(t)(\mathcal{L}A)^\dagger) \tag{3.10}$$

$$= -i\,\text{tr}(\hat{\rho}(t)(\mathcal{L}A)) = \langle -i\mathcal{L}A \rangle. \tag{3.11}$$

In summary,

$$\hat{\rho}(t) = e^{i\mathcal{L}t}\hat{\rho}(0), \quad \frac{\mathrm{d}}{\mathrm{d}t}\langle A \rangle = \langle -i\mathcal{L}A \rangle. \tag{3.12}$$

Notice that we have used the Euler/Schrödinger picture, where the state evolves with the observable fixed. We could also work in the Lagrange/Heisenberg picture, where the observable evolves with the state fixed, in which case the ensemble entropy is conserved.

- Classically, an ensemble is a history-recording distribution $\rho(\mathbf{q}(t), \mathbf{p}(t), t) = \rho(\mathbf{q}(0), \mathbf{p}(0), 0)$:

$$\lim_{\delta t \to 0} \frac{\rho(\mathbf{q}(t + \delta t), \mathbf{p}(t + \delta t), t + \delta t) - \rho(\mathbf{q}(t), \mathbf{p}(t), t)}{\delta t} = 0. \tag{3.13}$$

The observable is a time-dependent function $A(\mathbf{q}(t), \mathbf{p}(t)) = A_t(\mathbf{q}(0), \mathbf{p}(0))$ that follows Hamilton's equation:

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = -\{H, A_t\} = -i\mathcal{L}A_t. \tag{3.14}$$

The expectation value evolves in the same way in both pictures.

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A_t \rangle = \lim_{\delta t \to 0} \int \rho(\mathbf{q}(0), \mathbf{p}(0), 0) \frac{A_{t+\delta t}(\mathbf{q}(0), \mathbf{p}(0)) - A_t(\mathbf{q}(0), \mathbf{p}(0))}{\delta t} \mathrm{d}\mathbf{q}(0)\mathrm{d}\mathbf{p}(0)$$

$$= \langle -i\mathcal{L}A_t \rangle. \tag{3.15}$$

- In QM, a Heisenberg ensemble is a Heisenberg mixed state $\hat{\rho} = \sum_i |\psi_i\rangle p_i \langle\psi_i|$:

$$\lim_{\delta t \to 0} \frac{\hat{\rho} - \hat{\rho}}{\delta t} = 0. \tag{3.16}$$

The observable is a time-dependent operator A_t that follows Heisenberg's equation:

$$\frac{\mathrm{d}A_t}{\mathrm{d}t} = i[H, A_t] = -i\mathcal{L}A_t. \tag{3.17}$$

The expectation value evolves in the same way in both pictures.

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle A_t \rangle = \lim_{\delta t \to 0} \text{tr}\left(\hat{\rho}\frac{A_{t+\delta t} - A_t}{\delta t}\right)$$

$$= \langle -i\mathcal{L}A_t \rangle. \tag{3.18}$$

We may now answer the first question posed at the beginning, namely the definition of equilibrium. At equilibrium, the density ρ commutes with the Hamiltonian ($\mathcal{L}\rho = 0$). One possible solution is such that ρ is a function of H, in which case all constant-energy states are equally likely. This is what happens in the microcanonical ensemble! If the system has other conserved quantities, ρ commutes with H as long as it is a function of these conserved variables, in which case all microstates at a specific set of values of these macroscopic variables are equally likely.

Microscopically, the equation of motion has time-reversal symmetry. Therefore, the best we can hope for is to show that ρ_t stays in the vicinity of ρ_{eq} for the majority of time. Whether this is justified is the famous problem of ergodicity. Naively, one might think that macroscopic quantities are averages of long samples over time anyway, so that the representative point of the system uniformly samples the accessible states. However, in the few systems where it is possible to prove an ergodic theorem, the regression time is usually too long for our purposes. As such, these proofs "have so far little to do with the reality of macroscopic equilibrium", and we have to accept that the ergodicity hypothesis is only an assumption.

From now on, we will focus on classical systems and work in the Euler/Schrödinger picture.

3.2 The BBGKY Hierarchy

The Liouville equation, although formally quite simple, is impossible to solve due to the intractible amount of degrees of freedom. We need an equivalent formulation from which it is easier to make approximations. Here, the keen observation is that the dynamical variables of practical interest are often sums/averages of microscopic variables involving a small number of particles. For instance, the total energy is the sum of energies of individual paritcles, which is trivially related to the average energy of a typical particle. Thus, as far as the energy is concerned, we can take a mean-field approach, focusing on the effective action on one particle due to the environment and the other particles.

Given a distribution $\rho(\mathbf{q}, \mathbf{p}, t)$, the probability of finding any s particles at $(\mathbf{q}_1, \mathbf{p}_1), \cdots, (\mathbf{q}_s, \mathbf{p}_s)$ is:

$$f_s(\mathbf{q}_1, \mathbf{p}_1, \cdots, \mathbf{q}_s, \mathbf{p}_s, t) = \frac{N!}{(N-s)!} \int \rho(\mathbf{q}, \mathbf{p}, t) \prod_{i=s+1}^{N} \mathrm{d}\mathbf{q}_i \mathrm{d}\mathbf{p}_i = \frac{N!}{(N-s)!} \rho_s(\mathbf{q}_1, \mathbf{p}_1, \cdots, \mathbf{q}_s, \mathbf{p}_s, t). \quad (3.19)$$

The Hamiltonian can be separated into three parts: a term H_s involving the s particles only, a term H_{N-s} involving the rest of the particles, and a term H_{int} involving interactions between both groups. The time evolution of ρ_s follows the Liouville equation: (recall that in the E/S picture, time evolution is a partial derivative)

$$\frac{\partial \rho_s}{\partial t} = \int \{H_s + H_{N-s} + H_{\mathrm{int}}, \rho\} \prod_{i=s+1}^{N} \mathrm{d}\mathbf{q}_i \mathrm{d}\mathbf{p}_i. \quad (3.20)$$

- Since H_s is independent of the other particles,

$$\int \{H_s, \rho\} \prod_{i=s+1}^{N} \mathrm{d}\mathbf{q}_i \mathrm{d}\mathbf{p}_i = \left\{H_s, \int \rho \prod_{i=s+1}^{N} \mathrm{d}\mathbf{q}_i \mathrm{d}\mathbf{p}_i\right\} = \{H_s, \rho_s\}. \quad (3.21)$$

- Since H_{N-s} depends on the other particles only, using Hermiticity of $\{H_{N-s}, \cdot\}$ (i.e., IBP),

$$\int \{H_{N-s}, \rho\} \prod_{i=s+1}^{N} \mathrm{d}\mathbf{q}_i \mathrm{d}\mathbf{p}_i = -\int \rho \{H_{N-s}, 1\} \prod_{i=s+1}^{N} \mathrm{d}\mathbf{q}_i \mathrm{d}\mathbf{p}_i = 0. \quad (3.22)$$

Often, the Hamiltonian takes the form $H = \sum_{i=1}^{N} \left(\mathbf{p}_i^2/2m + U(\mathbf{q}_i)\right) + \frac{1}{2} \sum_{i<j} V(\mathbf{q}_i - \mathbf{q}_j)$. In this case, the interaction term becomes: (the second term vanishes by IBP since V is independent of $\mathbf{p}$)

$$\int \{H_{\mathrm{int}}, \rho\} \prod_{i=s+1}^{N} \mathrm{d}\mathbf{q}_i \mathrm{d}\mathbf{p}_i = \int \mathrm{d}\mathbf{q}_i \mathrm{d}\mathbf{p}_i \sum_{k=1}^{s} \sum_{j=s+1}^{N} \left[\frac{\partial \rho}{\partial \mathbf{p}_k} \cdot \frac{\partial V(\mathbf{q}_k - \mathbf{q}_j)}{\partial \mathbf{q}_k} + \frac{\partial \rho}{\partial \mathbf{p}_j} \cdot \frac{\partial V(\mathbf{q}_k - \mathbf{q}_j)}{\partial \mathbf{q}_j}\right]$$

$$= (N-s) \sum_{k=1}^{s} \int \mathrm{d}\mathbf{q}_{s+1} \mathrm{d}\mathbf{p}_{s+1} \frac{\partial V(\mathbf{q}_k - \mathbf{q}_j)}{\partial \mathbf{q}_k} \cdot \frac{\partial}{\partial \mathbf{p}_k} \int \prod_{i=s+2}^{N} \mathrm{d}\mathbf{q}_i \mathrm{d}\mathbf{p}_i \, \rho. \quad (3.23)$$

Therefore, we obtain the BBGKY hierarchy, which is equivalent to the Liouville equation:

$$\frac{\partial f_s}{\partial t} - \{H_s, f_s\} = \sum_{k=1}^{s} \int \mathrm{d}\mathbf{q}_{s+1} \mathrm{d}\mathbf{p}_{s+1} \frac{\partial V(\mathbf{q}_k - \mathbf{q}_{s+1})}{\partial \mathbf{q}_k} \cdot \frac{\partial f_{s+1}}{\partial \mathbf{p}_k}. \quad (3.24)$$

The s-particle distribution evolves like a free system, except for the effective action due to the $(s+1)$-th particle. This is true as long as there are only pair interactions.

We can now use physical arguments to cut off the series at some point.

Example: Mean field approximation and the Vlasov equation. In a mean field theory, we neglect the correlations between one microstate and another, so that $\rho_2(\mathbf{q}_1, \mathbf{p}_1, \mathbf{q}_2, \mathbf{p}_2, t) \approx \rho_1(\mathbf{q}_1, \mathbf{p}_1, t)\rho_1(\mathbf{q}_2, \mathbf{p}_2, t)$ and $f_2 \approx \frac{N-1}{N} f_1 f_1 \approx f_1 f_1$. Then, the BBGKY series is cut off, and we are left with a non-linear equation of f_1:

$$\frac{\partial f_1}{\partial t} - \{H_1, f_1\} = \int \mathrm{d}\mathbf{q}_2 \mathrm{d}\mathbf{p}_2 \frac{\partial V(\mathbf{q}_1 - \mathbf{q}_2)}{\partial \mathbf{q}_1} \cdot \frac{\partial f_1(\mathbf{q}_1, \mathbf{p}_1, t)}{\partial \mathbf{p}_1} f_1(\mathbf{q}_2, \mathbf{p}_2, t), \quad (3.25)$$

or, after some simplifications,

$$\frac{\partial f_1}{\partial t} + \frac{\partial f_1}{\partial \mathbf{q}_1} \cdot \mathbf{v}_1 + \frac{\partial f_1}{\partial \mathbf{p}_1} \cdot \left[\mathbf{F}_1^{(\mathrm{ext})} + \int \mathrm{d}\mathbf{q}_2 \mathrm{d}\mathbf{p}_2 \, f_1(\mathbf{q}_2, \mathbf{p}_2, t) \mathbf{F}_{1, \mathrm{from \, 2}}\right] = 0. \quad (3.26)$$

3.3 The Boltzmann Equation

In this section, we follow [Kardar]. Recall the BBGKY hierarchy:

$$\left[\frac{\partial}{\partial t} + \sum_{k=1}^{s}\left(\mathbf{v}_k \cdot \frac{\partial}{\partial \mathbf{q}_k} + \mathbf{F}_k^{(\text{ext})} \cdot \frac{\partial}{\partial \mathbf{p}_k}\right) + \sum_{1 \le j < k \le s} \mathbf{F}_{j,k} \cdot \left(\frac{\partial}{\partial \mathbf{p}_j} - \frac{\partial}{\partial \mathbf{p}_k}\right)\right] f_s(\{\mathbf{q}, \mathbf{p}\}_{k=1}^{s}, t)$$

$$= \int \mathrm{d}\mathbf{q}_{s+1}\mathrm{d}\mathbf{p}_{s+1}\left[\sum_{k=1}^{s} \mathbf{F}_{k,s+1} \cdot \frac{\partial}{\partial \mathbf{p}_k}\right] f_{s+1}(\{\mathbf{q}, \mathbf{p}\}_{k=1}^{s}, \mathbf{q}_{s+1}, \mathbf{p}_{s+1}, t), \quad (3.27)$$

where $\mathbf{v}_k := \mathbf{p}_k/m$, $\mathbf{F}_k^{(\text{ext})} := -\partial U(\mathbf{q}_k)/\partial \mathbf{q}_k$, and $\mathbf{F}_{j,k} := -\partial V(\mathbf{q}_j - \mathbf{q}_k)/\partial \mathbf{q}_j = -\mathbf{F}_{k,j}$.

- The time derivative $\partial/\partial t \sim 1/\tau$ corresponds to the time scale over which we study the evolution of our system.

- The drift terms $\mathbf{v} \cdot \partial/\partial \mathbf{q} \sim 1/\tau_e$, $\mathbf{F}^{(\text{ext})} \cdot \partial/\partial \mathbf{p} \sim 1/\tau_e$ correspond to the time scale L/v over which a molecule travels across the system.

- The collision terms $\mathbf{F} \cdot \partial/\partial \mathbf{p} \sim 1/\tau_c$ corresponds to the time scale d/v over which molecular scattering occurs, which is very small for short-range interactions.

- Since $f_{s+1}/f_s \sim n$, the $(s+1)$-particle marginalization contributes a factor $\sim nd^3$ because it is only non-vanishing over the range of molecular interactions. Hence, the RHS $\sim 1/\tau_\times$ where $\tau_\times = \tau_c/nd^3 \gg \tau_c$ for short-range interactions.

Typically, $\tau_c \ll \tau_\times \ll \tau_e$, so that the BBGKY equations split into two types: for $s = 1$, there are no collision terms on the LHS; for $s \ge 2$, there are collision terms on the LHS, so that the RHS can be neglected. Since we are usually interested in f_1, we focus on the first two equations:

$$\begin{cases} \left[\dfrac{\partial}{\partial t} + \mathbf{v}_1 \cdot \dfrac{\partial}{\partial \mathbf{q}_1} + \mathbf{F}_1^{(\text{ext})} \cdot \dfrac{\partial}{\partial \mathbf{p}_1}\right] f_1 = \displaystyle\int \mathrm{d}\mathbf{q}_2\mathrm{d}\mathbf{p}_2 \left[\mathbf{F}_{1,2} \cdot \dfrac{\partial}{\partial \mathbf{p}_1}\right] f_2, \\[2mm] \left[\dfrac{\partial}{\partial t} + \mathbf{v}_1 \cdot \dfrac{\partial}{\partial \mathbf{q}_1} + \mathbf{v}_2 \cdot \dfrac{\partial}{\partial \mathbf{q}_2} + \mathbf{F}_{1,2} \cdot \left(\dfrac{\partial}{\partial \mathbf{p}_1} - \dfrac{\partial}{\partial \mathbf{p}_2}\right)\right] f_2 = 0. \end{cases} \quad (3.28)$$

Define the center-of-mass coordinates $\mathbf{Q} = (\mathbf{q}_1 + \mathbf{q}_2)/2$ and $\mathbf{q} = \mathbf{q}_2 - \mathbf{q}_1$. The second equation becomes:

$$\left[\frac{\partial}{\partial t} + \frac{\mathbf{v}_1 + \mathbf{v}_2}{2} \cdot \frac{\partial}{\partial \mathbf{Q}} - (\mathbf{v}_1 - \mathbf{v}_2) \cdot \frac{\partial}{\partial \mathbf{q}} + \mathbf{F}_{1,2} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right)\right] f_2 = 0. \quad (3.29)$$

Of these four terms, the last two are of the order $1/\tau_c$, which is much larger than $1/\tau_e$ or $1/\tau$. Therefore, the first equation becomes (after adding a vanishing boundary term $\int \mathbf{F}_{1,2} \cdot \partial/\partial \mathbf{p}_2$):

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{q}_1} + \mathbf{F}_1^{(\text{ext})} \cdot \frac{\partial}{\partial \mathbf{p}_1}\right] f_1 = \int \mathrm{d}^3\mathbf{p}_2 \mathrm{d}^3\mathbf{q} \left[(\mathbf{v}_1 - \mathbf{v}_2) \cdot \frac{\partial}{\partial \mathbf{q}}\right] f_2. \quad (3.30)$$

Since $\mathbf{v}_1 - \mathbf{v}_2 = \partial \mathbf{q}/\partial t$,

$$\begin{aligned} \text{RHS} &= \int \mathrm{d}^3\mathbf{p}_2\mathrm{d}^2\mathbf{q}_\perp|\mathbf{v}_1 - \mathbf{v}_2|\mathrm{d}t\frac{\partial f_2}{\partial t} \\ &= \int \mathrm{d}^3\mathbf{p}_2\mathrm{d}^2\mathbf{q}_\perp|\mathbf{v}_1 - \mathbf{v}_2|(f_2^{(\text{after})}(\mathbf{q}_1, \mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_\perp, t) - f_2^{(\text{before})}(\mathbf{q}_1, \mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_\perp, t)) \\ &= \int \mathrm{d}^3\mathbf{p}_2\mathrm{d}^2\mathbf{q}_\perp|\mathbf{v}_1 - \mathbf{v}_2|(f_2^{(\text{before})}(\mathbf{q}_1, \mathbf{p}_1', \mathbf{p}_2', \mathbf{q}_\perp, t) - f_2^{(\text{before})}(\mathbf{q}_1, \mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_\perp, t)), \quad (3.31) \end{aligned}$$

where we made use of $\mathrm{d}f_2/\mathrm{d}t = 0$ during streaming in the last step.

Up to now, although we have made quite a few approximations, everything is still time-reversal invariant. Now, we turn a blind eye to $\mathbf{q}_\perp$ (coarse graining), and impose the molecular chaos assumption that before each collision occurs, the two particles are uncorrelated:

$$f_2^{(\text{before})}(\mathbf{q}_1, \mathbf{p}_1, \mathbf{p}_2, \mathbf{q}_\perp, t) = f_1(\mathbf{q}_1, \mathbf{p}_1, t)f_1(\mathbf{q}_1, \mathbf{p}_2, t). \quad (3.32)$$

The molecular chaos assumption is not time-reversal invariant, because it forcifully erases any correlation produced by previous collisions. This way, we obtain the Boltzmann equation:

$$\left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{q}_1} + \mathbf{F}_1^{(\text{ext})} \cdot \frac{\partial}{\partial \mathbf{p}_1}\right] f_1(\mathbf{q}_1, \mathbf{p}_1, t)$$

$$= \int \mathrm{d}^3\mathbf{p}_2 \mathrm{d}\Omega \left|\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right| |\mathbf{v}_1 - \mathbf{v}_2| \left(f_1(\mathbf{q}_1, \mathbf{p}_1', t) f_1(\mathbf{q}_1, \mathbf{p}_2', t) - f_1(\mathbf{q}_1, \mathbf{p}_1, t) f_1(\mathbf{q}_1, \mathbf{p}_2, t)\right). \quad (3.33)$$

3.4 The H-Theorem

For a (approximated) reduced density $f_1(\mathbf{q}, \mathbf{q}, t)$ satisfying the Boltzmann equation, it can be shown that the entropy associated with this distribution always increases over time. This is known as the H-theorem. To prove this, define the functional:

$$H(t) = \int \mathrm{d}\mathbf{q}_1 \mathrm{d}\mathbf{p}_1 \, f_1(\mathbf{q}_1, \mathbf{p}_1, t) \ln f_1(\mathbf{q}_1, \mathbf{p}_1, t). \quad (3.34)$$

Consider its time derivative:

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \int \mathrm{d}\mathbf{q}_1 \mathrm{d}\mathbf{p}_1 \frac{\partial f_1}{\partial t} (\ln f_1 + 1)$$

$$= \int \mathrm{d}\mathbf{q}_1 \mathrm{d}\mathbf{p}_1 \frac{\partial f_1}{\partial t} \ln f_1$$

$$= \int \mathrm{d}\mathbf{q}_1 \mathrm{d}\mathbf{p}_1 \ln f_1 \left(\frac{\partial U(\mathbf{q}_1)}{\partial \mathbf{q}_1} \cdot \frac{\partial f_1}{\partial \mathbf{p}_1} - \frac{\mathbf{p}_1}{m} \cdot \frac{\partial f_1}{\partial \mathbf{q}_1}\right)$$

$$+ \int \mathrm{d}^3\mathbf{q}_1 \mathrm{d}^3\mathbf{p}_1 \mathrm{d}^3\mathbf{p}_2 \mathrm{d}^2\sigma |\mathbf{v}_1 - \mathbf{v}_2| \left(f_1(\mathbf{p}_1') f_1(\mathbf{p}_2') - f_1(\mathbf{p}_1) f_1(\mathbf{p}_2)\right) \ln f_1(\mathbf{p}_1), \quad (3.35)$$

Since the streaming terms vanish by successive IBPs, by symmetry under $(\mathbf{p}_1 \leftrightarrow \mathbf{p}_2, \mathbf{p}_1' \leftrightarrow \mathbf{p}_2')$,

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{1}{2} \int \mathrm{d}^3\mathbf{q}_1 \mathrm{d}^3\mathbf{p}_1 \mathrm{d}^3\mathbf{p}_2 \mathrm{d}^2\sigma |\mathbf{v}_1 - \mathbf{v}_2| \left(f_1(\mathbf{p}_1') f_1(\mathbf{p}_2') - f_1(\mathbf{p}_1) f_1(\mathbf{p}_2)\right) \ln \left(f_1(\mathbf{p}_1) f_1(\mathbf{p}_2)\right). \quad (3.36)$$

As [Weinberg] pointed out, time-reversal symmetry is NOT necessary in completing the proof. Write the differential cross section for fixed $(\mathbf{p}_1, \mathbf{p}_2)$ in terms of scattering amplitudes:

$$\mathrm{d}^2\sigma |\mathbf{v}_1 - \mathbf{v}_2| = \mathcal{C} \mathrm{d}^3\mathbf{p}_1' \mathrm{d}^3\mathbf{p}_2' |\mathcal{M}_{\mathbf{p}_1\mathbf{p}_2 \to \mathbf{p}_1'\mathbf{p}_2'}|^2 \delta^{(4)}(p - p'). \quad (3.37)$$

It's possible to prove the H-theorem using the Born approximation or PT-symmetry, which implies $|\mathcal{M}_{\mathbf{p}_1\mathbf{p}_2 \to \mathbf{p}_1'\mathbf{p}_2'}|^2 = |\mathcal{M}_{\mathbf{p}_1'\mathbf{p}_2' \to \mathbf{p}_1\mathbf{p}_2}|^2$. However, it suffices to use unitarity alone for the underlying microscopic evolutions, which says (for elastic scattering so that all products are two-particle states)

$$\mathcal{C}' \, \mathrm{Im}\, \mathcal{M}_{\mathbf{p}_1\mathbf{p}_2 \to \mathbf{p}_1\mathbf{p}_2} = \int \mathrm{d}^3\mathbf{p}_1' \mathrm{d}^3\mathbf{p}_2' |\mathcal{M}_{\mathbf{p}_1\mathbf{p}_2 \to \mathbf{p}_1'\mathbf{p}_2'}|^2 \delta^{(4)}(p - p') = \int \mathrm{d}^3\mathbf{p}_1' \mathrm{d}^3\mathbf{p}_2' |\mathcal{M}_{\mathbf{p}_1'\mathbf{p}_2' \to \mathbf{p}_1\mathbf{p}_2}|^2 \delta^{(4)}(p - p').$$
$$(3.38)$$

Using it and changing labels $(\mathbf{p}_1 \leftrightarrow \mathbf{p}_1', \mathbf{p}_2 \leftrightarrow \mathbf{p}_2')$ for the second term in $\mathrm{d}H/\mathrm{d}t$,

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{1}{2} \int \mathrm{d}^3\mathbf{q}_1 \mathrm{d}^3\mathbf{p}_1 \mathrm{d}^3\mathbf{p}_2 \mathrm{d}^2\sigma |\mathbf{v}_1 - \mathbf{v}_2| f_1(\mathbf{p}_1') f_1(\mathbf{p}_2') \ln \frac{f_1(\mathbf{p}_1) f_1(\mathbf{p}_2)}{f_1(\mathbf{p}_1') f_1(\mathbf{p}_2')} \quad (3.39)$$

$$\leq \frac{1}{2} \int \mathrm{d}^3\mathbf{q}_1 \mathrm{d}^3\mathbf{p}_1 \mathrm{d}^3\mathbf{p}_2 \mathrm{d}^2\sigma |\mathbf{v}_1 - \mathbf{v}_2| \left(f_1(\mathbf{p}_1') f_1(\mathbf{p}_2') - f_1(\mathbf{p}_1) f_1(\mathbf{p}_2)\right), \quad (3.40)$$

where we have used the fact that $y \ln(x/y) \leq x - y$ for $x > 0$ and $y > 0$. Now, repeat the process for the second term,

$$\frac{\mathrm{d}H}{\mathrm{d}t} \leq \frac{1}{2} \int \mathrm{d}^3\mathbf{q}_1 \mathrm{d}^3\mathbf{p}_1 \mathrm{d}^3\mathbf{p}_2 \mathrm{d}^2\sigma |\mathbf{v}_1 - \mathbf{v}_2| \left(f_1(\mathbf{p}_1') f_1(\mathbf{p}_2') - f_1(\mathbf{p}_1') f_1(\mathbf{p}_2')\right) = 0. \quad (3.41)$$

With the Boltzmann equation and the H-theorem established, we may now answer the remaining two questions posed at the beginning, at least for the approximated one-particle reduced density. A system with short-range pair-interactions satisfying the molecular chaos assumption can be approximated as a one-particle reduced density f_1 following the Boltzmann equation, and it does evolve irreversibly towards an equilibrium state.

3.5 Equilibrium

Recall that we now have three scales to look at the system:

- Microscopically, the system satisfies the Liouville equation; there is no notion of equilibrium.

- Macroscopically, the system is described by thermodynamics; there is the notion of global equilibrium.

- Mesoscopically, the system satisfies the Boltzmann equation and is described by hydronamics; there is the notion of local equilibrium.

Whether global or local, a system at equilibrium satisfies $\mathrm{d}H/\mathrm{d}t = 0$, which is equivalent to the detailed balance condition:

$$f_1(\mathbf{q}_1, \mathbf{p}_1, t) f_1(\mathbf{q}_1, \mathbf{p}_2, t) = f_1(\mathbf{q}_1, \mathbf{p}_1', t) f_1(\mathbf{q}_1, \mathbf{p}_2', t). \tag{3.42}$$

In other words, the quantity $\ln f_1(\mathbf{q}, \mathbf{p}, t)$ is an additive conserved quantity during a collision. Since an elastic collision has five additive conserved quantities (particle number, kinetic energy, three components of momentum),

$$\ln f_1(\mathbf{q}, \mathbf{p}, t) = -\alpha(\mathbf{q}, t) - \boldsymbol{\gamma}(\mathbf{q}, t) \cdot \mathbf{p} - \beta(\mathbf{q}, t) \frac{\mathbf{p}^2}{2m}. \tag{3.43}$$

After some recombination, we may write

$$f_1(\mathbf{q}, \mathbf{p}, t) = \mathcal{N}(\mathbf{q}, t) \exp\left(-\beta(\mathbf{q}, t)\left(\frac{(\mathbf{p} - \boldsymbol{\pi}(\mathbf{q}, t))^2}{2m} + U(\mathbf{q})\right)\right). \tag{3.44}$$

Any distribution of the above form is in local equilibrium: it remains intact during a collision (the RHS of the Boltzmann equation vanishes). However, its time derivative is not zero since there are also streaming terms. For a system at rest to be in global equilibrium, we need $\{H_1, f_1\} = 0$, which implies $\mathcal{N}(\mathbf{q}, t) \equiv \mathcal{N}$, $\beta(\mathbf{q}, t) \equiv \beta$, and $\boldsymbol{\pi}(\mathbf{p}, t) \equiv 0$, which is the Boltamann distribution.

To see the physical meaning of these parameters, consider the global equilibrium of a gas constrained by $U(\mathbf{q})$ in a box of volumn V.

- Normalization $N = \int \mathrm{d}^3 q \mathrm{d}^3 p \, f_1(\mathbf{q}, \mathbf{p})$ implies:

$$N = \mathcal{N}V \int \mathrm{d}^3\mathbf{p} \exp\left(-\beta \frac{\mathbf{p}^2}{2m}\right) = \mathcal{N}V \left(\frac{2\pi m}{\beta}\right)^{3/2} \implies \mathcal{N} = n \left(\frac{\beta}{2\pi m}\right)^{3/2}. \tag{3.45}$$

- The Gaussian distribution $\rho_1 = f_1/N$ is characterized by $\langle \mathbf{p} \rangle = \boldsymbol{\pi}$ and $\langle \mathbf{p}^2 \rangle = 3m/\beta$.

- Consider two types of gases A, B in the same box. Denote the collision terms as:

$$C_{\alpha,\beta} = \int \mathrm{d}^3\mathbf{p}_2 \mathrm{d}\Omega \left|\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right| |\mathbf{v}_1 - \mathbf{v}_2| (f_1^{(\alpha)}(\mathbf{p}_1') f_1^{(\beta)}(\mathbf{p}_2') - f_1^{(\alpha)}(\mathbf{p}_1) f_1^{(\beta)}(\mathbf{p}_2)). \tag{3.46}$$

The Boltzmann equations become:

$$\begin{cases} \partial_t f_1^{(A)} - \{H_1^{(A)}, f_1^{(A)}\} = C_{A,A} + C_{A,B}, \\ \partial_t f_1^{(B)} - \{H_1^{(B)}, f_1^{(B)}\} = C_{B,A} + C_{B,B}. \end{cases} \tag{3.47}$$

For the system to be in global equilibrium, in addition to $C_{\alpha,\alpha} = 0$ which implies $f_1^{(\alpha)} \propto e^{-\beta_\alpha H_1^{(\alpha)}}$, we need

$$C_{A,B} = 0 \implies \beta_A H_1^{(A)}(\mathbf{p}_1') + \beta_B H_1^{(B)}(\mathbf{p}_2') = \beta_A H_1^{(A)}(\mathbf{p}_1) + \beta_B H_1^{(B)}(\mathbf{p}_2). \tag{3.48}$$

Since $H_1^{(A)} + H_1^{(B)}$ is conserved during a collision, the above equation is equivalent to $\beta_A = \beta_B = \beta$, so that β plays the role of an empirical temperature. Then, following Maxwell's argument to compute the pressure of an ideal gas, we easily obtain $\beta = 1/k_B T$.

Therefore, we see that a system in local equilibrium is described by:

$$f_1(\mathbf{q}, \mathbf{p}, t) = n(\mathbf{q}, t)(2\pi m k_B T(\mathbf{q}, t))^{-3/2} \exp\left(-\frac{1}{k_B T(\mathbf{q}, t)} \left(\frac{(\mathbf{p} - \langle \mathbf{p} \rangle(\mathbf{q}, t))^2}{2m} + U(\mathbf{q})\right)\right). \tag{3.49}$$

4 Hydronamics

After the system has relaxed to local equilibrium over time scale $\tau_\times$, it evolves towards a global equilibrium through hydronamic equations of motion.

4.1 Local Balance Equations

As discussed earlier, the local equilibrium is described by the local quantities $n(\mathbf{q}, t)$, $\boldsymbol{\pi}(\mathbf{q}, t)$, and $T(\mathbf{q}, t)$, corresponding to the three conserved quantities during collisions, namely, particle number, momentum, and kinetic energy. Therefore, the hydronamic evolution is completely captured by the equations of motion of these quantities, which we proceed to establish.

First, we consider the general case, where $\chi(\mathbf{q}, \mathbf{p}, t)$ is any additive invariant during a collision:

$$\chi(\mathbf{q}, \mathbf{p}_1, t) + \chi(\mathbf{q}, \mathbf{p}_2, t) = \chi(\mathbf{q}, \mathbf{p}_1', t) + \chi(\mathbf{q}, \mathbf{p}_2', t). \tag{4.1}$$

We are mostly interested in three cases: particle number $\chi = 1$, momentum $\vec{\chi} = \mathbf{p}$, and kinetic energy $\chi = \mathbf{p}^2/2m$. None of these depend on $\mathbf{q}$ or t. However, we have included the spacetime dependence in the general form $\chi(\mathbf{q}, \mathbf{p}, t)$, to make the following discussion as general as possible (e.g., it applies to systems inhomogeneous in space or time).

Using the same trick as in the proof of the H-theorem for χ instead of $\ln f_1$, we obtain:

$$\int d^3\mathbf{p}_1 d^3\mathbf{p}_2 d^2\sigma |\mathbf{v}_1 - \mathbf{v}_2| (f_1(\mathbf{p}_1')f_1(\mathbf{p}_2') - f_1(\mathbf{p}_1)f_2(\mathbf{p}_2))\chi(\mathbf{p}_1) = 0. \tag{4.2}$$

We stress that for the above expression to be true, unitarity at the microscopic level alone suffices. Comparing with the Boltzmann equation, we have:

$$0 = \int d^3\mathbf{p}_1 \chi(\mathbf{q}, \mathbf{p}_1, t) \left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{q}} + \mathbf{F}_1^{(\text{ext})} \cdot \frac{\partial}{\partial \mathbf{p}_1} \right] f_1(\mathbf{q}, \mathbf{p}_1, t). \tag{4.3}$$

This could be massaged into the following form:

$$\int d^3\mathbf{p}_1 \left(\left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{q}} + \mathbf{F}_1^{(\text{ext})} \cdot \cancel{\frac{\partial}{\partial \mathbf{p}_1}} \right] (\chi f_1) - f_1 \left[\frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{q}} + \mathbf{F}_1^{(\text{ext})} \cdot \frac{\partial}{\partial \mathbf{p}_1} \right] \chi \right) = 0. \tag{4.4}$$

Here, the slashed term vanishes since it is a total derivative.

Recall that our normalization is $\int d^3\mathbf{p}_1 f_1(\mathbf{q}, \mathbf{p}, t) = n(\mathbf{q}, t)$ so that the expectation value $\langle \mathcal{O} \rangle$ of any local operator $\mathcal{O}(\mathbf{q}, \mathbf{p})$ satisfies:

$$\langle \mathcal{O} \rangle (\mathbf{q}, t) = \frac{1}{n(\mathbf{q}, t)} \int d^3\mathbf{p}_1 f_1(\mathbf{q}, \mathbf{p}_1, t) \mathcal{O}(\mathbf{q}, \mathbf{p}). \tag{4.5}$$

In this form,

$$\frac{\partial}{\partial t}(n\langle\chi\rangle) + \nabla_{\mathbf{q}} \cdot (n\langle\mathbf{v}\chi\rangle) - n\langle\dot{\chi}\rangle - n\langle\mathbf{v} \cdot \nabla_{\mathbf{q}}\chi\rangle - n\mathbf{F}_1^{(\text{ext})} \cdot \langle\nabla_{\mathbf{p}}\chi\rangle = 0. \tag{4.6}$$

Now, we apply the general formula to the special cases.

- Particle number $\chi = 1$.

$$\frac{\partial}{\partial t}n + \nabla_{\mathbf{q}} \cdot (n\langle\mathbf{v}\rangle) = 0. \tag{4.7}$$

Define the velocity field $\mathbf{u}(\mathbf{q}, t) = \langle\mathbf{v}\rangle(\mathbf{q}, t)$.

$$\frac{\partial}{\partial n} + \mathbf{u} \cdot \nabla_{\mathbf{q}}n = -n\nabla_{\mathbf{q}} \cdot \mathbf{u}. \tag{4.8}$$

- Momentum of internal motion $\vec{\chi} = \mathbf{c}$, where $\mathbf{c}(\mathbf{q}, \mathbf{p}, t) = \mathbf{v} - \mathbf{u}(\mathbf{q}, t)$ so that $\langle\mathbf{c}\rangle(\mathbf{q}) = 0$.

$$\nabla_{\mathbf{q}} \cdot (n\langle(\mathbf{c} + \mathbf{u})\mathbf{c}\rangle) - n\langle\dot{\mathbf{c}}\rangle - n\langle(\mathbf{c} + \mathbf{u}) \cdot \nabla_{\mathbf{q}}\mathbf{c}\rangle - \frac{n}{m}\mathbf{F}_1^{(\text{ext})} = 0. \tag{4.9}$$

After some simplification,

$$\nabla_{\mathbf{q}} \cdot (n\langle\mathbf{c}\mathbf{c}\rangle) + n\frac{\partial}{\partial t}\mathbf{u} + n\mathbf{u} \cdot \nabla_{\mathbf{q}}\mathbf{u} - \frac{n}{m}\mathbf{F}_1^{(\text{ext})} = 0. \tag{4.10}$$

Define the pressure tensor $\hat{P} = mn\langle\mathbf{c}\mathbf{c}\rangle$.

$$\frac{\partial}{\partial t}\mathbf{u} + \mathbf{u} \cdot \nabla_{\mathbf{q}}\mathbf{u} = \frac{\mathbf{F}_1^{(\text{ext})}}{m} - \frac{1}{mn}\nabla_{\mathbf{q}} \cdot \hat{P}. \tag{4.11}$$

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- Energy of internal motion $\chi = m\mathbf{c}^2/2$. Define the local internal energy $\varepsilon = \langle m\mathbf{c}^2/2 \rangle$.

$$\frac{\partial}{\partial t}(n\varepsilon) + \nabla_{\mathbf{q}} \cdot \left(n\langle(\mathbf{c} + \mathbf{u})\frac{m\mathbf{c}^2}{2}\rangle\right) + nm\dot{\mathbf{u}} \cdot \langle\mathbf{c}\rangle + nm\langle(\mathbf{c} + \mathbf{u}) \cdot \nabla_{\mathbf{q}}\mathbf{u} \cdot \mathbf{c}\rangle - n\mathbf{F}_1^{(\text{ext})} \cdot \langle\mathbf{c}\rangle = 0. \quad (4.12)$$

Since $\langle\mathbf{c}\rangle = 0$,

$$\frac{\partial}{\partial t}(n\varepsilon) + \nabla_{\mathbf{q}} \cdot (n\mathbf{u}\varepsilon) + \nabla_{\mathbf{q}} \cdot \left(n\langle\mathbf{c}\frac{m\mathbf{c}^2}{2}\rangle\right) + \nabla_{\mathbf{q}}\mathbf{u} : \hat{P} = 0. \quad (4.13)$$

Define the local heat flux $\mathbf{h} = n\frac{m}{2}\langle\mathbf{c}\mathbf{c}^2\rangle$ and the rate of strain $\hat{u}_{\alpha\beta} = \frac{1}{2}(\partial_{q_\alpha}u_\beta + \partial_{q_\beta}u_\alpha)$.

$$\frac{\partial}{\partial t}\varepsilon + \mathbf{u} \cdot \nabla_{\mathbf{q}}\varepsilon = -\frac{1}{n}\nabla_{\mathbf{q}} \cdot \mathbf{h} - \frac{1}{n}\hat{P} : \hat{u}. \quad (4.14)$$

We have now established all the hydrodynamic equations of motion. In order to solve them, we need expression for $\hat{P}$ and $\mathbf{h}$, which are either determined phenomenologically or calculated from the density f_1.

4.2 The Chapman-Enskog Expansion

Recall that the LHS of the Boltzmann equation describes the hydrodynamic evolution of time scale τ_e and that the RHS of the Boltzmann equation describes collisions of time scale $\tau_\times$. When $\tau_\times \ll \tau_e$, we are justified to expand perturbatively around local equilibrium.

Consider the first-order ansatz $f_1 = f_1^{(0)} + f_1^{(1)}$. We choose $f_1^{(0)}$ so that it captures all the local equilibrium properties of f_1:

$$f_1^{(0)}(\mathbf{q}, \mathbf{p}, t) = n(\mathbf{q}, t)(2\pi mk_BT(\mathbf{q}, t))^{-3/2}\exp\left(-\frac{(\mathbf{p} - m\mathbf{u}(\mathbf{q}, t))^2}{2mk_BT(\mathbf{q}, t)}\right), \quad (4.15)$$

$$\int \mathrm{d}^3\mathbf{p}f_1(\mathbf{q}, \mathbf{p}, t)\begin{pmatrix}1\\\mathbf{v}\\\mathbf{v}^2\end{pmatrix} = \int \mathrm{d}^3\mathbf{p}f_1^{(0)}(\mathbf{q}, \mathbf{p}, t)\begin{pmatrix}1\\\mathbf{v}\\\mathbf{v}^2\end{pmatrix}, \quad \int \mathrm{d}^3\mathbf{p}f_1^{(1)}(\mathbf{q}, \mathbf{p}, t)\begin{pmatrix}1\\\mathbf{v}\\\mathbf{v}^2\end{pmatrix} = 0. \quad (4.16)$$

Here, we consider the interior of the box, so that $U(\mathbf{q}) = 0$. Denote the RHS of the Boltamann equation as the collision bilinear $\mathcal{C}[f_1|f_1]$. Being at local equilibrium, $f_1^{(0)}$ satisfies $\mathcal{C}[f_1^{(0)}|f_1^{(0)}] = 0$. The first-order correction $f_1^{(1)}$ thus satisfies, alongside the above-mentioned constraints, the following equation:

$$\frac{\partial}{\partial t}f_1^{(0)} + \mathbf{v} \cdot \nabla_{\mathbf{q}}f_1^{(0)} + \mathbf{F}^{(\text{ext})} \cdot \nabla_{\mathbf{p}}f_1^{(0)} = \mathcal{C}[f_1^{(0)}|f_1^{(1)}] + \mathcal{C}[f_1^{(1)}|f_1^{(0)}]. \quad (4.17)$$

At the zeroth order, recall the definition $\mathbf{c} := \mathbf{v} - \langle\mathbf{v}\rangle$.

$$\hat{P} := mn\langle\mathbf{c}\mathbf{c}\rangle = nk_BT\hat{I}, \quad \varepsilon = \frac{m}{2}\langle\mathbf{c}^2\rangle = \frac{3}{2}k_BT, \quad \mathbf{h} := \frac{mn}{2}\langle\mathbf{c}\mathbf{c}^2\rangle = 0. \quad (4.18)$$

Since the collision terms vanish identically at this order, the system is non-dissipative. This can also be seen from the equations of motion:

$$\begin{cases}\dfrac{\mathrm{D}}{\mathrm{D}t}n = -n\nabla_{\mathbf{q}} \cdot \mathbf{u} \\[2mm] m\dfrac{\mathrm{D}}{\mathrm{D}t}\mathbf{u} = \mathbf{F}_1^{(\text{ext})} - \dfrac{1}{n}\nabla_{\mathbf{q}}(nk_BT) \\[2mm] \dfrac{\mathrm{D}}{\mathrm{D}t}\varepsilon = -k_BT\nabla_{\mathbf{q}} \cdot \mathbf{u}\end{cases} \implies \frac{\mathrm{D}}{\mathrm{D}t}\ln(nT^{-3/2}) = 0. \quad (4.19)$$

Here, $\mathrm{D}/\mathrm{D}t := \partial/\partial t + \mathbf{u} \cdot \nabla_{\mathbf{q}}$ is the material derivative. Since $\ln(nT^{-3/2})$ is the local ensemble entropy (up to a constant), we see that it never changes along the flow of a piece of matter.

At the first order, we employ the relaxation time approximation, which replaces the collision terms $\mathcal{C}[f_1^{(0)}|f_1^{(1)}] + \mathcal{C}[f_1^{(1)}|f_1^{(0)}]$ with $-f_1^{(1)}/\tau_\times$. The first-order correction is thus:

$$f_1^{(1)} = -\tau_\times f_1^{(0)}\left(\frac{m}{k_BT}\hat{u} : \left(\mathbf{c}\mathbf{c} - \frac{1}{3}\mathbf{c}^2\hat{I}\right) + \frac{\mathbf{c} \cdot \nabla_{\mathbf{q}}T}{T}\left(\frac{m\mathbf{c}^2}{2k_BT} - \frac{5}{2}\right)\right). \quad (4.20)$$

After quite some simplifying efforts,

$$\hat{P} = nk_B T \hat{I} - 2nk_B T \tau_\times \left(\hat{u} - \frac{\hat{I}}{3} \nabla_{\mathbf{q}} \cdot \mathbf{u} \right), \quad \mathbf{h} = -\frac{5}{2} \frac{nk_B^2 T \tau_\times}{m} \nabla_{\mathbf{q}} T. \tag{4.21}$$

The first order solution captures the essential evolution towards a global equilibrium. To see this, consider small deviations around a stationary global equilibrium without external forces ($\mathbf{F}_1^{(\text{ext})} = 0$):

$$n(\mathbf{q}, t) = \bar{n} + \nu(\mathbf{q}, t), \quad T(\mathbf{q}, t) = \bar{T} + \theta(\mathbf{q}, t), \quad \mathbf{u}(\mathbf{q}, t) = 0 + \mathbf{u}(\mathbf{q}, t). \tag{4.22}$$

The linearized equations of motion satisfy $\mathrm{D}/\mathrm{D}t = \partial/\partial t + \mathcal{O}(|\mathbf{u}|)$. Fourier transform the variables $\{\nu, \theta, \mathbf{u}\}$ using $\tilde{A}(\mathbf{k}, \omega) = \int \mathrm{d}^3 \mathbf{q} \mathrm{d}t \, e^{i(\mathbf{k} \cdot \mathbf{q} - \omega t)} A(\mathbf{q}, t)$. The hydrodynamic equations become:

$$\omega \begin{pmatrix} \tilde{\nu} \\ \tilde{\mathbf{u}} \\ \tilde{\theta} \end{pmatrix} = \begin{pmatrix} 0 & \bar{n}\mathbf{k} \cdot \hat{I} & 0 \\ \frac{k_B \bar{T}}{m\bar{n}}\mathbf{k} \cdot \hat{I} & \boxed{-i\frac{k_B \bar{T} \tau_\times}{m}(\mathbf{k}^2 \hat{I} + \frac{1}{3}\mathbf{k}\mathbf{k})} & \frac{k_B}{m}\mathbf{k} \cdot \hat{I} \\ 0 & \frac{2}{3}\bar{T}\mathbf{k} \cdot \hat{I} & \boxed{-i\frac{5k_B \bar{T}\mathbf{k}^2 \tau_\times}{3m}} \end{pmatrix} \begin{pmatrix} \tilde{\nu} \\ \tilde{\mathbf{u}} \\ \tilde{\theta} \end{pmatrix}. \tag{4.23}$$

The boxed terms don't exist at zeroth order, where all eigenvalues are real. Due to first-order corrections, all eigenvalues are modified with negative imaginary parts, in the sense that if $|\lambda\rangle$ is an eigenvector of the zeroth-order matrix $M^{(0)}$,

$$\mathrm{Im}\langle \lambda | M - M^{(0)} | \lambda \rangle < 0. \tag{4.24}$$

This indicates that all deviations from the global equilibrium are damped.