

Summary of SI2520 Non-Equilibrium Statistical Mechanics

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Abstract

This is a summary of SI2520 Non-equilibrium statistical mechanics.

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1 A Little Bit About Stochastic Processes

The Characteristic Function For a continuous probability distribution we define the characteristic function

$$G(k) = \int dx e^{ikx} P(x).$$

This function satisfies

$$\left. \frac{1}{i^n} \frac{d^n G}{dk^n} \right|_{k=0} = \langle X^n \rangle.$$

The Cumulant-Generating Function Likewise we define the cumulant-generating function $\ln(G)$. We expand it according to

$$\ln(G) = \sum_{m=0}^m \frac{(ik)^m}{m!} \langle \langle X^m \rangle \rangle.$$

From this relations between the cumulants and the moments can be derived.

Discrete Characteristic Functions For functions with a discrete state space we define the characteristic function

$$F(z) = \langle z^X \rangle.$$

Derivatives of this function evaluated at 1 will produce moments.

Stochastic Processes A stochastic process is a function of a random variable. We use the notation $f(X, t)$, and outcomes of X corresponds to functions

$$f(x, t) = f_x(t).$$

The moments of a stochastic process are

$$\left\langle \prod_i f(X, t_i) \right\rangle = \int dx P(x) \prod_i f_x(t_i).$$

Probability Distributions for Stochastic Processes The probability distribution for a stochastic process is defined as

$$P(x, t) = \langle \delta(x - X(t)) \rangle.$$

Similarly a joint probability distribution is defined as

$$P(x_1, t_1; \dots; x_N, t_N) = \left\langle \prod_{i=1}^N \delta(x_i - X(t_i)) \right\rangle.$$

Conditional probabilities may be defined for stochastic processes as well, and from basic probability theory we have

$$P(x_1, t_1; x_0, t_0) = P(x_1, t_1 \mid x_0, t_0) P(x_0, t_0).$$

Using the notation

$$P(x_1, t_1; \dots; x_N, t_N \mid y_1, \tau_1; \dots; y_M, \tau_M)$$

we have the convention that the events are ordered from latest to earliest with the τ corresponding to events before the t .

Markov Processes A Markov process is a process such that

$$P(x_1, t_1; \dots; x_N, t_N \mid y_1, \tau_1; \dots; y_M, \tau_M) = P(x_1, t_1; \dots; x_N, t_N \mid y_1, \tau_1).$$

For such processes we have

$$\begin{aligned} P(x_1, t_1; \dots; x_N, t_N) &= P(x_1, t_1 \mid x_2, t_2; \dots; x_N, t_N) P(x_2, t_2; \dots; x_N, t_N) \\ &= P(x_1, t_1 \mid x_2, t_2) P(x_2, t_2 \mid x_3, t_3; \dots; x_N, t_N) P(x_3, t_3; \dots; x_N, t_N) \\ &= \dots \\ &= P(x_N, t_N) \prod_{i=1}^{N-1} P(x_i, t_i \mid x_{i+1}, t_{i+1}). \end{aligned}$$

The Chapman-Kolgomorov Equation In general we have

$$P(x_1, t_1) = \int dx_2 P(x_1, t_1; x_2, t_2) = \int dx_2 P(x_1, t_1 \mid x_2, t_2) P(x_2, t_2),$$

and similarly for a conditional probability

$$P(x_1, t_1 \mid x_3, t_3) = \int dx_2 P(x_1, t_1; x_2, t_2 \mid x_3, t_3) = \int dx_2 P(x_1, t_1 \mid x_2, t_2; x_3, t_3) P(x_2, t_2 \mid x_3, t_3).$$

In particular, for a Markov process, we find

$$P(x_1, t_1 \mid x_3, t_3) = \int dx_2 P(x_1, t_1 \mid x_2, t_2) P(x_2, t_2 \mid x_3, t_3),$$

which is the Chapman-Kolgomorov equation.

The Focker-Planck Equation The Focker-Planck equation is a partial differential equation describes the evolution of the probability distribution for a Markov process. Given an initial condition at x_0, t_0 , the Chapman-Kolmogorov equation implies

$$P(x, t + \delta t \mid x_0, t_0) = \int dx' P(x, t + \delta \mid x', t) P(x', t \mid x_0, t_0).$$

To proceed we will need some assumptions about the stochastic process $x(t)$. We define $\delta x(t) = x(t + \delta t) - x(t)$ and choose the assumptions

$$\langle \delta x(t) \rangle = A(x(t)) \delta t, \quad \langle (\delta x(t))^2 \rangle = B(x(t)) \delta t,$$

as well as higher-order moments being of order 2 or more in terms of δt .

By definition we have

$$\begin{aligned} P(x, t + \delta \mid x', t) &= \langle \delta(x - x' - \delta x(t)) \rangle \\ &\approx \left\langle \delta(x - x') + \delta x(t) \partial_x \delta(x - x') + \frac{1}{2} (\delta x(t))^2 \partial_x^2 \delta(x - x') \right\rangle \\ &= \delta(x - x') + \partial_x \delta(x - x') \langle \delta x(t) \rangle + \frac{1}{2} \partial_x^2 \delta(x - x') \langle (\delta x(t))^2 \rangle \\ &= \delta(x - x') + \partial_x \delta(x - x') A(x(t)) \delta t + \frac{1}{2} \partial_x^2 \delta(x - x') B(x(t)) \delta t. \end{aligned}$$

Inserting this into the Chapman-Kolmogorov equation and using our knowledge of distribution theory we find

$$\begin{aligned} P(x, t + \delta t \mid x_0, t_0) &= \int dx' \left(\delta(x - x') + \partial_x \delta(x - x') A(x(t)) \delta t + \frac{1}{2} \partial_x^2 \delta(x - x') B(x(t)) \delta t \right) P(x', t \mid x_0, t_0) \\ &= P(x, t \mid x_0, t_0) + \left(\frac{1}{2} \partial_x^2 (B(x(t)) P(x, t \mid x_0, t_0)) - \partial_x (A(x(t)) P(x, t \mid x_0, t_0)) \right) \delta t. \end{aligned}$$

Simplifying notation a little, we have

$$P(x, t + \delta t) = P(x, t) + \left(\frac{1}{2} \partial_x^2 (B(x)P(x, t)) - \partial_x (A(x)P(x, t)) \right) \delta t,$$

and in the limit of infinitesimal time steps

$$\partial_t P(x, t) = \frac{1}{2} \partial_x^2 (B(x)P(x, t)) - \partial_x (A(x)P(x, t)).$$

The Master Equation Consider a Markov process with discrete state space. The Chapman-Kolgomorov equation then takes the form

$$P(x, t \mid x_0, t_0) = \sum_{x'} P(x, t \mid x', t') P(x', t' \mid x_0, t_0).$$

From this point we will omit the initial condition in the notation. We assume the transition probabilities to be stationary, i.e. to only depend on time differences according to

$$P(x, t \mid x', t') = P_{t-t'}(x \mid x').$$

For a small time step we may expand according to

$$P_{\delta t}(x \mid x') \approx (1 - \gamma(x')\delta t)\delta_{x,x'} + w(x \mid x')\delta t,$$

where we may assume the first term to contain all information about staying in the same spot, and thus $w(x \mid x) = 0$. Probability conservation implies

$$1 = \sum_x P_{\delta t}(x \mid x') = 1 - \gamma(x')\delta t + \sum_x w(x \mid x')\delta t,$$

and thus

$$\gamma(x') = \sum_x w(x \mid x'),$$

written in integral form in the notes. We now have

$$\begin{aligned} P_{t+\delta t}(x) &= \sum_{x'} P_{\delta t}(x \mid x') P_t(x') \\ &= \sum_{x'} ((1 - \gamma(x')\delta t)\delta_{x,x'} + w(x \mid x')\delta t) P_t(x'), \end{aligned}$$

and thus

$$\begin{aligned} \frac{1}{\delta t} (P_{t+\delta t} - P_t) &= -\gamma(x)P_t(x) + \sum_{x'} w(x \mid x')P_t(x') \\ &= \sum_{x'} w(x \mid x')P_t(x') - w(x' \mid x)P_t(x). \end{aligned}$$

Labelling the positions with integer indices we arrive at the master equation

$$\partial_t P_n = \sum_m W_{nm} P_m - W_{nn} P_n.$$

Alternatively, in matrix form we may write

$$\partial_t P = \Gamma P, \quad \Gamma_{nm} = W_{nm} - \delta_{nm} \sum_k W_{kn}.$$

Formally the solution is

$$P(t) = P(0)e^{\Gamma t}.$$

While Γ must have the same left and right eigenvalues, the corresponding eigenvectors may differ. Another property it has is

$$\sum_n \Gamma_{nm} = 0,$$

as

$$\frac{d}{dt} \sum_n P_n = \sum_n \sum_m \Gamma_{nm} P_m = \sum_m P_m \sum_n \Gamma_{nm} = 0,$$

and for this to be true for any set of initial probabilities the statement in question must hold. This implies that the vector with only ones is a left eigenvector of Γ with eigenvalue 0. To show this, call this vector v . We then have

$$(v\Gamma)_n = \sum_m v_m \Gamma_{mn} = \sum_m \Gamma_{mn} = 0.$$

This implies that there exists a right eigenvector with the same eigenvalue, meaning that this kind of systems has at least one stationary state.

The equilibrium condition for a state is

$$\sum_m W_{nm} P_m = \sum_m W_{mn} P_n,$$

but a stronger equilibrium condition is that of detailed balance - namely,

$$W_{nm} P_m = W_{mn} P_n.$$

This generally holds for systems with time reversal symmetry. Its interpretation is that there is an equal exchange of probability between different sites at equilibrium.

One-Step Processes A one-step process is a special case of the above where the process may only move a single step in the chain of possible states. The process is labeled by transition probabilities α_n to the right and β_n to the left.

2 Basic Concepts

Diffusion and Random Walks Macroscopic diffusion is governed by the diffusion equation

$$\partial_t \rho = D \nabla^2 \rho.$$

In particular, with the initial condition $\rho(\mathbf{x}, t_0) = \delta(\mathbf{x} - \mathbf{x}_0)$ we find

$$\rho(\mathbf{x}, t) = (4\pi D(t - t_0))^{-\frac{d}{2}} e^{-\frac{|\mathbf{x} - \mathbf{x}_0|^2}{4D(t - t_0)}}.$$

Can we re-obtain this result from microscopic dynamics? One way to do this is to consider a random walk with coordinates

$$x^i(t + \Delta t) = x^i(t) + \Delta x_n^i,$$

where the Δx_n^i are random variables assumed to be independent and from the same probability distribution. It turns out that all the information we need is contained in the first two moments

$$\langle \Delta x_n^i \rangle = 0, \quad \langle (\Delta x_n^i)^2 \rangle = \sigma^2,$$

as with this recursion we find

$$x^i(t) = x_0^i + \sum_n \Delta x_n^i.$$

For a large number of steps N the coordinates then follow a normal distribution. Its expectation value is

$$\langle x^i(t) \rangle = \left\langle x_0^i + \sum_n \Delta x_n^i \right\rangle = x_0^i.$$

Its variance is

$$\begin{aligned} \langle (x^i(t) - \langle x^i(t) \rangle)^2 \rangle &= \left\langle \left(\sum_n \Delta x_n^i \right)^2 \right\rangle \\ &= \sum_{m,n} \langle \Delta x_m^i \Delta x_n^i \rangle \\ &= \sum_{m=n} \langle \Delta x_m^i \Delta x_n^i \rangle + \sum_{m \neq n} \langle \Delta x_m^i \Delta x_n^i \rangle \\ &= N\sigma^2, \end{aligned}$$

where we have used the fact that the steps are independent and the covariance therefore is 0, implying

$$\begin{aligned} \langle (\Delta x_m^i - \langle \Delta x_m^i \rangle)(\Delta x_n^i - \langle \Delta x_n^i \rangle) \rangle &= \langle \Delta x_m^i \Delta x_n^i \rangle - \langle \Delta x_m^i \rangle \langle \Delta x_n^i \rangle - \langle \langle \Delta x_m^i \rangle \Delta x_n^i \rangle + \langle \langle \Delta x_m^i \rangle \langle \Delta x_n^i \rangle \rangle \\ &= \langle \Delta x_m^i \Delta x_n^i \rangle = 0. \end{aligned}$$

To rewrite this in the appropriate form, we introduce the time as $t = N\Delta t$ and define

$$\frac{\sigma^2}{\Delta t} t = 2Dt,$$

meaning that things have the right form somehow.

Irreversibility and Classical Mechanics The example with random walks showed that the diffusion result was produced under the assumption that the microscopic process did not have time reversal symmetry. Classical mechanics, however, does. How do we reconcile the two?

One ad hoc answer is that classical dynamics, while allowing for dynamics with time reversal, will not necessarily admit this with a high probability, accounting for why it is not observed.

A more computational example might be found by defining the statistical entropy

$$S = -k_B \int d\mathbf{x} f(\mathbf{x}, t) \ln(f(\mathbf{x}, t)).$$

f is the probability density in phase space, and according to Liouville's theorem we have

$$\partial_f^t = \{\mathcal{H}, f\},$$

where \mathcal{H} is the Hamiltonian. Defining the velocity field $\mathbf{v} = \frac{d\mathbf{x}}{dt}$ in phase space and using Hamilton's equations we may alternatively write the above as

$$\partial_f^t = -\mathbf{v} \cdot \vec{\nabla}_{\mathbf{x}} f.$$

As

$$\vec{\nabla} \cdot_{\mathbf{x}} \mathbf{v} = \partial_{q_i} \partial_{p_i} \mathcal{H} - \partial_{p_i} \partial_{q_i} \mathcal{H} = 0,$$

we have

$$\partial_f^t = -\vec{\nabla} \cdot_{\mathbf{x}} (f\mathbf{v}).$$

The derivative of the entropy is thus

$$\begin{aligned} \partial_S^t &= -k_B \int d\mathbf{x} \partial_f^t \ln(f) + \partial_f^t \\ &= k_B \int d\mathbf{x} \vec{\nabla} \cdot_{\mathbf{x}} (f\mathbf{v})(\ln(f) + 1). \end{aligned}$$

The latter term may be converted to a surface term using Gauss' theorem, and choosing boundaries at infinity it produces no contribution. Similarly for the other term we may write

$$\begin{aligned}\partial_S^t &= k_B \int d\mathbf{x} \vec{\nabla} \cdot_{\mathbf{x}} (f \ln(f) \mathbf{v}) - f \mathbf{v} \cdot \vec{\nabla}_{\mathbf{x}} \ln(f) \\ &= -k_B \int d\mathbf{x} f \mathbf{v} \cdot \frac{1}{f} \vec{\nabla}_{\mathbf{x}} f \\ &= -k_B \int d\mathbf{x} \mathbf{v} \cdot \vec{\nabla}_{\mathbf{x}} f.\end{aligned}$$

Repeating a previous step, we find that this term gives no contribution either, meaning $\partial_S^t = 0$.

Brownian Motion and the Langevin Equation To describe Brownian motion we consider particles much heavier than the molecules in the medium in which they are immersed and perform the anzats

$$m \frac{dv^i}{dt} = R_i(t),$$

where the $R_i(t)$ are stochastic processes with the underlying random variable being the initial position of the particle (I think). In order to produce Brownian motion we expect $\langle R_i(t) \rangle = 0$. Next we introduce the autocorrelation function

$$k(t, t') = \langle (R_i(t) - \langle R_i(t) \rangle)(R_i(t') - \langle R_i(t') \rangle) \rangle = \langle R_i(t) R_i(t') \rangle - \langle R_i(t) \rangle \langle R_i(t') \rangle.$$

It measures for how long deviations from the mean force remain correlated, and thus the time scales of the fluctuations and typical amplitudes of the force. In the case of a single time scale being relevant, we name it the autocorrelation time and denote it τ_c . For Brownian motion this time scale is the typical time between collisions. In the relevant limits in which we are working we expect the correlations in forces at different times to be irresolvable, and thus

$$k(t, t') = \langle R_i(t) R_i(t') \rangle = \Gamma \delta(t - t').$$

$\sqrt{\Gamma}$ is a typical intensity of the fluctuations in the force. If we assume the stochastic processes to be Gaussian, we have now completely specified them.

Does the anzats work? No! By computing expectation values, we see that constant drift is allowed, which is certainly not what we expect. The liquid will in fact resist the motion of the particle with a velocity-dependent force, which we will remedy by adding a first-order correction. By also incorporating an external force \mathbf{F} we arrive at the Langevin equation

$$m \frac{dv^i}{dt} = R^i(t) + F^i - \alpha v^i.$$

The general solution is

$$v^i(t) = e^{-\gamma t} v_0^i + \frac{1}{m} \int_0^t ds e^{-\gamma(t-s)} (R^i(s) + F^i(s)),$$

which we can verify according to

$$\begin{aligned}m \frac{dv^i}{dt} &= -m\gamma e^{-\gamma t} v_0^i + R^i(t) + F^i(t) - \frac{\gamma}{m} \int_0^t ds e^{-\gamma(t-s)} (R^i(s) + F^i(s)) \\ &= -m\gamma v^i(t) + R^i(t) + F^i(t) \\ &= -\alpha v^i(t) + R^i(t) + F^i(t).\end{aligned}$$

What kind of behaviour is produced now? To begin with, let us assume there are no external forces. The expectation value then evolves according to

$$m \frac{d\langle v^i \rangle}{dt} = -\alpha \langle v^i \rangle,$$

with solution

$$\langle v^i \rangle = v_0^i e^{-\frac{t}{\tau_v}}, \quad \tau_v = \frac{1}{\gamma} = \frac{m}{\alpha}.$$

To be consistent with our assumptions, we thus require $\tau_v \gg \tau_c$. Next we have

$$\begin{aligned} \langle (v^i(t) - \langle v^i(t) \rangle)^2 \rangle &= \left\langle \left(\frac{1}{m} \int_0^t ds e^{-\gamma(t-s)} R^i(s) \right)^2 \right\rangle \\ &= \frac{1}{m^2} \int_0^t ds \int_0^t du e^{-\gamma(t-s)} e^{-\gamma(t-u)} \langle R^i(s) R^i(u) \rangle \\ &= \frac{\Gamma}{m^2} \int_0^t ds \int_0^t du e^{-\gamma(2t-s-u)} \delta(s-u) \\ &= \frac{\Gamma}{m^2} \int_0^t ds e^{-2\gamma(t-s)} \\ &= \frac{\Gamma}{2\gamma m^2} e^{-2\gamma t} (e^{2\gamma t} - 1) \\ &= \frac{\Gamma}{2\gamma m^2} (1 - e^{-2\gamma t}). \end{aligned}$$

At long times, when equilibrium is established, we have $\langle v^i(t) \rangle = 0$. At this point we expect

$$\frac{1}{2} m \langle v^2 \rangle = \frac{d}{2} k_B T.$$

This implies

$$\Gamma = 2m\gamma k_B T.$$

We pause at this result for a second, noting that the random forces increase in intensity with temperature. This is expected as the molecular motion increases in intensity with temperature. We also note that there is an equivalence between the rate of dissipation and the intensity of the fluctuations, a special case of the fluctuation-dissipation theorem.

We can also introduce the velocity correlation function

$$C(t, t') = \langle v(t)v(t') \rangle - \langle v(t) \rangle \langle v(t') \rangle,$$

and we find

$$\begin{aligned} C(t, t') &= \frac{1}{m^2} \int_0^t ds \int_0^{t'} du e^{-\gamma(t-s)} e^{-\gamma(t'-u)} \langle R^i(s) R^i(u) \rangle \\ &= \frac{\Gamma}{m^2} \int_0^t ds \int_0^{t'} du e^{-\gamma(t+t'-s-u)} \delta(s-u) \\ &= \frac{\Gamma}{m^2} \int_0^t ds \theta(t' - s) e^{-\gamma(t+t'-2s)} \\ &= \frac{\Gamma}{m^2} \int_0^{\min(t, t')} ds e^{-\gamma(t+t'-2s)}. \end{aligned}$$

We may without loss of generality assume $t > t'$, for which we find

$$C(t, t') = \frac{\Gamma}{m^2} e^{-\gamma(t+t')} \int_0^{t'} ds e^{2\gamma s} = \frac{\Gamma}{2\gamma m^2} e^{-\gamma(t+t')} (e^{2\gamma t'} - 1) = \frac{\Gamma}{2\gamma m^2} e^{-\gamma(t-t')} (1 - e^{-2\gamma t'}).$$

Consider now the limit of large times where $t - t'$ is fixed. In this limit we find

$$C(t, t') = \frac{\Gamma}{2\gamma m^2} e^{-\gamma(t-t')}.$$

The dependence on the time difference is expected as this limit concerns correlations between two velocities at equilibrium, and that should only depend on the time difference. Note that due to the previously occurring minimum, its dependence is in fact on $|t - t'|$. Denoting this function as $C(t - t')$ we have

$$\int_{-\infty}^{\infty} dt C(t) = \frac{\Gamma}{\gamma^2 m^2} = \frac{2k_B T}{\gamma m},$$

or

$$\frac{1}{\alpha} = \frac{1}{2k_B T} \int_{-\infty}^{\infty} dt C(t).$$

In other words, there is a relation between correlation functions and friction coefficients. This applies generally.

Next, the position in the absence of external forces is

$$\begin{aligned} x^i(t) &= x_0^i + \int_0^t ds \left(e^{-\gamma s} v_0^i + \frac{1}{m} \int_0^s du e^{-\gamma(s-u)} R^i(u) \right) \\ &= x_0^i + \frac{v_0^i}{\gamma} (1 - e^{-\gamma t}) + \frac{1}{m} \int_0^t ds \int_0^s du e^{-\gamma(s-u)} R^i(u), \end{aligned}$$

from which we compute

$$\langle x^i(t) \rangle = x_0^i + \frac{v_0^i}{\gamma} (1 - e^{-\gamma t}).$$

Next the correlation function is

$$\begin{aligned} \langle x^i(t) x^i(t') - \langle x^i(t) \rangle \langle x^i(t') \rangle \rangle &= \frac{1}{m^2} \int_0^t ds \int_0^s du \int_0^{t'} ds' \int_0^{s'} du' e^{-\gamma(s-u)} e^{-\gamma(s'-u')} \langle R^i(u) R^i(u') \rangle \\ &= \frac{1}{m^2} \int_0^t ds \int_0^s du \int_0^{t'} ds' \int_0^{s'} du' e^{-\gamma(s+s'-u-u')} \langle R^i(u) R^i(u') \rangle. \end{aligned}$$

In particular, for $t = t'$ we find

$$\begin{aligned}
\langle x^i(t)x^i(t') - \langle x^i(t) \rangle \langle x^i(t') \rangle \rangle &= \frac{\Gamma}{m^2} \int_0^t ds \int_0^s du \int_0^t ds' \int_0^{s'} du' e^{-\gamma(s+s'-u-u')} \delta(u-u') \\
&= \frac{\Gamma}{m^2} \int_0^t ds \int_0^s du \int_0^t ds' e^{-\gamma(s+s'-2u)} \theta(s'-u) \\
&= \frac{\Gamma}{m^2} \int_0^t ds \int_0^s du \int_u^t ds' e^{-\gamma(s+s'-2u)} \\
&= \frac{\Gamma}{m^2} \int_0^t ds e^{-\gamma s} \int_0^s du e^{2\gamma u} \int_u^t ds' e^{-\gamma s'} \\
&= \frac{\Gamma}{\gamma m^2} \int_0^t ds e^{-\gamma s} \int_0^s du e^{2\gamma u} (e^{-\gamma u} - e^{-\gamma t}) \\
&= \frac{\Gamma}{\gamma^2 m^2} \int_0^t ds e^{-\gamma s} \left(e^{\gamma s} - 1 - \frac{1}{2} e^{-\gamma t} (e^{2\gamma s} - 1) \right) \\
&= \frac{\Gamma}{\gamma^2 m^2} \int_0^t ds \left(1 - e^{-\gamma s} - \frac{1}{2} e^{-\gamma t} (e^{\gamma s} - e^{-\gamma s}) \right) \\
&= \frac{\Gamma}{\gamma^2 m^2} \left(t + \frac{1}{\gamma} (e^{-\gamma t} - 1) - \frac{1}{2\gamma} e^{-\gamma t} (e^{\gamma t} - 1 + e^{-\gamma t} - 1) \right) \\
&= \frac{2k_B T}{\gamma m} \left(t + \frac{1}{\gamma} (e^{-\gamma t} - 1) - \frac{1}{2\gamma} (1 - 2e^{-\gamma t} + e^{-2\gamma t}) \right) \\
&= \frac{2k_B T}{\gamma m} \left(t + \frac{1}{\gamma} (e^{-\gamma t} - 1) - \frac{1}{2\gamma} (1 - e^{-\gamma t})^2 \right).
\end{aligned}$$

At large times we find

$$\langle x^i(t)x^i(t') - \langle x^i(t) \rangle \langle x^i(t') \rangle \rangle = \frac{2k_B T}{\gamma m} \left(t - \frac{3}{2\gamma} \right) \approx \frac{2k_B T}{\gamma m} t.$$

Comparing with the previously obtained random walk result we find

$$D = \frac{k_B T}{\gamma m} t.$$

The Focker-Planck Equation for the Langevin Equation For a stochastic process of the form

$$dx = a(x) dt + b(x) dW$$

where $W(t)$ is a Wiener process we have

$$\langle dx \rangle = a(x) dt, \quad \langle (dx)^2 \rangle \approx b^2(x) dt,$$

where we have used the Ito prescription. For the Langevin equation, here in the form

$$\frac{dv}{dt} = -\gamma v + \frac{\sqrt{\Gamma}}{m} \eta(t),$$

we have

$$\partial_t P = \gamma \partial_v (vP) + \frac{\Gamma}{2m^2} \partial_v^2 P.$$

In particular, the Gaussian distribution expected at equilibrium is a stationary solution.

The Pauli Master Equation Consider a quantum system with a set of possible states. Using the eigenbasis of the Hamiltonian the elements of the density matrix are

$$\rho_{nm} = c_n(0)c_m^*(0)e^{-i\frac{E_n-E_m}{\hbar}t}.$$

If the system is weakly coupled to a surrounding environment, that can be hard to incorporate. However, one can think of it like this: If the energy exchanges with the surroundings are large compared to the eigenenergies, the phase of off-diagonal elements in the density matrix fluctuates, this fluctuation being on a time scale τ_ϕ . If the relevant time scales of the dynamics of the system are much larger than τ_ϕ , we expect the phase to be uniformly distributed, yielding that the time average of the off-diagonal matrix elements is

$$\langle \rho_{nm} \rangle = 0.$$

This means that the density matrix is diagonal, and its non-zero elements can now be thought of as probabilities. We can thus apply the master equation to such a system. The transition rates are usually calculated with time-independent perturbation theory. One basic result which is often used is Fermi's golden rule

$$W_{nm} = \frac{2\pi}{\hbar} |\langle n|V|m \rangle|^2 \delta(E_n - E_m).$$

The Boltzmann Equation Consider some classical system (with many degrees of freedom) moving with some Hamiltonian. The phase space probability distribution, which in principle describes this system, is hard to handle. Instead we would like to work with the one-body distribution $f(\mathbf{r}, \mathbf{p}, t)$ which describes the number of particle at a particular position with a particular momentum. Formally it satisfies

$$f(\mathbf{r}, \mathbf{q}, t) = \sum_i \langle \delta(\mathbf{x}_i - \mathbf{r}) \delta(\mathbf{p}_i - \mathbf{q}) \rangle = N \int \prod_{i=2}^N d^d \mathbf{x}_i d^d \mathbf{p}_i \frac{1}{h^2} \rho(\mathbf{r}, \mathbf{x}_2, \dots, \mathbf{x}_N; \mathbf{q}, \mathbf{p}_2, \dots, \mathbf{p}_N).$$

It should then satisfy

$$\int d^3 \mathbf{p} f(\mathbf{r}, \mathbf{p}, t) = n(\mathbf{r}, t), \quad \int d^3 \mathbf{r} n = N.$$

f flows through this constructed phase space with time. Liouville's theorem states that phase space volume is preserved, hence

$$f(\mathbf{r}, \mathbf{p}, t) d\mathbf{r} d\mathbf{p} = f(\mathbf{r} + \dot{\mathbf{r}} dt, \mathbf{p} + \dot{\mathbf{p}} dt, t + dt) d\mathbf{r}' d\mathbf{p}'.$$

Neglecting collisions, all forces are external. Defining $\mathbf{v} = \dot{\mathbf{r}}$ and $\mathbf{F} = \dot{\mathbf{p}}$, we can then Taylor expand the above to find

$$\partial_t f + \mathbf{v} \cdot \vec{\nabla}_{\mathbf{x}} f + \mathbf{F} \cdot \vec{\nabla}_{\mathbf{p}} f = 0.$$

We may now also introduce Liouville operator $L = \partial_t + \mathbf{v} \cdot \vec{\nabla}_{\mathbf{x}} + \mathbf{F} \cdot \vec{\nabla}_{\mathbf{p}}$.

When accounting for collisions and other scattering events, we write this as

$$Lf = (\partial_t f)_{\text{coll}}.$$

We will focus on two-particle scattering events. These are caused by an interaction potential $V(\mathbf{r}, \mathbf{r}')$. We coarse grain over the time and length scale of the collision, the latter meaning that the typical time between two collisions involving the same particle should be much longer than the collision time. This is achieved if the density is low.

We distinguish between two kinds of events: those that increase and decrease $f(\mathbf{r}, \mathbf{p}, t)$. We need two quantities to proceed. The first is the scattering rate $\omega(\mathbf{p}_1, \mathbf{p}_2 \rightarrow \mathbf{p}'_1, \mathbf{p}'_2)$. The second is the probability of two particles with momenta \mathbf{p}_1 and \mathbf{p}_2 to be at \mathbf{r} at the same time. This is computed from the two-particle distribution function

$$\begin{aligned} f_2(\mathbf{r}, \mathbf{q}; \mathbf{r}', \mathbf{q}'; t) &= \sum_i \sum_{j \neq i} \langle \delta(\mathbf{x}_i - \mathbf{r}) \delta(\mathbf{p}_i - \mathbf{q}) \delta(\mathbf{x}_j - \mathbf{r}') \delta(\mathbf{p}_j - \mathbf{q}') \rangle \\ &= N(N-1) \int \prod_{i=3}^N d^d \mathbf{x}_i d^d \mathbf{p}_i \frac{1}{h^2} \rho(\mathbf{r}, \mathbf{r}', \mathbf{x}_3, \dots, \mathbf{x}_N; \mathbf{q}, \mathbf{q}', \mathbf{p}_3, \dots, \mathbf{p}_N). \end{aligned}$$

We can then write down

$$(\partial_t f)_{\text{coll}}(\mathbf{r}, \mathbf{p}, t) = \int d^3 \mathbf{p}_2 \int d^3 \mathbf{p}'_1 \int d^3 \mathbf{p}'_2 \omega(\mathbf{p}'_1, \mathbf{p}'_2 \rightarrow \mathbf{p}, \mathbf{p}_2) f_2(\mathbf{r}, \mathbf{p}'_1; \mathbf{r}, \mathbf{p}'_2; t) - \omega(\mathbf{p}, \mathbf{p}_2 \rightarrow \mathbf{p}'_1, \mathbf{p}'_2) f_2(\mathbf{r}, \mathbf{p}; \mathbf{r}, \mathbf{p}_2; t)$$

using a master equation-like argument. This does not really help, as the determination of f now rests on determining f_2 . One could imagine propagating this argument by letting f_2 depend on f_3 , all the way back to ρ , which is precisely what we do not want. Instead we introduce the assumption of molecular chaos, namely $f_2(\mathbf{r}_1, \mathbf{p}_1; \mathbf{r}_2, \mathbf{p}_2; t) = f(\mathbf{r}_1, \mathbf{p}_1; t) f(\mathbf{r}_2, \mathbf{p}_2; t)$. This assumption manifests an assumption that the evolution of the system is chaotic, and two incoming particles in a collision are therefore uncorrelated. We also assume the dynamics of the system to have both time reversal and parity symmetry. The first implies

$$\omega(\mathbf{p}_1, \mathbf{p}_2 \rightarrow \mathbf{p}'_1, \mathbf{p}'_2) = \omega(-\mathbf{p}'_1, -\mathbf{p}'_2 \rightarrow -\mathbf{p}_1, -\mathbf{p}_2),$$

while the second implies

$$\omega(-\mathbf{p}'_1, -\mathbf{p}'_2 \rightarrow -\mathbf{p}_1, -\mathbf{p}_2) = \omega(\mathbf{p}'_1, \mathbf{p}'_2 \rightarrow \mathbf{p}_1, \mathbf{p}_2).$$

The transition rate is thus symmetric. We thus obtain

$$(\partial_t f)_{\text{coll}}(\mathbf{r}, \mathbf{p}, t) = \int d^3 \mathbf{p}_2 \int d^3 \mathbf{p}'_1 \int d^3 \mathbf{p}'_2 \omega(\mathbf{p}, \mathbf{p}_2 \rightarrow \mathbf{p}'_1, \mathbf{p}'_2) (f(\mathbf{r}, \mathbf{p}'_1, t) f(\mathbf{r}, \mathbf{p}'_2, t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_2, t)).$$

We proceed by interpreting the coordinates and momenta as those of point particles, and require conservation of energy and momentum. If all the particles have identical masses, we then find

$$(\mathbf{p}_1 + \mathbf{p}_2)^2 = \mathbf{p}_1^2 + \mathbf{p}_2^2 + 2\mathbf{p}_1 \cdot \mathbf{p}_2,$$

and energy conservation implies the scalar product to be conserved. This further implies that the length of the momentum difference is conserved, and thus

$$\mathbf{p}'_2 - \mathbf{p}'_1 = |\mathbf{p}_2 - \mathbf{p}_1| \mathbf{\Omega},$$

where $\mathbf{\Omega}$ is some unit vector. This means that we can specify the collision by specifying the incoming momenta and the scattering direction of the difference.

We can also introduce the differential cross-section, defined as $\frac{\partial \sigma}{\partial \Omega}$ being the ratio of incoming and outgoing intensities in some interval of solid angle, corrected for travelling time. Somehow we find that

$$(\partial_t f)_{\text{coll}}(\mathbf{r}, \mathbf{p}, t) = \int d^3 \mathbf{p}_2 \int d\Omega \frac{\partial \sigma}{\partial \Omega} |\mathbf{v} - \mathbf{v}_2| (f(\mathbf{r}, \mathbf{p}'_1, t) f(\mathbf{r}, \mathbf{p}'_2, t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_2, t)).$$

The final equation, named the Boltzmann equation, is thus

$$\partial_t f + \mathbf{v} \cdot \vec{\nabla}_{\mathbf{x}} f + \mathbf{F} \cdot \vec{\nabla}_{\mathbf{p}} f = \int d^3 \mathbf{p}_2 \int d\Omega \frac{\partial \sigma}{\partial \Omega} |\mathbf{v} - \mathbf{v}_2| (f(\mathbf{r}, \mathbf{p}'_1, t) f(\mathbf{r}, \mathbf{p}'_2, t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_2, t)).$$

The Boltzmann H Theorem Consider the function

$$H = \int d^3 \mathbf{r} \int d^3 \mathbf{p} f \ln(f).$$

As the integral of f itself is constant we have

$$\begin{aligned} \frac{dH}{dt} &= \int d^3 \mathbf{r} \int d^3 \mathbf{p} \partial_t f \ln(f) \\ &= \int d^3 \mathbf{r} \int d^3 \mathbf{p} \ln(f) \left(-\mathbf{v} \cdot \vec{\nabla}_{\mathbf{x}} f - \mathbf{F} \cdot \vec{\nabla}_{\mathbf{p}} f \right) \\ &\quad + \int d^3 \mathbf{r} \int d^3 \mathbf{p} \ln(f) \int d^3 \mathbf{p}_2 \int d\Omega \frac{\partial \sigma}{\partial \Omega} |\mathbf{v} - \mathbf{v}_2| (f(\mathbf{r}, \mathbf{p}'_1, t) f(\mathbf{r}, \mathbf{p}'_2, t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_2, t)). \end{aligned}$$

As the velocity field in (this projection of) phase space is divergence-free, we can somehow eliminate the first term and find

$$\frac{dH}{dt} = \int d^3\mathbf{r} \int d^3\mathbf{p} \ln(f) \int d^3\mathbf{p}_2 \int d\Omega \frac{\partial\sigma}{\partial\Omega} |\mathbf{v} - \mathbf{v}_2| (f(\mathbf{r}, \mathbf{p}'_1, t) f(\mathbf{r}, \mathbf{p}'_2, t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_2, t)).$$

The integrand is now entirely symmetric under the switch of \mathbf{p} and \mathbf{p}_2 , assuming we also switch the f in the logarithm. We thus find

$$\frac{dH}{dt} = \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{p} \int d^3\mathbf{p}_2 \int d\Omega \frac{\partial\sigma}{\partial\Omega} |\mathbf{v} - \mathbf{v}_2| (f(\mathbf{r}, \mathbf{p}'_1, t) f(\mathbf{r}, \mathbf{p}'_2, t) - f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_2, t)) \ln(f(\mathbf{r}, \mathbf{p}, t) f(\mathbf{r}, \mathbf{p}_2, t)).$$

The cross section is symmetric under parity and time reversal, hence we may switch the primed and non-primed momenta to find

$$\frac{dH}{dt} = \frac{1}{4} \int d^3\mathbf{r} \int d^3\mathbf{p} \int d^3\mathbf{p}_2 \int d\Omega \frac{\partial\sigma}{\partial\Omega} |\mathbf{v} - \mathbf{v}_2| (f(\mathbf{p}'_1) f(\mathbf{p}'_2) - f(\mathbf{p}) f(\mathbf{p}_2)) (\ln(f(\mathbf{p}) f(\mathbf{p}_2)) - \ln(f(\mathbf{p}'_1) f(\mathbf{p}'_2))),$$

where redundant variables have been suppressed. This must be negative, as the expression $(y-x)(\ln(y)-\ln(x))$ is non-negative.

This result implies that entropy is increasing. How come? It is due to the assumption of molecular chaos, causing loss of information.

Conservation Laws Consider a local observable χ with a corresponding density

$$n = \int d^3\mathbf{p} \chi f.$$

For χ to be conserved, n should be conserved in collisions. In other words,

$$(\partial_t n)_{\text{coll}} = \int d^3\mathbf{p} \chi (\partial_t n)_{\text{coll}} = 0.$$

To show that this is in fact the case, we repeat the derivation of the H theorem, netting us a term $\chi(\mathbf{p}) + \chi(\mathbf{p}_2) - \chi(\mathbf{p}'_1) - \chi(\mathbf{p}'_2)$, meaning that if χ is conserved in collisions, then $(\partial_t n)_{\text{coll}} = 0$.

Local Equilibrium While the only explicit conserved quantities of (almost-ideal) gas Hamiltonians are momentum and energy, the logarithm of the equilibrium distribution $\ln(f^0)$ is also conserved. This must mean

$$\ln(f^0) = \beta(\mu + \mathbf{v} \cdot \mathbf{p} - \varepsilon),$$

with the different variables being chemical potential and reciprocal temperature, or

$$f^0 \propto e^{-\frac{\beta}{2m}(\mathbf{p}-m\mathbf{v})^2}.$$

This is the state of equilibrium. In local equilibrium the various quantities are allowed to vary in space. It turns out that such a solution is not affected by collisions, but as it does not solve the Boltzmann equation, it is affected by the streaming terms. Thus, after local equilibrium is established, there is hydrodynamic evolution of these macroscopic observables.

The Relaxation Time Approximation In the relaxation time approximation, one arrives at an expression of the form

$$(\partial_t f)_{\text{coll}} = -\frac{f - f^0}{\tau}.$$

The quantity $f - f^0$ evolves exponentially in this approach as f^0 is not affected by collision terms.

3 Quantum Systems

The Reduced Density Matrix The reduced density matrix is found by tracing out a particular set of degrees of freedom from a total density matrix.