Summary of SI2520 Non-Equilibrium Statistical Mechanics

Yashar Honarmandi
yasharh@kth.se

March 16, 2021

Abstract

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

Contents

1 A Litte Bit About Probability Theory

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

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

This function satisfies

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

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

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

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

$$\left\langle \prod_i f(X,t_i) \right\rangle = \int \mathrm{d}x\, P(x) \prod_i f_x(t_i).$$

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

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

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

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

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

Wiener Processes In this course we will be studying equations of the form

$$\frac{\mathrm{d}x}{\mathrm{d}t} = a(x;t) + b(x;t)\eta(t),$$

where η is a stochastic process that satisfies

$$\langle \eta(t) \rangle \,,\ \left\langle \eta(t)\eta(t') \right\rangle = \delta(t-t').$$

This equation is not well-defined, however, due to the Dirac delta. However, as the integral of η is continuous, we can define

$$W = \int_{t_0}^{t} \mathrm{d}t'\, \eta(t').$$

It satisfies

$$\langle W(t) \rangle = 0,\ \left\langle W(t)W(t') \right\rangle = \int_{t_0}^{t} \mathrm{d}\tau \int_{t_0}^{t'} \mathrm{d}\tau' \left\langle \eta(\tau)\eta(\tau') \right\rangle = \int_{t_0}^{t} \mathrm{d}\tau \int_{t_0}^{t'} \mathrm{d}\tau'\, \delta(\tau-\tau') = \int_{t_0}^{t} \mathrm{d}\tau\, \theta(t'-\tau) = \min(t-t_0, t'-t_0).$$

From this we can consider infinitesimal increments

$$\mathrm{d}W = W(t+\mathrm{d}t) - W(t) = \int_{t}^{t+\mathrm{d}t} \mathrm{d}t'\, \eta(t'),$$

which satisfy

$$\langle \mathrm{d}W \rangle = 0,\ \left\langle \mathrm{d}W\,(t)\, \mathrm{d}W\,(t') \right\rangle = \delta(t-t')\,\mathrm{d}t\,.$$

This is a warning sign that care should be taken when doing calculus with such processes. Using this, we reformulate the equation we wanted to study as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = a(x;t) + b(x;t)\,\mathrm{d}W\,,$$

where we take the previous version to be a shorthand for this one. This can be formally integrated as

$$x(t) = x(t_0) + \int_{t_0}^{t} \mathrm{d}t'\, a(x;t) + \int_{t_0}^{t} \mathrm{d}W(t')\, b(x;t).$$

Integral Prescription The last integral in the previous section introduces a complication, as it is not uniquely defined. Namely, depending on how you define your Riemann sum you might get different results. Two choices we will discuss here are the Ito prescription, which chooses function values from the left of the interval, and the Stratonovich prescription, which chooses them from the right.

To relate the two, consider the expression

$$I = \int_{t_0}^{t} \mathrm{d}W\, b(x;t).$$

In the two prescriptions, distinguished by a subscript, we have

$$I_{\mathrm{I}} = \sum_{i=0}^{n-1} b(x(t_i);t_i)\Delta W(t_i),\ I_{\mathrm{S}} = \sum_{i=0}^{n-1} b(x(t_{i+1});t_{i+1})\Delta W(t_i).$$

We have

$$b(x(t_{i+1});t_{i+1}) = b(x(t_i);t_i) + \alpha\Delta' W(t_i),$$

where Δ' indicates a different realization of the Wiener process. In the limit of the increments vanishing we find

$$\langle I_{\rm I}\rangle = \left\langle \int_{t_0}^{t} {\rm d}W(\tau)\, b(x(\tau);\tau) \right\rangle = 0,$$
$$\langle I_{\rm S}\rangle = \int_{t_0}^{t} {\rm d}\tau\, \alpha(\tau).$$

The Ito prescription thus allows us to ignore the b term in such equations when taking expectation values.

Markov Processes A Markov process is a process such that

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

For such processes we have

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

The Chapman-Kolgomorov Equation In general we have

$$P(x_1,t_1) = \int {\rm d}x_2\, P(x_1,t_1;x_2,t_2) = \int {\rm d}x_2\, P(x_1,t_1 \mid x_2,t_2)P(x_2,t_2),$$

and similarly for a conditional probability

$$P(x_1,t_1 \mid x_3,t_3) = \int {\rm d}x_2\, P(x_1,t_1;x_2,t_2 \mid x_3,t_3) = \int {\rm d}x_2\, P(x_1,t_1 \mid x_2,t_2;x_3,t_3)P(x_2,t_2 \mid x_3,t_3).$$

In particular, for a Markov process, we find

$$P(x_1,t_1 \mid x_3,t_3) = \int {\rm d}x_2\, P(x_1,t_1 \mid x_2,t_2)P(x_2,t_2 \mid x_3,t_3),$$

which is the Chapman-Kolgomorov equation.

The Fokker-Planck Equation The Fokker-Planck equation is a partial differential equation that 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

$$P(x,t+\delta t \mid x_0,t_0) = \int {\rm d}x'\, P(x,t+\delta \mid x',t)P(x',t \mid x_0,t_0).$$

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

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

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

By definition we have

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

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

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

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

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

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

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

Alternatively, in matrix form we may write

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

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

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

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

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

as we recursively 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, according to the central limit theorem. Their expectation values are

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

Their variances are

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

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

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

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

$$\frac{\sigma^2}{\Delta t}(t - t_0) = 2D(t - t_0).$$

We then find

$$P(\mathbf{x}) = \frac{1}{(4\pi D(t - t_0))^{\frac{d}{2}}} e^{-\frac{|\mathbf{x}-x_0|^2}{4D(t-t_0)}},$$

which is the correct result.

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.

Entropy and Classical Mechanics Consider the statistical entropy

$$S = -k_{\mathrm{B}} \int \mathrm{d}\mathbf{x}\, f(\mathbf{x},t) \ln(f(\mathbf{x},t)),$$

where f is the probability density in phase space. According to Liouville's theorem we have

$$\partial_t f = \{\mathcal{H}, f\},$$

where $\mathcal{H}$ is the Hamiltonian. Defining the velocity field $\mathbf{v} = \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t}$ in phase space and using Hamilton's equations we may alternatively write the above as

$$\partial_t f = -\mathbf{v} \cdot \vec{\boldsymbol{\nabla}}_{\mathbf{x}} f.$$

As

$$\vec{\boldsymbol{\nabla}}_{\mathbf{x}} \cdot \mathbf{v} = \partial_{q^i}\partial_{p_i}\mathcal{H} - \partial_{p^i}\partial_{q_i}\mathcal{H} = 0,$$

we have

$$\partial_t f = -\vec{\boldsymbol{\nabla}}_{\mathbf{x}} \cdot (f\mathbf{v}).$$

The derivative of the entropy is thus

$$\begin{aligned}\partial_t S &= -k_{\mathrm{B}} \int \mathrm{d}\mathbf{x} \ln(f)\partial_t f + \partial_t f \\ &= k_{\mathrm{B}} \int \mathrm{d}\mathbf{x}\, (\ln(f)+1)\vec{\boldsymbol{\nabla}}_{\mathbf{x}} \cdot (f\mathbf{v}).\end{aligned}$$

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

$$\begin{aligned}\partial_t S &= k_{\mathrm{B}} \int \mathrm{d}\mathbf{x}\, \vec{\boldsymbol{\nabla}}_{\mathbf{x}} \cdot (f\ln(f)\mathbf{v}) - f\mathbf{v}\cdot\vec{\boldsymbol{\nabla}}_{\mathbf{x}}\ln(f) \\ &= -k_{\mathrm{B}} \int \mathrm{d}\mathbf{x}\, f\mathbf{v}\cdot\frac{1}{f}\vec{\boldsymbol{\nabla}}_{\mathbf{x}} f \\ &= -k_{\mathrm{B}} \int \mathrm{d}\mathbf{x}\, \mathbf{v}\cdot\vec{\boldsymbol{\nabla}}_{\mathbf{x}} f,\end{aligned}$$

where we removed an intermediate surface term. The previous steps show that the remaining term may also be converted to a surface term, 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

$$m\frac{\mathrm{d}v^i}{\mathrm{d}t} = R^i(t),$$

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 force correlations at different times to be irresolvable, and thus

$$k(t,t') = \left\langle R^i(t)R^i(t')\right\rangle = \Gamma\delta(t-t').$$

$\sqrt{\Gamma}$ 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

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

The formal solution is

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

which we can verify according to

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

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

$$m\frac{\mathrm{d}\left\langle v^i\right\rangle}{\mathrm{d}t} = -\alpha\left\langle v^i\right\rangle,$$

with solution

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

To be consistent with our assumptions, we thus require $\tau_v \gg \tau_\mathrm{c}$. Next we have

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

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

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

This implies

$$\Gamma = 2m\gamma k_{\mathrm{B}}T.$$

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

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

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

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

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 occuring minimum, its dependence is in fact on $|t-t'|$. Denoting this function as $C(t-t')$ we have

$$\int_{-\infty}^{\infty} \mathrm{d}t\, C(t) = \frac{\Gamma}{\gamma^2 m^2} = \frac{2k_{\mathrm{B}}T}{\gamma m},$$

or

$$\frac{1}{\alpha} = \frac{1}{2k_{\mathrm{B}}T}\int_{-\infty}^{\infty} \mathrm{d}t\, C(t).$$

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

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

from which we compute

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

Next the correlation function is

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

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

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

At large times we find

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

Comparing with the previously obtained random walk result we find

$$D = \frac{k_{\mathrm{B}}T}{\gamma m}t.$$

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

$$\mathrm{d}x = a(x)\,\mathrm{d}t + b(x)\,\mathrm{d}W$$

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

$$\langle \mathrm{d}x \rangle = a(x)\,\mathrm{d}t\,,\ \left\langle (\mathrm{d}x)^2 \right\rangle \approx b^2(x)\,\mathrm{d}t\,,$$

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

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

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

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

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

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

It should then satisfy

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

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

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

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

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

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

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 $\omega(\mathbf{p}_1, \mathbf{p}_2 \to \mathbf{p}_1', \mathbf{p}_2')$. 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

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

We can then write down

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

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

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

while the second implies

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

The transition rate is thus symmetric. We thus obtain

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

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

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

where $\boldsymbol{\Omega}$ 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

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

The final equation, named the Boltzmann equation, is thus

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

The Boltzmann H Theorem Consider the function

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

As the integral of f itself is constant we have

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

The streaming part is zero, yielding, as was shown previously, yielding

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

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

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

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

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{1}{4}\int \mathrm{d}^3\mathbf{r} \int \mathrm{d}^3\mathbf{p} \int \mathrm{d}^3\mathbf{p}_2 \int \mathrm{d}\Omega\, \frac{\partial\sigma}{\partial\Omega}|\mathbf{v}-\mathbf{v}_2|\left(f(\mathbf{p}_1')f(\mathbf{p}_2') - f(\mathbf{p})f(\mathbf{p}_2)\right)\left(\ln(f(\mathbf{p})f(\mathbf{p}_2)) - \ln\big(f(\mathbf{p}_1')f(\mathbf{p}_2')\big)\right),$$

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

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

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

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

To show that this is in fact the case, we repeat the derivation done for the H theorem. Ignoring streaming terms we find

$$\partial_t n = \int \mathrm{d}^3\mathbf{p}\,\chi(\mathbf{r},\mathbf{p}) \int \mathrm{d}^3\mathbf{p}_2 \int \mathrm{d}\Omega\, \frac{\partial\sigma}{\partial\Omega}|\mathbf{v}-\mathbf{v}_2|\left(f(\mathbf{p}_1')f(\mathbf{p}_2') - f(\mathbf{p})f(\mathbf{p}_2)\right).$$

Applying the symmetry of the integral as well as time reversal and parity symmety we find

$$\partial_t n = \int \mathrm{d}^3\mathbf{p} \int \mathrm{d}^3\mathbf{p}_2 \int \mathrm{d}\Omega\, \frac{\partial\sigma}{\partial\Omega}|\mathbf{v}-\mathbf{v}_2|\left(f(\mathbf{p}_1')f(\mathbf{p}_2') - f(\mathbf{p})f(\mathbf{p}_2)\right)\left(\chi(\mathbf{r},\mathbf{p}) + \chi(\mathbf{r},\mathbf{p}_2) - \chi(\mathbf{r},\mathbf{p}_1') - \chi(\mathbf{r},\mathbf{p}_2')\right),$$

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 $\ln\left(f^0\right)$ is also conserved. This must mean

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

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 Idea For this consideration of quantum systems, the idea is to have the system interact with some bath containing an enormous number of degrees of freedom relative to those of the system.

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.

Product Operators We recall that for a tensor product, the expectation value of the product is the product of the expectation values. This means that expectation values of system observables make sense.

Schmidt Decomposition Consider a system in contact with a bath. A general state can be written as

$$|\Psi\rangle = \sum_a \sum_\alpha \Psi_{a\alpha}\,|a\rangle \otimes |\alpha\rangle\,,$$

where the latin and greek indices indicate states in the system and bath respectively. We may equivalently consider a state as specified by a matrix Ψ with elements $\Psi_{a\alpha}$. The singular value decomposition of Ψ is

$$\Psi = U\Lambda V^\dagger$$

for some set of matrices U, Λ and V such that Λ is a rectangular diagonal matrix with positive elements and U and V are unitary. We may then write

$$\Psi_{a\alpha} = \sum_b U_{ab}(\Lambda V^\dagger)_{b\alpha} = \sum_b \sum_\beta U_{ab}\Lambda_{b\beta}(V^\dagger)_{\beta\alpha}.$$

Because Λ is diagonal, summing over β only gives a contribution when $b = \beta$, hence

$$\Psi_{a\alpha} = \sum_b U_{ab}\lambda_b (V^\dagger)_{b\alpha},$$

and

$$\begin{aligned}|\Psi\rangle &= \sum_a \sum_\alpha \sum_b U_{ab}\lambda_b (V^\dagger)_{b\alpha} |a\rangle \otimes |\alpha\rangle \\ &= \sum_b \lambda_b \sum_a U_{ab} |a\rangle \otimes \sum_\alpha (V^\dagger)_{b\alpha} |\alpha\rangle .\end{aligned}$$

Because U and V are unitary, the above product contains two proper states. Naming them $|b\rangle_{\mathrm{S}}$ and $|b\rangle_{\mathrm{B}}$ we have

$$|\Psi\rangle = \sum_b \lambda_b |b\rangle_{\mathrm{S}} \otimes |b\rangle_{\mathrm{B}} .$$

One thing that was somewhat brushed over in this treatment is the kind of summation performed in the decomposition. Its limits depend on the structure of Ψ. This case is valid for when Ψ has more columns than rows, but if the other were to be the case, we could use a similar treatment to obtain a sum over greek indices instead. The point is that we are summing over the singular values, the number of which is equal to the smaller of the sizes of Ψ.

The Schrödinger Langevin Equation We will now perform a similar consideration as that done in the classical case, namely extending the Schrödinger equation to

$$i\frac{\mathrm{d}}{\mathrm{d}t}|\Psi\rangle = (H - iW + i\eta(t)V)|\Psi\rangle .$$

W is a Hermitian damping term and η is a random process such that

$$\langle\langle \eta(t) \rangle\rangle = 1, \ \left\langle\left\langle \eta(t)\eta^\star(t') \right\rangle\right\rangle = \delta(t - t'),$$

where we are now referring to averages over the random process rather than quantum mechanical expectation values. This term then corresponds to a noise term. A time step δt yields

$$|\Psi\rangle_{t+\delta t} = \left(1 - (iH + W)\delta t + \int_t^{t+\delta t} \mathrm{d}t' \, \eta(t')V\right)|\Psi\rangle_t .$$

Using this we may compute the norm of $|\Psi\rangle$ after this time step according to

$$\begin{aligned}\langle\Psi|\Psi\rangle_{t+\delta t} =& \langle\Psi| \left(1 + (iH - W)\delta t + \int_t^{t+\delta t} \mathrm{d}t' \, \eta^\star(t')V^\dagger\right) \left(1 - (iH + W)\delta t + \int_t^{t+\delta t} \mathrm{d}t' \, \eta(t')V\right)|\Psi\rangle \\ =& \langle\Psi|(1 + (iH - W)\delta t)\,(1 - (iH + W)\delta t)|\Psi\rangle \\ &+ \langle\Psi|(1 + (iH - W)\delta t) \left(\int_t^{t+\delta t} \mathrm{d}t' \, \eta(t')V\right)|\Psi\rangle + \langle\Psi| \left(\int_t^{t+\delta t} \mathrm{d}t' \, \eta^\star(t')V^\dagger\right)(1 - (iH + W)\delta t)|\Psi\rangle \\ &+ \langle\Psi| \int_t^{t+\delta t} \mathrm{d}t' \int_t^{t+\delta t} \mathrm{d}t'' \, \eta(t')\eta^\star(t'')V^\dagger V|\Psi\rangle .\end{aligned}$$

Averaging over the random process removes the two terms in the middle. To first order in the time step we therefore have

$$\begin{aligned}\langle\Psi|\Psi\rangle_{t+\delta t} =& \ \langle\Psi|(1 + -2W\delta t)|\Psi\rangle + \langle\Psi| \int_t^{t+\delta t} \mathrm{d}t' \int_t^{t+\delta t} \mathrm{d}t'' \, \delta(t' - t'')V^\dagger V|\Psi\rangle \\ =& \ \langle\Psi|(1 - 2W\delta t)|\Psi\rangle + \langle\Psi| \int_t^{t+\delta t} \mathrm{d}t' \, V^\dagger V|\Psi\rangle \\ =& \ \langle\Psi|(1 - 2W\delta t)|\Psi\rangle + \delta t \, \langle\Psi|V^\dagger V|\Psi\rangle ,\end{aligned}$$

and requiring the norm to be preserved by the time step implies

$$W = \frac{1}{2}V^\dagger V.$$

In summary, the Schrödinger Langevin equation is

$$i\frac{\mathrm{d}}{\mathrm{d}t}\left|\Psi\right\rangle = \left(H - \frac{i}{2}V^\dagger V + i\eta(t)V\right)\left|\Psi\right\rangle.$$

The Lindblad Equation Using the Schrödinger Langevin equation we may derive a time evolution equation for the density matrix. We have the time evolution operator

$$U(t,t_0) = e^{-i\left((H-\frac{i}{2}V^\dagger V)(t-t_0)+i\int_{t_0}^{t}\mathrm{d}t'\eta(t')V\right)},$$

and thus

$$\rho(t) = U(t,t_0)\rho(t_0)U^\dagger(t,t_0).$$

In particular, for a small time step δt we may expand to find

$$\begin{aligned}\rho(t+\delta t) =& \left(1 - i\left(\left(H - \frac{i}{2}V^\dagger V\right)\delta t + i\int_t^{t+\delta t}\mathrm{d}t'\,\eta(t')V\right)\right)\rho(t)\left(1 + i\left(\left(H + \frac{i}{2}V^\dagger V\right)\delta t - i\int_t^{t+\delta t}\mathrm{d}t'\,\eta^\star(t')V^\dagger\right)\right)\\ =&\rho(t) - i\left(\left(H - \frac{i}{2}V^\dagger V\right)\delta t + i\int_t^{t+\delta t}\mathrm{d}t'\,\eta(t')V\right)\rho(t) + i\rho(t)\left(\left(H + \frac{i}{2}V^\dagger V\right)\delta t - i\int_t^{t+\delta t}\mathrm{d}t'\,\eta^\star(t')V^\dagger\right)\\ &+ \int_t^{t+\delta t}\mathrm{d}t'\int_t^{t+\delta t}\mathrm{d}t''\,\eta(t')\eta^\star(t'')V\rho(t)V^\dagger.\end{aligned}$$

Averaging over the noise yields

$$\begin{aligned}\rho(t+\delta t) &= \rho(t) - i\left(\left(H - \frac{i}{2}V^\dagger V\right)\delta t\right)\rho(t) + i\rho(t)\left(\left(H + \frac{i}{2}V^\dagger V\right)\delta t\right) + \int_t^{t+\delta t}\mathrm{d}t'\int_t^{t+\delta t}\mathrm{d}t''\,\delta(t'-t'')V\rho(t)V^\dagger\\ &= \rho(t) + i\delta t\left(-\left(H - \frac{i}{2}V^\dagger V\right)\rho(t) + \rho(t)\left(H + \frac{i}{2}V^\dagger V\right)\right) + \int_t^{t+\delta t}\mathrm{d}t'\,V\rho(t)V^\dagger\\ &= \rho(t) + \delta t\left(-i[H,\rho(t)] - \frac{1}{2}\Big\{V^\dagger V,\rho(t)\Big\} + V\rho(t)V^\dagger\right),\end{aligned}$$

and in the limit of infinitesimal time steps we obtain the Lindblad equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho = -i[H,\rho(t)] - \frac{1}{2}\Big\{V^\dagger V,\rho(t)\Big\} + V\rho(t)V^\dagger.$$

It may be generalized to a set of interactions with the surroundings by applying a linearity and choosing a basis for the space of operators such that

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho = -i[H,\rho(t)] + \sum_\alpha V_\alpha\rho(t)V_\alpha^\dagger - \frac{1}{2}\Big\{V_\alpha^\dagger V_\alpha,\rho(t)\Big\}.$$

Third Quantization Let K be the space of operators on Hilbert space. Then the Liouville operator

$$L:\ \rho \to -i[H,\rho(t)] + \sum_\alpha 2V_\alpha\rho(t)V_\alpha^\dagger - \Big\{V_\alpha^\dagger V_\alpha,\rho(t)\Big\},$$

which appears in the Lindblad equation (with a different normalization of the jump operators), is a map on K. Solving for the dynamics of elements in K is difficult in general, but we will present a way to do it for a particular type of Hamiltonians. This is called third quantization.

A Hamiltonian is quadratic if it is quadratic in creation and annihilation operators. In the case of a non-interacting Hamiltonian, it takes the form

$$H = \sum_{i,j=1}^{N} \begin{bmatrix} c_i^\dagger & c_i \end{bmatrix} \begin{bmatrix} h_{ij} & \Delta_{ij} \\ \Delta_{ij}^\star & h_{ij}^\star \end{bmatrix} \begin{bmatrix} c_j \\ c_j^\dagger \end{bmatrix}.$$

We rewrite this by introducing creation operators for so-called Majorana fermions

$$w_{2j-1} = c_j + c_j^\dagger,\ w_{2j} = i(c_j - c_j^\dagger),$$

of which there are $2N$. We have

$$w_{2j-1}^\dagger = c_j^\dagger + c_j = w_{2j-1},\ w_{2j}^\dagger = -i(c_j^\dagger - c_j) = w_{2j}.$$

Assuming the fundamental operators to be fermionic, we have

$$\begin{aligned}
\{w_{2j-1}, w_{2k-1}\} &= \left\{c_j + c_j^\dagger, c_k + c_k^\dagger\right\} \\
&= \{c_j, c_k\} + \left\{c_j, c_k^\dagger\right\} + \left\{c_j^\dagger, c_k\right\} + \left\{c_j^\dagger, c_k^\dagger\right\} \\
&= 2\delta_{jk}, \\
\{w_{2j-1}, w_{2k}\} &= i\left\{c_j + c_j^\dagger, c_k - c_k^\dagger\right\} \\
&= i\left(\{c_j, c_k\} - \left\{c_j, c_k^\dagger\right\} + \left\{c_j^\dagger, c_k\right\} - \left\{c_j^\dagger, c_k^\dagger\right\}\right) \\
&= 0, \\
\{w_{2j}, w_{2k}\} &= -\left\{c_j - c_j^\dagger, c_k - c_k^\dagger\right\} \\
&= -\left(\{c_j, c_k\} - \left\{c_j, c_k^\dagger\right\} - \left\{c_j^\dagger, c_k\right\} + \left\{c_j^\dagger, c_k^\dagger\right\}\right) \\
&= 2\delta_{jk}.
\end{aligned}$$

We may therefore conclude

$$\{w_j, w_k\} = 2\delta_{jk}.$$

This implies $w_i^2 = 1$.

Returning to the Hamiltonian, we find that it takes the form

$$\begin{aligned}
H =& \sum_{i,j=1}^{N} h_{ij} c_i^\dagger c_j + h_{ij}^\star c_i c_j^\dagger + \Delta_{ij} c_i^\dagger c_j^\dagger + \Delta_{ij}^\star c_i c_j \\
=& \frac{1}{4} \sum_{i,j=1}^{N} h_{ij}(w_{2i-1} + iw_{2i})(w_{2j-1} - iw_{2j}) + h_{ij}^\star(w_{2i-1} - iw_{2i})(w_{2j-1} + iw_{2j}) \\
&+ \frac{1}{4} \sum_{i,j=1}^{N} \Delta_{ij}(w_{2i-1} + iw_{2i})(w_{2j-1} + iw_{2j}) + \Delta_{ij}^\star(w_{2i-1} - iw_{2i})(w_{2j-1} - iw_{2j}) \\
=& \frac{1}{4} \sum_{i,j=1}^{N} w_{2i-1}w_{2j-1}(h_{ij} + h_{ij}^\star + \Delta_{ij} + \Delta_{ij}^\star) + w_{2i-1}w_{2j}(-ih_{ij} + ih_{ij}^\star + i\Delta_{ij} - \Delta_{ij}^\star) \\
&+ \frac{1}{4} \sum_{i,j=1}^{N} w_{2i}w_{2j-1}(ih_{ij} - ih_{ij}^\star + i\Delta_{ij} - i\Delta_{ij}) + w_{2i}w_{2j}(h_{ij} + h_{ij}^\star - \Delta_{ij} - \Delta_{ij}^\star) \\
=& \frac{1}{4} \sum_{i,j=1}^{2N} w_i A_{ij} w_j
\end{aligned}$$

for some as of yet undetermined matrix A. The commutation relations imply

$$w_i A_{ij} w_j = 2A_{ij}\delta_{ij} - w_j A_{ij} w_i,$$

hence

$$\begin{aligned} H &= \frac{1}{8}\sum_{i,j=1}^{2N} w_i A_{ij} w_j + 2A_{ij}\delta_{ij} - w_j A_{ij} w_i \\ &= \frac{1}{4}\operatorname{tr}(A) + \frac{1}{8}\sum_{i,j=1}^{2N} w_i A_{ij} w_j - w_j A_{ij} w_i \\ &= \frac{1}{4}\operatorname{tr}(A) + \frac{1}{8}\sum_{i,j=1}^{2N} (A_{ij} - A_{ji}) w_i w_j, \end{aligned}$$

hence we may simplify by redefining A. Choosing it to be traceless corresponds to redefining the zero level. We also see that we may choose A to be antisymmetric. Extracting a factor i and choosing A to be real, we find H to be Hermitian, and the final form is

$$H = \frac{i}{4}\sum_{i,j=1}^{2N} w_i A_{ij} w_j.$$

We want the Liouvillian to be quadratic as well, hence the jump operators must be of the form

$$L_\mu = \sum_i (l_\mu)_i w_i.$$

On Fock space we construct operators with products of creation and annihilation operators. We want to do the same on K, and therefore need a basis on it. We use normal kets to denote elements in K, although double wedge brackets are more commonly used. We construct the basis from operator products

$$w_1^{\alpha_1} \dots w_{2N}^{\alpha_{2N}},\ \alpha_i \in \{0, 1\}.$$

The basis is thus comprised of elements

$$w_1^{\alpha_1} \otimes w_2^{\alpha_2} \otimes \dots \otimes w_{2N}^{\alpha_{2N}} = |w_{\boldsymbol{\alpha}}\rangle$$

such that

$$|w_{\boldsymbol{\alpha}}\rangle\,(w_{\boldsymbol{\alpha}'}) = |w_{\boldsymbol{\alpha}+\boldsymbol{\alpha}' \bmod 2}\rangle\,,$$

where the vector addition is carried out modulo 2 due to the w squaring to the identity. The dimension of K is identifiable from the above as $D = 2^{2N} = 4^N$. We also define the inner product on K as

$$\langle x|y\rangle = \frac{1}{D}\operatorname{tr}\Big(x^\dagger y\Big),$$

where the trace is carried out over K. Using this we have

$$\begin{aligned} \langle w_{\boldsymbol{\alpha}}|w_{\boldsymbol{\alpha}'}\rangle &= \frac{1}{D}\operatorname{tr}\Big((w_1^{\alpha_1})^\dagger (w_{2N}^{\alpha_{2N}})^\dagger w_1^{\alpha_1'} \dots w_{2N}^{\alpha_{2N}'}\Big) \\ &= \frac{1}{D}\operatorname{tr}\Big(w_1^{\alpha_1} w_1^{\alpha_1'} \dots w_{2N}^{\alpha_{2N}} w_{2N}^{\alpha_{2N}'}\Big). \end{aligned}$$

There are two possibilities. If $\boldsymbol{\alpha} = \boldsymbol{\alpha}'$ then all operators are merged to form powers of zero or two, and we are left with the trace of the identity, which is equal to D. In the other case there exists at least one operator which is not cancelled in the multiplication with the operator. This is equivalent to

$$\Big|(w_1^{\alpha_1})^\dagger (w_{2N}^{\alpha_{2N}})^\dagger w_1^{\alpha_1'} \dots w_{2N}^{\alpha_{2N}'}\Big\rangle\,(w_{\boldsymbol{\beta}}) = |w_{\boldsymbol{\gamma}}\rangle\,,\ \boldsymbol{\gamma} \neq \boldsymbol{\beta},$$

which implies that $(w_1^{\alpha_1})^\dagger (w_{2N}^{\alpha_{2N}})^\dagger w_1^{\alpha_1'} \dots w_{2N}^{\alpha_{2N}'}$ has no diagonal elements in K, and its trace must be zero. In conclusion, we have

$$\langle w_{\boldsymbol{\alpha}}|w_{\boldsymbol{\alpha}'}\rangle = \delta_{\boldsymbol{\alpha},\boldsymbol{\alpha}'}$$

We also introduce creation and annihilation operators on K according to

$$c_j \left|w_\alpha\right\rangle = \delta_{\alpha_j,1} \left|w_j w_\alpha\right\rangle .$$

The state on the right is given by

$$\left|w_j w_{\boldsymbol{\alpha}}\right\rangle = (-1)^{\sum\limits_{l<j} \alpha_l} \left|w_{\boldsymbol{\alpha}+\alpha_j \bmod 2}\right\rangle .$$

To find the creation operator, we consider its matrix elements

$$\begin{aligned}\langle w_{\boldsymbol{\alpha}'}|c_j^\dagger|w_{\boldsymbol{\alpha}}\rangle &= \langle w_{\boldsymbol{\alpha}}|c_j|w_{\boldsymbol{\alpha}'}\rangle^\star \\ &= \delta_{\alpha_j',1} \langle w_j w_{\boldsymbol{\alpha}'}|w_{\boldsymbol{\alpha}}\rangle .\end{aligned}$$

Writing it out in terms of the trace we have

$$\langle w_j w_{\boldsymbol{\alpha}'}|w_{\boldsymbol{\alpha}}\rangle = \frac{1}{D}\operatorname{tr}\Big(w_{2N}^{\alpha_{2N}'} \dots w_1^{\alpha_1'} w_j w_1^{\alpha_1} \dots w_{2N}^{\alpha_{2N}}\Big) = \langle w_{\boldsymbol{\alpha}'}|w_j w_{\boldsymbol{\alpha}}\rangle ,$$

hence

$$\langle w_{\boldsymbol{\alpha}'}|c_j^\dagger|w_{\boldsymbol{\alpha}}\rangle = \delta_{\alpha_j',1} \langle w_{\boldsymbol{\alpha}'}|w_j w_{\boldsymbol{\alpha}}\rangle .$$

In order to infer an operator identity, we need to contain $\boldsymbol{\alpha}'$ to the bra. We do this by applying orthonormality of the basis. We thus write this as

$$\begin{aligned}\delta_{\alpha_j',1} \langle w_{\boldsymbol{\alpha}'}|w_j w_{\boldsymbol{\alpha}}\rangle &= \delta_{\alpha_j',1}\delta_{\boldsymbol{\alpha}',\boldsymbol{\alpha}+\alpha_j \bmod 2} \\ &\propto \delta_{\alpha_j',1}\delta_{\alpha_j',\alpha_j+1 \bmod 2} \\ &= \delta_{1,\alpha_j+1 \bmod 2} \\ &= \delta_{\alpha_j,0}.\end{aligned}$$

We thus see that we may replace the extra delta in the primed components with one in the unprimed once, yielding

$$\langle w_{\boldsymbol{\alpha}'}|c_j^\dagger|w_{\boldsymbol{\alpha}}\rangle = \delta_{\alpha_j,0} \langle w_{\boldsymbol{\alpha}'}|w_j w_{\boldsymbol{\alpha}}\rangle \implies c_j^\dagger \left|w_{\boldsymbol{\alpha}}\right\rangle = \delta_{\alpha_j,0} \left|w_j w_{\boldsymbol{\alpha}}\right\rangle .$$

To verify the anticommutation relations between these operators, we first note that the action of two operators with different indices produce a state $|w_j w_k w_{\boldsymbol{\alpha}}\rangle$ with a prefactor which is independent of the order. We find

$$c_j c_k \left|w_{\boldsymbol{\alpha}}\right\rangle = C \left|w_j w_k w_{\boldsymbol{\alpha}}\right\rangle = -C \left|w_k w_j w_{\boldsymbol{\alpha}}\right\rangle = -c_k c_j \left|w_{\boldsymbol{\alpha}}\right\rangle$$

for any state, and the same applies if adjoints are added to any operator. This implies

$$\{c_k, c_j\} = \left\{c_k^\dagger, c_j^\dagger\right\} = 0.$$

We also have

$$c_j c_j^\dagger \left|w_{\boldsymbol{\alpha}}\right\rangle = \delta_{\alpha_j,0} c_j \left|w_j w_{\boldsymbol{\alpha}}\right\rangle = \delta_{\alpha_j,0}\delta_{\alpha_j+1 \bmod 2,1} \left|w_{\boldsymbol{\alpha}}\right\rangle .$$

The two Kronecker deltas are equivalent, so we may drop one. Similar arguments for the reverse order yield

$$\left\{c_j, c_j^\dagger\right\} \left|w_{\boldsymbol{\alpha}}\right\rangle = (\delta_{\alpha_j,0} + \delta_{\alpha_j,1}) \left|w_{\boldsymbol{\alpha}}\right\rangle ,$$

which is always equal to $|w_{\boldsymbol{\alpha}}\rangle$. We thus conclude

$$\left\{c_j, c_k^\dagger\right\} = \delta_{jk},$$

Returning to the Liouvillean, we note that as it is linear, we only need to compute $L\left|w_{\boldsymbol{\alpha}}\right\rangle$. It takes the form

$$\begin{aligned}L\rho &= -i[H,\rho] + \sum_{\mu} 2L_{\mu}\rho L_{\mu}^{\dagger} - \left\{L_{\mu}^{\dagger}L_{\mu},\rho\right\} \\ &= \frac{1}{4}\sum_{j,k} A_{ij}[w_j w_k,\rho] + \sum_{\mu}\sum_{j,k} 2(l_{\mu})_j (l_{\mu})_k^{\star} w_j \rho w_k - (l_{\mu})_j^{\star}(l_{\mu})_k\{w_j w_k,\rho\}\end{aligned}$$

for a general operator. For the Hamiltonian part we find

$$\begin{aligned}[w_j w_k, \left|w_{\boldsymbol{\alpha}}\right\rangle] &= \left|w_j w_k w_{\boldsymbol{\alpha}}\right\rangle - \left|w_{\boldsymbol{\alpha}} w_j w_k\right\rangle \\ &= \left(1 - (-1)^{\sum\limits_{m\neq j}\alpha_m}(-1)^{\sum\limits_{n\neq k}\alpha_n}\right)\left|w_j w_k w_{\boldsymbol{\alpha}}\right\rangle \\ &= \left(1-(-1)^{\alpha_k+\alpha_l}\right)\left|w_j w_k w_{\boldsymbol{\alpha}}\right\rangle,\end{aligned}$$

where the last equality is a result of j and k being the only operators that are commuted through once. This is only non-zero if $\alpha_j \neq \alpha_k$, hence we may write

$$[w_j w_k, \left|w_{\boldsymbol{\alpha}}\right\rangle] = 2\left(\delta_{\alpha_j,0}\delta_{\alpha_k,1} + \delta_{\alpha_j,1}\delta_{\alpha_k,0}\right)\left|w_j w_k w_{\boldsymbol{\alpha}}\right\rangle.$$

This can be written in terms of creation and annihilation operators as

$$[w_j w_k, \left|w_{\boldsymbol{\alpha}}\right\rangle] = 2\left(c_j^{\dagger}c_k + c_j c_k^{\dagger}\right)(1-\delta_{ij})\left|w_{\boldsymbol{\alpha}}\right\rangle,$$

where the rightmost factor accounts for the fact that the Kronecker deltas prohibit $i=j$. Using the anticommutation relations we find

$$\begin{aligned}[w_j w_k, \left|w_{\boldsymbol{\alpha}}\right\rangle] &= 2\left(c_j^{\dagger}c_k - c_k^{\dagger}c_j + \delta_{jk}\right)(1-\delta_{jk})\left|w_{\boldsymbol{\alpha}}\right\rangle \\ &= 2\left(c_j^{\dagger}c_k - c_k^{\dagger}c_j + \delta_{jk} - \delta_{jk}\left(c_j^{\dagger}c_k - c_j c_k^{\dagger} + \delta_{jk}\right)\right)\left|w_{\boldsymbol{\alpha}}\right\rangle \\ &= 2\left(c_j^{\dagger}c_k - c_k^{\dagger}c_j - \delta_{jk}c_j^{\dagger}c_k + \delta_{jk}c_j c_k^{\dagger}\right)\left|w_{\boldsymbol{\alpha}}\right\rangle \\ &= 2\left(c_j^{\dagger}c_k - c_k^{\dagger}c_j - \delta_{jk}c_j^{\dagger}c_j + \delta_{jk}c_j c_j^{\dagger}\right)\left|w_{\boldsymbol{\alpha}}\right\rangle \\ &= 2\left(c_j^{\dagger}c_k - c_k^{\dagger}c_j\right)\left|w_{\boldsymbol{\alpha}}\right\rangle,\end{aligned}$$

and

$$\begin{aligned}-i[H,\left|w_{\boldsymbol{\alpha}}\right\rangle] &= \frac{1}{2}\sum_{j,k} A_{jk}\left(c_j^{\dagger}c_k - c_k^{\dagger}c_j\right)\left|w_{\boldsymbol{\alpha}}\right\rangle \\ &= \frac{1}{2}\sum_{j,k}\left(A_{jk}c_j^{\dagger}c_k - A_{kj}c_j^{\dagger}c_k\right)\left|w_{\boldsymbol{\alpha}}\right\rangle.\end{aligned}$$

The jump terms are given by

$$\sum_{\mu}\sum_{j,k}(l_{\mu})_j^{\star}(l_{\mu})_k\left(2w_j\left|w_{\boldsymbol{\alpha}}\right\rangle w_k - \{w_k w_j, \left|w_{\boldsymbol{\alpha}}\right\rangle\}\right) = \sum_{\mu}\sum_{j,k}(l_{\mu})_j^{\star}(l_{\mu})_k\left(2\left|w_j w_{\boldsymbol{\alpha}} w_k\right\rangle - \left|\{w_k w_j, w_{\boldsymbol{\alpha}}\}\right\rangle\right),$$

and we want to study the operator part, which we denote $L_{j,k}\left|w_{\boldsymbol{\alpha}}\right\rangle$. We have

$$\begin{aligned}L_{j,k}\left|w_{\boldsymbol{\alpha}}\right\rangle &= 2(-1)^{\sum\limits_{m\neq k}\alpha_m}\left|w_j w_k w_{\boldsymbol{\alpha}}\right\rangle - \left|w_k w_j w_{\boldsymbol{\alpha}}\right\rangle - (-1)^{\sum\limits_{m\neq j}\alpha_m + \sum\limits_{m\neq k}\alpha_m}\left|w_k w_j w_{\boldsymbol{\alpha}}\right\rangle \\ &= 2(-1)^{|\boldsymbol{\alpha}|+\alpha_k}\left|w_j w_k w_{\boldsymbol{\alpha}}\right\rangle - \left(1+(-1)^{\alpha_k+\alpha_j}\right)\left|w_k w_j w_{\boldsymbol{\alpha}}\right\rangle,\end{aligned}$$

where we have introduced

$$|\boldsymbol{\alpha}| = \sum_m \alpha_m$$

and used the fact that $(-1)^{2\alpha_k} = 1$. We need the number operator

$$N = \sum_j c_j^\dagger c_j,$$

which extracts one if $\alpha_j = 1$ and zero otherwise, for each operator in the product. Its eigenvalues are thus $|\boldsymbol{\alpha}|$. As we are working in its eigenbasis, we may replace $|\boldsymbol{\alpha}|$ with N wherever it is found. We will also need the rewriting

$$\begin{aligned}\left(c_k^\dagger + c_k\right)|w_{\boldsymbol{\alpha}}\rangle &= (\delta_{\alpha_k,0} + \delta_{\alpha_k,1})\,|w_k w_{\boldsymbol{\alpha}}\rangle = |w_k w_{\boldsymbol{\alpha}}\rangle\,,\\ \left(c_k^\dagger - c_k\right)|w_{\boldsymbol{\alpha}}\rangle &= (\delta_{\alpha_k,0} - \delta_{\alpha_k,1})\,|w_k w_{\boldsymbol{\alpha}}\rangle = (-1)^{\alpha_k}\,|w_k w_{\boldsymbol{\alpha}}\rangle\,.\end{aligned}$$

We now have

$$\begin{aligned}L_{j,k}\,|w_{\boldsymbol{\alpha}}\rangle =& 2e^{i\pi N}\left(c_j^\dagger + c_j\right)\left(c_k^\dagger - c_k\right)|w_{\boldsymbol{\alpha}}\rangle - \left(c_k^\dagger + c_k\right)\left(c_j^\dagger + c_j\right)|w_{\boldsymbol{\alpha}}\rangle - \left(c_k^\dagger - c_k\right)\left(c_j^\dagger - c_j\right)|w_{\boldsymbol{\alpha}}\rangle\\
=& \left(2e^{i\pi N}\left(c_j^\dagger c_k^\dagger - c_j^\dagger c_k + c_j c_k^\dagger - c_j c_k\right) - \left(c_k^\dagger c_j^\dagger + c_k c_j^\dagger + c_k^\dagger c_j + c_k c_j\right) - \left(c_k^\dagger c_j^\dagger - c_k c_j^\dagger - c_k^\dagger c_j + c_k c_j\right)\right)|w_{\boldsymbol{\alpha}}\rangle\\
=& \left(2e^{i\pi N}\left(c_j^\dagger c_k^\dagger - \frac{1}{2}\left(c_j^\dagger c_k + \delta_{jk} - c_k c_j^\dagger\right) + \frac{1}{2}\left(c_j c_k^\dagger + \delta_{jk} - c_k^\dagger c_j\right) - c_j c_k\right) - 2c_k^\dagger c_j^\dagger - 2c_k c_j\right)|w_{\boldsymbol{\alpha}}\rangle\\
=& 2\left(e^{i\pi N}\left(c_j^\dagger c_k^\dagger + \frac{1}{2}\left(c_k c_j^\dagger + c_j c_k^\dagger - c_k^\dagger c_j - c_j^\dagger c_k\right) - c_j c_k\right) + c_j^\dagger c_k^\dagger + c_j c_k\right)|w_{\boldsymbol{\alpha}}\rangle\\
=& 2\left(c_j^\dagger c_k^\dagger\left(1 + e^{i\pi N}\right) + c_j c_k\left(1 - e^{i\pi N}\right) + \frac{1}{2}e^{i\pi N}\left(c_k c_j^\dagger + c_j c_k^\dagger - c_k^\dagger c_j - c_j^\dagger c_k\right)\right)|w_{\boldsymbol{\alpha}}\rangle\\
=& \left(\left(2c_j^\dagger c_k^\dagger - c_j^\dagger c_k - c_k^\dagger c_j\right)\left(1 + e^{i\pi N}\right) + \left(2c_j c_k - c_j c_k^\dagger - c_k c_j^\dagger\right)\left(1 - e^{i\pi N}\right)\right)|w_{\boldsymbol{\alpha}}\rangle\\
&+ \left(c_j^\dagger c_k + c_k^\dagger c_j + c_j c_k^\dagger + c_k c_j^\dagger\right)|w_{\boldsymbol{\alpha}}\rangle\\
=& \left(\left(2c_j^\dagger c_k^\dagger - c_j^\dagger c_k - c_k^\dagger c_j\right)\left(1 + e^{i\pi N}\right) + \left(2c_j c_k - c_j c_k^\dagger - c_k c_j^\dagger\right)\left(1 - e^{i\pi N}\right) + 2\delta_{jk}\right)|w_{\boldsymbol{\alpha}}\rangle\,.\end{aligned}$$

Introducing the parity $(-1)^N$ of a particular state, the operators $\frac{1}{2}\left(1 \pm e^{i\pi N}\right)$ are projectors onto the subspaces with particular parity. $L_{j,k}$ thus preserves the parity of incoming states. As all states in the basis have well-defined parities, K is a direct sum over the subspaces with different parities. We may thus restrict the following considerations to the two subspaces separately.

Returning to the dissipator, it takes the form

$$\sum_\mu \sum_{j,k} (l_\mu)_j^\star (l_\mu)_k \left(\left(2c_j^\dagger c_k^\dagger - c_j^\dagger c_k - c_k^\dagger c_j\right)\left(1 + e^{i\pi N}\right) + \left(2c_j c_k - c_j c_k^\dagger - c_k c_j^\dagger\right)\left(1 - e^{i\pi N}\right) + 2\delta_{jk}\right)|w_{\boldsymbol{\alpha}}\rangle\,.$$

We now define

$$M_{jk} = \sum_\mu (l_\mu)_j^\star (l_\mu)_k,$$

which defines a Hermitian matrix, as

$$M_{kj}^\star = \sum_\mu (l_\mu)_k (l_\mu)_j^\star = M_{jk}.$$

On the subspace with positive parity, the dissipator is thus

$$\sum_{j,k} M_{jk}\left(4c_j^\dagger c_k^\dagger - 2c_j^\dagger c_k - 2c_k^\dagger c_j + 2\delta_{jk}\right)|w_{\boldsymbol{\alpha}}\rangle = \sum_{j,k}\left(2(M_{jk} - M_{kj})c_j^\dagger c_k^\dagger - 2(M_{jk} + M_{kj})c_j^\dagger c_k + 2M_{jk}\delta_{jk}\right)|w_{\boldsymbol{\alpha}}\rangle\,.$$

As M is Hermitian, this is equal to

$$\begin{aligned}&2\,\mathrm{tr}(M)\,|w_{\boldsymbol{\alpha}}\rangle + \sum_{j,k}\left(4i\,\mathrm{Im}(M_{jk})c_j^\dagger c_k^\dagger - 4\,\mathrm{Re}(M_{jk})c_j^\dagger c_k\right)|w_{\boldsymbol{\alpha}}\rangle\\
=&2\,\mathrm{tr}(M)\,|w_{\boldsymbol{\alpha}}\rangle + \sum_{j,k}\left(4i\,\mathrm{Im}(M_{jk})c_j^\dagger c_k^\dagger - 2(\mathrm{Re}(M_{jk})c_j^\dagger c_k - \mathrm{Re}(M_{kj})c_j c_k^\dagger)\right)|w_{\boldsymbol{\alpha}}\rangle\,.\end{aligned}$$

On this subspace, the Liouvillean then takes the form

$$L\left|w_{\boldsymbol{\alpha}}\right\rangle = 2\operatorname{tr}(M)\left|w_{\boldsymbol{\alpha}}\right\rangle + \sum_{j,k}\left(\frac{1}{2}\left(A_{jk}c_j^\dagger c_k - A_{kj}c_j^\dagger c_k\right) + 4i\operatorname{Im}(M_{jk})c_j^\dagger c_k^\dagger - 2\operatorname{Re}(M_{jk})c_j^\dagger c_k + 2\operatorname{Re}(M_{kj})c_j c_k^\dagger\right)\left|w_{\boldsymbol{\alpha}}\right\rangle.$$

We can employ a somewhat more efficient notation by converting to vector notation, which yields

$$L = \frac{1}{2}\begin{bmatrix}c^\dagger & c\end{bmatrix}\begin{bmatrix}A - 4\operatorname{Re}(M) & 8i\operatorname{Im}(M) \\ 0 & -A^T + 4\operatorname{Re}(M^T)\end{bmatrix}\begin{bmatrix}c \\ c^\dagger\end{bmatrix} - \frac{1}{2}\operatorname{tr}(A - 4M),$$

where the vectors on the left and right contain all creation and annihilation operators.

On the subspace with negative parity, the dissipator is instead

$$\begin{aligned}
&\sum_{j,k} M_{jk}\left(2\left(2c_jc_k - c_jc_k^\dagger - c_kc_j^\dagger\right) + 2\delta_{jk}\right)\left|w_{\boldsymbol{\alpha}}\right\rangle \\
=&2\operatorname{tr}(M)\left|w_{\boldsymbol{\alpha}}\right\rangle + \sum_{j,k}\left(2(M_{jk} - M_{kj})c_jc_k - 2(M_{jk} + M_{kj})c_jc_k^\dagger\right)\left|w_{\boldsymbol{\alpha}}\right\rangle \\
=&2\operatorname{tr}(M)\left|w_{\boldsymbol{\alpha}}\right\rangle + \sum_{j,k}\left(4i\operatorname{Im}(M_{jk})c_jc_k - 4\operatorname{Re}(M_{jk})c_jc_k^\dagger\right)\left|w_{\boldsymbol{\alpha}}\right\rangle \\
=&2\operatorname{tr}(M)\left|w_{\boldsymbol{\alpha}}\right\rangle + \sum_{j,k}\left(4i\operatorname{Im}(M_{jk})c_jc_k - 2\operatorname{Re}(M_{jk})c_jc_k^\dagger + 2\operatorname{Re}(M_{kj})c_j^\dagger c_k\right)\left|w_{\boldsymbol{\alpha}}\right\rangle,
\end{aligned}$$

and the Liouvillean is

$$L = \frac{1}{2}\begin{bmatrix}c^\dagger & c\end{bmatrix}\begin{bmatrix}A - 4\operatorname{Re}(M) & 0 \\ 8i\operatorname{Im}(M) & -A^T + 4\operatorname{Re}(M^T)\end{bmatrix}\begin{bmatrix}c \\ c^\dagger\end{bmatrix} - \frac{1}{2}\operatorname{tr}(A - 4M).$$

What have we achieved by this? The problem of studying dynamics on K has been reduced from diagonalizing a $4^N \times 4^N$ matrix to diagonalizing two $2N \times 2N$ matrices.

Quantum Quenching We will now develop a Monte Carlo method for solving the Lindblad equation by noting that the jump operators represent jumps whereas the remaining terms in the Schrödinger Langevin equation represent continuous time evolution given by the operator

$$J = H - \frac{i}{2}\sum_\alpha L_\alpha^\dagger L_\alpha.$$

Time evolving for a short time and assuming no jumps to occur we find

$$\langle\Psi|\Psi\rangle_{t+\delta t} = \langle\Psi|\Psi\rangle_t + \langle\Psi|-iJ\delta t + iJ^\dagger\delta t|\Psi\rangle = 1 + i\delta t\langle\Psi|J^\dagger - J|\Psi\rangle = 1 - \delta t\langle\Psi|\sum_\alpha L_\alpha^\dagger L_\alpha|\Psi\rangle,$$

assuming the Hamiltonian to be self-adjoint and the state to initially be normalized. To interpret this, we define

$$p_0 = 1 - \delta t\langle\Psi|\sum_\alpha L_\alpha^\dagger L_\alpha|\Psi\rangle$$

and

$$p_\alpha = \delta t\langle\Psi|L_\alpha^\dagger L_\alpha|\Psi\rangle,$$

which satisfy

$$p_0 + \sum_\alpha p_\alpha = 1,$$

and our interpretation is thus that p_0 is the probability of no jump happening and p_α being the probability that the jump given by L_α happened. This defines a Monte Carlo algorithm to time evolve a quantum state:

1. Given some initial state, a system Hamiltonian and jump operators, compute p_0 and all p_α.

2. Get a random number between 0 and 1.

3. If $r < p_0$, no jump has occured, meaning that one time evolves using J. Otherwise, a jump occured. To determine which jump occured, identify the smallest ν such that $\sum_{\alpha=1}^{\nu} p_\alpha > r$ and evolve the state by simply multiplying by L_ν.

4. Normalize the state.

The Monte Carlo approach consists of performing a set of such evolutions from some initial state and compute the density matrix from a statistical overage over different runs.

Quantum Quenches In a quantum quench, one prepares a system in an eigenstate $|\Psi_0\rangle$ of some Hamiltonian H_0, and then switch the Hamiltonian to H_1 and let the system evolve. These two Hamiltonians generally do not share eigenstates, hence the system has non-trivial dynamics. This switch can be performed globally or locally.

A Conundrum of Thermalization Quantum mechanics preserves the purity of the density matrix, but the thermalized density matrix $\rho = \frac{1}{Z}e^{-\beta H}$ is always mixed. How, then, can quantum mechanics produce thermalization? It will turn out that this is the same problem as the one we faced with classical mechanics.

Von Neumann provided a suggestion for how to handle this in a previously-forgotten paper. In it he suggested that states themselves do not thermalize, but that expectation values of local observables do. This would require that the reduced density matrix for a system in consideration approaches that predicted by statistical mechanics.

Entanglement Entropy We define the von Neumann entanglement entropy as

$$S = -\operatorname{tr}_{\mathrm{S}}(\rho_{\mathrm{S}} \ln(\rho_{\mathrm{S}})) = -\operatorname{tr}_{\mathrm{B}}(\rho_{\mathrm{B}} \ln(\rho_{\mathrm{B}})).$$

Volume-Law Entanglement In order for systems to thermalize as we would like, we need the entanglement entropy to approach the thermal entropy. The thermal entropy is extensive, and thus scales as L^d, where d is the dimensionality. We therefore need there to exist states with this kind of entanglement. Such states have volume-law entanglement.

Random Matrix Theory Generally two things are needed for understanding the dynamics of a quantum system: The energy spacings, which dictate time evolution, and local matrix elements, which dictate how observables are calculated. Knowing this for a system of appreciable size is hard. Instead, random matrix theory involves replacing the Hamiltonian with an operator with random matrix elements. Given this, one can compute the distribution of level spacings $P(\Delta E)$.

There are a few different schemes. One is called the Gaussian orthonormal ensemble, and consists of all real Hamiltonians with elements drawn from a Gaussian distribution. The name comes from the realness being preserved by orthogonal transformations. Such Hamiltonians are time reversal symmetric.

Another scheme is called the Gaussian unitary scheme, and consists of complex (but self-adjoint) Hamiltonians with elements drawn from a Gaussian distribution.

Finally there is the Gaussian symplectic ensemble, which consists of Hamiltonians with elements drawn from a Gaussian distribution which are left invariant by a symplectic transformation, i.e. a transformation such that

$$S^T \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} S = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}.$$

Such Hamiltonians are invariant under transformations by operators T such that $T^2 = -1$.

In general the distribution is well approximated by the Wigner-Dyson distribution

$$P(s) = A_\beta s^\beta e^{-B_\beta s^2},$$

where A_β and B_β are determined by normalization and by fixing the mean. If the energy levels are independent, one instead expects them to follow a Poisson distribution. The former applies to chaotic dynamics, whereas the latter to integrable dynamics.

States and Matrix Elements in RMT In random matrix theory the eigenstates are random. Expanding in some basis we have

$$|\Psi\rangle = \sum_i \Psi_i |i\rangle .$$

For the Gaussian orthogonal and unitary cases the joint probability distributions of the expansion coefficients are products of Gaussians in each coefficients. To preserve normalization, we do however need to include

$$P_{\mathrm{GOE}}(\Psi_i) \propto \delta\left(\sum_j \Psi_j^2 -\right), \; P_{\mathrm{GUE}}(\Psi_i) \propto \delta\left(\sum_j |\Psi_j|^2 - 1\right).$$

This, as well as the issue of orthogonality, produces some correlation, but for sufficiently high dimensionalities of the Hilbert space this can be ignored. Hence we may take the joint probability distribution to be Gaussian.

Now let us consider matrix elements. In the eigenbasis $|i\rangle$ of the operator we have

$$O_{mn} = \langle m|O|n\rangle = \sum_i O_i \langle m|i\rangle \langle i|n\rangle = \sum_i O_i \Psi^\star_{m,i}\Psi_{n,i}.$$

Because the probability distribution is isotropic we have to leading order in the reciprocal dimensionality of Hilbert space

$$\overline{\Psi^\star_{m,i}\Psi_{n,i}} = \frac{1}{D}\delta_{mn}\delta_{ij},$$

where the bar denotes an average over the distribution of the coefficients. Thus

$$\overline{O}_{mn} = \sum_i O_i \overline{\Psi^\star_{m,i}\Psi_{n,i}} = \delta_{mn}\frac{1}{D}\sum_i O_i \equiv \bar{O}.$$

Higher-Order Expectation Values and Wick's Theorem Wick's theorem is a general statement on higher-order expectation values of the kind we will encounter here (and other things). The statement is

$$\overline{\Psi_{m_1}\ldots\Psi_{m_{2N}}} = \sum_{\text{pairs}} \overline{\Psi_{m_{k_1}}\Psi_{m_{k_2}}}\ldots\overline{\Psi_{m_{k_{2N-1}}}\Psi_{m_{k_{2N}}}},$$

where the summation is carried out over all possible unique ways to pair up the subscripts i and the indices m_k are paired indices. In the complex case we instead have

$$\overline{\Psi^\star_{i_1}\ldots\Psi^\star_{i_N}\Psi_{j_1}\ldots\Psi_{j_N}} = \sum_{P(1,\ldots,N)} \overline{\Psi_{i_{P(1)}}\Psi_{j_1}}\;\overline{\Psi_{i_{P(2)}}\Psi_{j_2}}\ldots\overline{\Psi_{i_{P(N)}}\Psi_{j_N}}.$$

Let us prove the real case first. A general Gaussian probability distribution for the coefficients is

$$P(\Psi) \propto e^{-\frac{1}{2}\Psi^T A\Psi},$$

where A is real, positive definite and symmetric (antisymmetric parts would not contribute). To normalize this, suppose that A is diagonalized by the orthogonal matrix P, and introduce the variable $x = P\Psi$. The Jacobian of this change of variables is 1 as the columns of P are orthonormal. We then have

$$\int \mathrm{d}^N\Psi\, C e^{-\frac{1}{2}\Psi^T A\Psi} = C\int \mathrm{d}^N x\, e^{-\frac{1}{2}x^T P^T APx} = C\int \mathrm{d}^N x\, e^{-\frac{1}{2}x^T Dx} = C\int \mathrm{d}^N x\, e^{-\frac{1}{2}\sum_i \lambda_i x_i^2},$$

where N is the dimension of the coefficient space and D is the diagonal matrix composed of the eigenvalues λ_i of A. The conditions on A imply that all eigenvalues are real and positive. This integral is separable, so we only need to look at one factor. We have

$$\int_{-\infty}^{\infty} \mathrm{d}x\, e^{-\frac{1}{2}\lambda_i x^2} = \sqrt{\frac{2}{\lambda_i}}\int_{-\infty}^{\infty} \mathrm{d}u\, e^{-u^2} = \sqrt{\frac{2\pi}{\lambda_i}},$$

and normalization implies

$$C = \sqrt{\frac{\prod_i \lambda_i}{(2\pi)^N}} = \sqrt{\frac{\det(A)}{(2\pi)^N}}.$$

To generate correlation functions, we introduce a generator-like function

$$F(j) = \int \mathrm{d}^N\Psi\, P(\Psi) e^{j^T\Psi}.$$

By its definition we find

$$\partial_{j_i} F\Big|_{j=0} = \int \mathrm{d}^N\Psi\, \Psi_i P(\Psi) e^{j^T\Psi}\Big|_{j=0} = \int \mathrm{d}^N\Psi\, \Psi_i P(\Psi) = \langle \Psi_i \rangle\,,$$

illustrating how we will use it to find expectation values. The general scheme is to apply successive derivatives with respect to the different components of j to find the corresponding correlation functions.

To compute F, we will introduce a j-dependent shift of the form $x = \Psi - Bj$, which yields

$$\begin{aligned}
F(j) &= \sqrt{\frac{\det(A)}{(2\pi)^N}} \int \mathrm{d}^N\Psi\, e^{-\frac{1}{2}\Psi^T A\Psi} e^{j^T\Psi} \\
&= \sqrt{\frac{\det(A)}{(2\pi)^N}} \int \mathrm{d}^N x\, e^{-\frac{1}{2}(x+Bj)^T A(x+Bj)} e^{j^T(x+Bj)} \\
&= e^{-\frac{1}{2}j^T B^T ABj + j^T Bj} \sqrt{\frac{\det(A)}{(2\pi)^N}} \int \mathrm{d}^N x\, e^{-\frac{1}{2}x^T Ax} e^{-\frac{1}{2}(x^T ABj + j^T B^T Ax) + j^T x}.
\end{aligned}$$

For any matrix, the fact that $AA^{-1} = A^{-1}A = 1$ implies that $(A^{-1})^T = (A^T)^{-1}$. In particular for a symmetrix matrix, the inverse matrix is also symmetric. Choosing $B = A^{-1}$ we find

$$\begin{aligned}
F(j) &= e^{-\frac{1}{2}j^T A^{-1}j + j^T A^{-1}j} \sqrt{\frac{\det(A)}{(2\pi)^N}} \int \mathrm{d}^N x\, e^{-\frac{1}{2}x^T Ax} e^{-\frac{1}{2}(x^T j + j^T x) + j^T x} \\
&= e^{\frac{1}{2}j^T A^{-1}j} \sqrt{\frac{\det(A)}{(2\pi)^N}} \int \mathrm{d}^N x\, e^{-\frac{1}{2}x^T Ax} = e^{\frac{1}{2}j^T A^{-1}j}.
\end{aligned}$$

Let us first study one particular correlation function. We have

$$\begin{aligned}
\partial_{j_m}\partial_{j_n} e^{\frac{1}{2}j^T A^{-1}j} =& \partial_{j_m}\left(\partial_{j_n}\left(\frac{1}{2}j^T A^{-1}j\right) e^{\frac{1}{2}j^T A^{-1}j}\right) \\
=& \partial_{j_m}\partial_{j_n}\frac{1}{2}\left(j^T A^{-1}j\right) e^{\frac{1}{2}j^T A^{-1}j} + \partial_{j_m}\frac{1}{2}\left(j^T A^{-1}j\right)\partial_{j_n}\frac{1}{2}\left(j^T A^{-1}j\right) e^{\frac{1}{2}j^T A^{-1}j} \\
=& \frac{1}{2}\partial_{j_m}\left((A^{-1})_{nb}j_b + (A^{-1})_{an}j_a\right) e^{\frac{1}{2}j^T A^{-1}j} \\
&+ \frac{1}{4}\left((A^{-1})_{mb}j_b + (A^{-1})_{am}j_a\right)\left((A^{-1})_{nb}j_b + (A^{-1})_{an}j_a\right) e^{\frac{1}{2}j^T A^{-1}j} \\
=& \frac{1}{2}\left((A^{-1})_{nm} + (A^{-1})_{mn}\right) e^{\frac{1}{2}j^T A^{-1}j} \\
&+ \frac{1}{4}\left((A^{-1})_{mb}j_b + (A^{-1})_{am}j_a\right)\left((A^{-1})_{nb}j_b + (A^{-1})_{an}j_a\right) e^{\frac{1}{2}j^T A^{-1}j}
\end{aligned}$$

where we employ Einstein summation over a and b. Evaluation at $j = 0$ means the latter terms vanish, leaving

$$\overline{\Psi_m\Psi_n} = \partial_{j_m}\partial_{j_n} e^{\frac{1}{2}j^T A^{-1}j}\Big|_{j=0} = \frac{1}{2}\left((A^{-1})_{nm} + (A^{-1})_{mn}\right) e^{\frac{1}{2}j^T A^{-1}j}\Big|_{j=0} = (A^{-1})_{mn},$$

reusing the fact that A^{-1} is symmetric.

Looking at the structure of the above argument we have all we need to prove the theorem. We write $F(j) = e^{g(j)}$, where $g(0) = 0$, all derivatives of g are zero at $j = 0$ and g is at most quadratic in all j_m. Supposing you want to calculate the expectation value of some product $\Psi_{m_1} \dots \Psi_{m_{2N}}$, that will amount to computing a sequence of derivatives of F and setting $j = 0$. At some point in the sequence of derivatives, any one term will have two factors: some product of derivatives of g, and e^j. The following derivatives act schematically according to the product rule. This scheme is illustrated in figure 1.

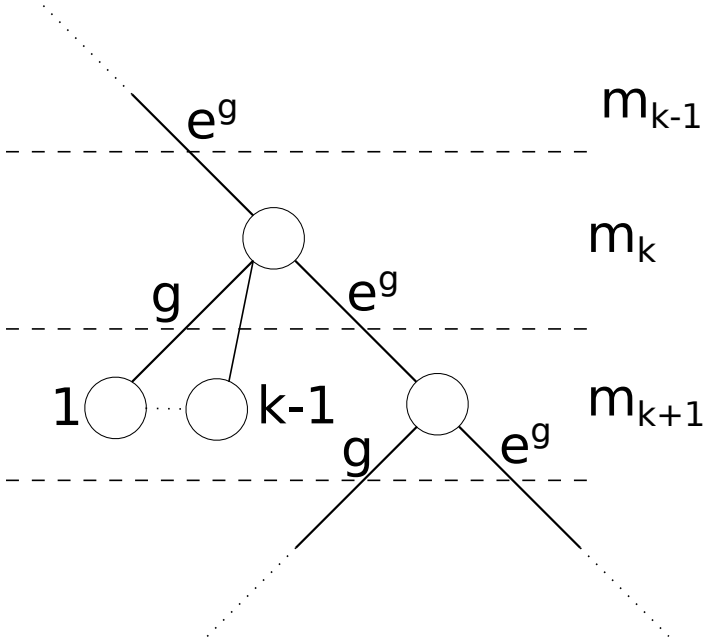

Figure 1: Illustration of the differentiation scheme.

The tree starts with e^g at the very top. From there, the derivatives produce a series of terms, one with derivatives of e^g and the rest with derivatives of the already present derivatives of g. The two are represented by steps to the left and right down the tree. Moving down the tree corresponds to starting with some term, represented by a node, and following the term generated by differentiating a particular factor in that term. In the figure we see a path that has thus far only included steps to the right, and therefore contains $k-1$ factors of derivatives of g, as well as e^g. We therefore have $k-1$ left nodes corresponding to terms with derivatives of´ these factors, as well as a right node corresponding to the term which has an extra derivative of g. As we have seen above, steps to the left after steps to the right produces correlation functions as factors, meaning that each left node in the figure has a correlation function as a factor - in this particular case factors $\overline{\Psi_{m_k}\Psi_{m_n}}$ for all $n < k$. Note that this implies that each of these $k-1$ have $k-2$ left nodes, and thus that the upper most node and all nodes that are preceded by an equal amount of left and right steps have no left nodes. Because the first derivatives of g are zero, the only contributions to the desired correlation function are found by considering valid paths with an equal number of steps to the right and left.

More explicitly, we are studying

$$\overline{\Psi_{m_1} \dots \Psi_{m_{2N}}} = \left(\prod_{k=1}^{2N} \partial_{j_{m_k}} \right) e^g \Big|_{j=0} = \left(\prod_{k=2N}^{1} \partial_{j_{m_k}} \right) e^g \Big|_{j=0} ,$$

where the latter simply denotes a reversal of order for convenience. The term corresponding to the uppermost node in figure 1 is equal to

$$e^g \prod_{a=1}^{k-1} \left(\frac{1}{2} (B_{m_a b} + B_{b m_a}) j_b \right),$$

where we use $B = A^{-1}$ for brevity. We now want to consider a step to the left. Stepping to node n from the

left we get the term

$$e^g\left(\partial_{j_{m_k}}\frac{1}{2}(B_{m_nb}+B_{bm_n})j_b\right)\prod_{a=1,\ a\neq n}^{k-1}\left(\frac{1}{2}(B_{m_ab}+B_{bm_a})j_b\right)=\frac{1}{2}(B_{m_nm_k}+B_{m_km_n})e^g\prod_{a=1,\ a\neq n}^{k-1}\left(\frac{1}{2}(B_{m_ab}+B_{bm_a})j_b\right)$$
$$=B_{m_nm_k}e^g\prod_{a=1,\ a\neq n}^{k-1}\left(\frac{1}{2}(B_{m_ab}+B_{bm_a})j_b\right)$$
$$=\overline{\Psi_{m_n}\Psi_{m_k}}e^g\prod_{a=1,\ a\neq n}^{k-1}\left(\frac{1}{2}(B_{m_ab}+B_{bm_a})j_b\right).$$

From this we first note the recursive structure of the tree, as the result of taking a step left is an expectation value and a function similar to the one we started with. The effect of taking a specific step to the left after a given number of steps to the right is thus to pick out a particular expectation value.

We may now use the structure of the diagram to infer the value of the desired expectation value. We note that the combination of the first step left and the second step right produces the correlation function $\overline{\Psi_{m_1}\Psi_{m_2}}$ and returning us to square one. Alternating between left and right thus pairs the Ψ_i in order. Taking two steps right before the first step left instead produces two terms with factors $\overline{\Psi_{m_1}\Psi_{m_3}}$ and $\overline{\Psi_{m_2}\Psi_{m_3}}$ while leaving a factor. Another step left pairs the remaining Ψ_m with Ψ_{m_4}. For $N=2$ there are three valid paths, which are the ones discussed above. They combine to form the statement of Wick's theorem for $N=2$. Repeating this argument for a larger structure, we find that in these paths, all possible pairings of Ψ_m are found exactly once, yielding

$$\overline{\Psi_{i_1}\dots\Psi_{i_{2N}}}=\sum_{\text{pairs}}\overline{\Psi_{i_{k_1}}\Psi_{i_{k_2}}}\dots\overline{\Psi_{i_{k_{2N-1}}}\Psi_{i_{k_{2N}}}}.$$

The complex case carries many similarities to the real case, so this will only be a repetition of the important details. First, we will have to use the probability distribution

$$P(\Psi)=Ce^{-\Psi^\dagger A\Psi},$$

where A is a Hermitian matrix. Computations with this distribution involves integration over the complex plane for each components. Letting a and b be the real and imaginary of some particular component ψ, integration over the complex plain maps onto integration over real space parametrized by a and b. We may now introduce independent variables $\psi=a+bi$ and $\psi^\star=a-bi$, which correspond to a rotation in ab-space, and integrate over these instead. We thus write the integral as an integral over $\mathrm{d}\Psi\,\mathrm{d}\Psi^\dagger$. Similarly to the real case, integration can be carried out by a change of variables specified by the unitary matrix U that diagonalizes A.

To extract expectation values, we use the function

$$F(v,w^\dagger)=\int\mathrm{d}\Psi\int\mathrm{d}\Psi^\dagger\,Ce^{-\Psi^\dagger A\Psi}e^{w^\dagger\Psi}e^{\Psi^\dagger v}.$$

We introduce shifted variables to find

$$F(v,w^\dagger)=\int\mathrm{d}\Psi\int\mathrm{d}\Psi^\dagger\,Ce^{-(\Psi^\dagger+w^\dagger W^\dagger)A(\Psi+Vv)}e^{w^\dagger(\Psi+Vv)}e^{(\Psi^\dagger+w^\dagger W^\dagger)v}$$
$$=e^{w^\dagger Vv+w^\dagger W^\dagger v-w^\dagger W^\dagger AVv}\int\mathrm{d}\Psi\int\mathrm{d}\Psi^\dagger\,Ce^{-\Psi^\dagger A\Psi-\Psi^\dagger AVv-w^\dagger W^\dagger A\Psi+w^\dagger\Psi+\Psi^\dagger v}.$$

Choosing $W^\dagger=V=A^{-1}$ we find

$$F(v,w^\dagger)=e^{w^\dagger A^{-1}v+w^\dagger A^{-1}v-w^\dagger A^{-1}v}\int\mathrm{d}\Psi\int\mathrm{d}\Psi^\dagger\,Ce^{-\Psi^\dagger A^{-1}\Psi-\Psi^\dagger v-w^\dagger\Psi+w^\dagger\Psi+\Psi^\dagger v}$$
$$=e^{w^\dagger A^{-1}v}\int\mathrm{d}\Psi\int\mathrm{d}\Psi^\dagger\,Ce^{-\Psi^\dagger A^{-1}\Psi}$$
$$=e^{w^\dagger A^{-1}v}.$$

By its definition, we have

$$\partial_{v_i} F\Big|_{w,v=0} = \int \mathrm{d}\Psi \int \mathrm{d}\Psi^\dagger \, \Psi_i^\star C e^{-\Psi^\dagger A \Psi} = \overline{\Psi_i^\star}, \;\; \partial_{w_i} F\Big|_{v,w=0} = \int \mathrm{d}\Psi \int \mathrm{d}\Psi^\dagger \, \Psi_i C e^{-\Psi^\dagger A \Psi} = \overline{\Psi_i},$$

and similarly for higher-order expectation values. Note the suppression of the adjointness of w. In particular we may repeat the arguments for the real case by writing F as e^g for $g = w^\dagger A^{-1} v$. As g is linear in w and v, we must have $\overline{\Psi_i \Psi_j} = \overline{\Psi_i^\star \Psi_j^\star} = 0$. Finally we find

$$\begin{aligned}
\overline{\Psi_i \Psi_j^\star} &= \partial_{v_j} \partial_{w_i} F\Big|_{v,w=0} \\
&= \partial_{v_j} \left((A)^{-1}_{ik} v_k e^g \right) \Big|_{v,w=0} \\
&= (A)^{-1}_{ij} e^g \Big|_{v,w=0} \\
&= (A)^{-1}_{ij}.
\end{aligned}$$

The argument for higher-order correlation functions used in the real case may also be applied to the complex case. As we see from the above, it is in fact even simpler. By writing

$$\overline{\Psi_{i_1} \dots \Psi_{i_N} \Psi^\star_{j_1} \dots \Psi^\star_{j_N}} = \left(\prod_{n=1}^N \partial_{v_{j_n}} \right) \left(\prod_{m=1}^N \partial_{w_{i_m}} \right) F\Big|_{v,w=0},$$

we note that g being linear in both v and w implies that the first N layers of the tree contain only right steps. As $g = 0$ for either v or w equal to zero, there must still be a balance between right and left steps, meaning that we only need to consider left steps in the lower half of the tree. In similar fashion to the real case, the first step to the left creates N nodes, each with a factor $\overline{\Psi_{i_1} \Psi^\star_{j_k}}$ for some k unique to that node in that particular level. Similar pairings occur down through the structure, and the final result is

$$\overline{\Psi^\star_{i_1} \dots \Psi^\star_{i_N} \Psi_{j_1} \dots \Psi_{j_N}} = \sum_{P(1,\dots,N)} \overline{\Psi_{i_{P(1)}} \Psi_{j_1}} \, \overline{\Psi_{i_{P(2)}} \Psi_{j_2}} \dots \overline{\Psi_{i_{P(N)}} \Psi_{j_N}}.$$