Outline: Momentum Hops and Time Dependence

Brownian Motion
- Define Situation
- Calculate momentum
- Calculate Variance
- Calculate Probability Distribution

Probability Distribution in Classical Mechanics
- Statistical and Hamiltonian Dynamics
- Probability Distributions in Dynamical Systems
- Time dependence of dynamical systems
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Classical Mechanics

Brownian motion again: toward a unique solution
- friction
- collisions
  - calculation set up
  - calculation continued
  - calculation concluded

A unique probability distribution

Summary

Boltzmann Equation
- Scattering
  - forward
  - backward
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Symmetries
- detailed balance-local equilibrium
- conservation of particle number
- H-theorem
- sign of dissipation term
- $dS/dt$

Homework
Brownian motion:

Robert Brown (1773-1858) saw particles of pollen “dance around” in fluid under microscope. This motion was caused by many tiny particles hitting the grains of pollen.

Albert Einstein (1905) explained this dancing by many, many collisions with molecules in fluid

\[
dp/dt = \ldots + \eta(t) - \frac{p}{\tau} \]

\(p = (p_x, p_y, p_z)\)
\(\eta = (\eta_x, \eta_y, \eta_z)\)
\(\eta(t)\) is a Gaussian random variable resulting from random kicks produced by collisions. Since the kicks have random directions \(<\eta(t)> = 0\). Different collisions are assumed to be statistically independent

\(<\eta_j(t) \eta_k(s)> = \Gamma \delta(t-s) \delta_{j,k}\)

The relaxation time, \(\tau\), describes friction slowing down as the particles moves through the medium. In contrast \(\Gamma\) describes the extra momentum picked up via the collisions. Both represent the same physical effect, little particles hitting our big one. However, they operate in a somewhat different fashion. The individual kicks point in every which direction and only in the long run produce any concerted change in momentum. On the other hand the term in \(\tau\) is a friction tending to continually push our particle toward smaller speeds relative to the medium.
Calculate momentum from \( \frac{dp}{dt} = \ldots + \eta(t) - p/\tau \)

\[
P(t) = \int_{-\infty}^{t} dt' \eta(t') \exp\left(-\frac{t - t'}{\tau}\right)
\]

Because \( P(t) \) is a sum of many random variables according to the central limit theorem, it must be a Gaussian random variable. Therefore it has a Gaussian probability distribution. In equilibrium, \( P(t) \) should have the variance, \( M_kT \), with \( M \) being the mass of the Brownian particle. In equilibrium it will have the Maxwell-Boltzmann probability distribution

\[
\rho(p) = \left(\frac{\beta}{2\pi M}\right)^{3/2} \exp\left[-\beta p^2/(2M)\right]
\]

Notice that if this works out for us, it will be our first “proof” that the ideas of Gibbs, Boltzmann, and Maxwell about the canonical distribution was correct. So we would have a proof that this “law” works, at least in this situation. In physics, we often use laws long before there is any substantial proof that they are correct. We use little bits of evidence, intuition, and guesswork and gradually convince ourselves that \( X \) “must be” right. If \( X \) is attractive, we hold on to that view until there is overwhelming evidence to the contrary.
Calculate Variance of $P(t)$

$$<p_j(t)p_k(s)> = \int_{-\infty}^{t} du \int_{-\infty}^{s} dv <\eta_j(t)\eta_k(s)>$$

$$\text{v.4}$$

$$<p_j(t)p_k(s)> = \int_{-\infty}^{t} du \int_{-\infty}^{s} dv \Gamma \delta_{j,k} \delta(u-v) \exp[-(t-u)/\tau - (s-v)/\tau]$$

$$\text{v.5}$$

...... if $t > s$ the integral over $u$ always gets a contribution from the delta-function so that this expression then becomes

$$<p_j(t)p_k(s)> = \int_{-\infty}^{s} dv \Gamma \delta_{j,k} \exp[-(t+s-2v)/\tau]$$

$$= \frac{\delta_{j,k}}{2} \Gamma \tau \exp[-|t-s|/\tau]$$

so we see that $p_j^2/(2M)$, where $M$ is the mass of the Brownian particle is on one hand given by

$$<\frac{p_j^2}{2M}> = \Gamma \tau / (4M)$$

On the other hand, we know that in classical physics this quantity is $kT/2$. Thus we obtain the relation between the two parameters in the Einstein model.

$$\Gamma \tau = 2MkT$$

$$\text{v.6}$$
\[ \Gamma \tau = 2MkT \]

Whenever this relation is satisfied, \( p \) has the right variance, \( MkT \), and the right Maxwell-Boltzmann probability distribution.

\[ \rho(p) = \left( \frac{\beta}{2\pi M} \right)^{3/2} \exp\left[ -\beta p^2 / (2M) \right] \]

More generally, if we have a Hamiltonian, \( H(p,r) \), for the one-particle system, the Maxwell-Boltzmann distribution takes the form

\[ \rho(p,r) = \exp\left[ -\beta H(p,r) \right] / Z, \]

where, the simplest case the Hamiltonian is

\[ H(p,r) = p^2 / (2M) + U(r) \]

Maxwell and Boltzmann expected that, in appropriate circumstances, if they waited long enough, a Hamiltonian system would get to equilibrium and they would end up with a Maxwell-Boltzmann probability distribution

**Question:** Should we not be able to derive this distribution from classical mechanics alone? Maybe we should have to assume that we must long enough to reach equilibrium? Anything more?

Something of the form \( v.7 \) is called by mathematicians a Gibbs measure and by physicists a Boltzmann distribution or often a Maxwell-Boltzmann distribution. Why? Should we care?
Statistical and Hamiltonian Dynamics

We have that the equilibrium $\rho = \exp(-\beta H)/Z$. How can this arise from time dependence of system? One very important possible time-dependence is given by Hamiltonian mechanics

$$\frac{dq_\alpha}{dt} = \frac{\partial H}{\partial p_\alpha}$$
$$\frac{dp_\alpha}{dt} = -\frac{\partial H}{\partial q_\alpha}$$

The simplest case is a particle moving in a potential field with a Hamiltonian

$$H = \frac{p^2}{2M} + U(r)$$

and consequently equations of motion

$$\frac{dp}{dt} = -\nabla U$$
$$\frac{dr}{dt} = \frac{p}{M}$$

The statistical mechanics of such situations is given by a probability density function $\rho(p,r,t)$ such that the probability of finding the particle in a volume element $dp\,dr$ about $p,r$ at time $t$ is $\rho(p,r,t)\,dp\,dr$. The next question is, what is the time-dependence of this probability density? Or maybe, how do we get equilibrium statistical mechanics as a consequence of this.
Time Dependence of Dynamical systems: A much more general problem

Instead of carrying around the variables $p$ and $r$, let me do something with much simpler formulas. I’m going to imagine solving the dynamical systems problem in which there is a differential equation $dX/dt = V(X(t), t)$ to get a solution $X(t)$. I will have a probability function $\rho(x,t) \, dx$ which is the probability that the solution will be in the interval $dx$ about $x$. This is a probability because, when we start out the initial data is not just one value of $x$ but a probability distribution, given by $\rho(x,0)$. So the situation at a later time must be described by a probability distribution then as well. So what is the time dependence of the probability distribution? One way to approach this problem is to ask what does the distribution mean. Specifically, if we have some function $g(X)$ of the particle coordinates at time $t$, that function has an average at time $t$ given by

$$\int dx \, g(x) \, \rho(x,t).$$

Naturally the average at time $t + dt$ is

$$\int dx \, g(x) \, \rho(x,t+dt).$$

That same average is obtained by taking the solution at time $t+dt$, which is

$$X(t+dt) \approx X(t) + V(X(t),t))dt$$

and calculate its average using the probability distribution which is appropriate at the earlier time, i.e. the average is

$$\int dx \, g(x+dt \, V(x,t)) \, \rho(x,t).$$

Equate those two expressions for the average

$$\int dx \, g(x) \, \rho(x,t+dt) = \int dx \, g(x+dt \, V(x,t)) \, \rho(x,t)$$

carry this result forward
Calculation Continued ..... 
\[ \int dx \, g(x) \, \rho(x,t+dt) = \int dx \, g(x+dt \, V(x,t)) \, \rho(x,t) \]

expand to first order in \( dt \)
\[ \int dx \, g(x) \, \rho(x,t) + dt \int dx \, g(x) \, \partial_t \rho(x,t) = \int dx \, g(x) \, \rho(x,t) + \int dx \, dt \, V(x,t) \, [d_x g(x)] \, \rho(x,t) \]

throw away the things that cancel against each other to get
\[ \int dx \, g(x) \, \partial_t \rho(x,t) - \int dx \, V(x,t) \, [\partial_x g(x)] \, \rho(x,t) = 0 \]

integrate by parts on the right hand side, using the fact that \( \rho(x,t) \) vanishes at \( x=\pm \infty \)
\[ \int dx \, g(x) \{ \partial_t \rho(x,t) + \partial_x [V(x,t) \, \rho(x,t)] \} = 0 \]

Notice that \( g(x) \) is arbitrary. If this left hand side is going to always to vanish, the \{ \} must vanish. We then conclude that \[ \partial_t \rho(x,t) + \partial_x [V(x,t) \, \rho(x,t)] = 0 \] That’s for one coordinate, \( x \).

If there are lots of coordinates this equation reads
\[ \partial_t \rho(x,t) + \rho(x,t) \sum_j (\partial_{x_j} \, V_j) + \sum_j V_j \partial_{x_j} \rho(x,t) = 0 \]

We call the second term on the left the **divergence** term. It describes the dilation of the volume element by the changes in the \( x \)'s caused by the time development. The last term is the direct result of the time-change in each coordinate \( X(t) \). Now we have the general result for the time development of the probability density. We go look at the Hamiltonian case which is rather special
Calculation concluded ....

\[\partial_t \rho(x, t) + \rho(x, t) \sum_j (\partial_{x_j} V_j) + \sum_j V_j \partial_{x_j} \rho(x, t) = 0\]

The Hamiltonian case is special. There are two kinds of coordinates 
\(x_j = q_\alpha\) with \(V_j = \partial_{p_\alpha} H\) and \(x_j = p_\alpha\) with \(V_j = -\partial_{q_\alpha} H\). In that case, the divergence term is 
\((\partial_{q_\alpha} \partial_{p_\alpha} H - \partial_{p_\alpha} \partial_{q_\alpha} H)\rho = 0\). This result, called Liouville’s theorem, says that the size of the volume element is independent of time. As a result the probability density obeys a special equation, with no divergence term

\[\partial_t \rho(p, q, t) + \sum_\alpha [(\partial_{p_\alpha} H) \partial_{q_\alpha} - (\partial_{q_\alpha} H) \partial_{p_\alpha}] \rho(p, q, t) = 0\]

The time derivative of any function of \(p\) and \(q\) is given in Hamiltonian mechanics by

\[
dX(p, q)/dt = \sum_\alpha [(\partial_{p_\alpha} H) \partial_{q_\alpha} - (\partial_{q_\alpha} H) \partial_{p_\alpha}] X(p, q)
\]

In particular if \(H\) is the Hamiltonian, assumed to be a function of the \(p\)'s and \(q\)'s but not containing any other \(t\)-dependence, then \(dH/dt=0\), i.e. \(H\) is independent of time. Further, if \(\rho\) is any function of a time-independent \(H\) and of any other conserved function of \(p\) and \(q\) (but not \(t\)) then \(\rho\) will be a solution of our equation. Thus, not only is the Boltzmann function a solution describing the equilibrium time-dependence of a Hamiltonian system, there are many other solutions as well.
Poisson Bracket

The Poisson Bracket is Defined by

\[ \{ f, g \} = \sum_{\alpha} \left[ \frac{\partial f}{\partial q_\alpha} \frac{\partial g}{\partial p_\alpha} - \frac{\partial g}{\partial q_\alpha} \frac{\partial f}{\partial p_\alpha} \right] \]

\[ \partial_t \rho = \{ H, \rho \} \quad \text{for any function of p’s and q’s, with no explicit time-dependence} \]

\[ dX/dt = \{ X, H \} \]

These Poisson brackets are rather like the commutators of quantum mechanics. For example \( \{ \{ f,g,h \}, \{ h,f,g \} + \{ g,h,f \} \} = 0 \). The same kind of relation is true for operators in quantum theory with \{ and \} replaced by \[ and \]. The bracket relations for classical time-dependence are very much like the time-dependence of operators and density matrices in quantum theory. This relation between quantum mechanics and the canonical version of classical mechanics is quite surprising and turns out to be quite deep.

Note the difference in sign between the relation for \( dX/dt \) and the one for \( \partial_t \rho \). I have gotten one of those signs wrong many times in my life. Think for a bit about why we write \( \partial_t \rho \) but \( dX/dt \). Why?
Any function of $H$ will do

To achieve equilibrium we can have the probability density be any function of the Hamiltonian and the other conserved quantities in the system. The following functions are in broad use. We assume one type of particle, with number $N$.

**Canonical ensemble:** $\rho = \exp(-\beta H)/Z(\beta)$ $N$ is fixed
This is the right ensemble to use if a small system with a known number of particles is weakly coupled to a larger system so that it might exchange energy but not particles with the larger system.

**Microcanonical ensemble:** $\rho = \delta(E-H)/\chi(E)$ $N$ is fixed
This is the right ensemble to use if the energy and number of particles in a small system are known.

**Grand Canonical ensemble:** $\rho = \exp[-\beta(H-\mu N)]/\Xi(\beta,\mu)$
This is the right ensemble to use if a small system is weakly coupled to a larger system so that it might exchange energy and particles with the larger system.

All ensembles are equivalent for a large system. Why?
**Say it again**

For the simplest case in which \( H = \frac{\mathbf{p}^2}{2M} + U(\mathbf{r}) \), the result of Hamiltonian mechanics is that the probability distribution \( \rho(\mathbf{p}, \mathbf{r}, t) \) has the time dependence

\[
\frac{\partial}{\partial t} \rho(\mathbf{p}, \mathbf{r}, t) + \left( \frac{\mathbf{p}}{M} \right) \cdot \nabla_{\mathbf{r}} \rho(\mathbf{p}, \mathbf{r}, t) - (\nabla_{\mathbf{r}} U) \cdot \nabla_{\mathbf{p}} \rho(\mathbf{p}, \mathbf{r}, t) = 0
\]

A time independent solution of this equation would be that \( \rho \) could be any function of \( H \). This result stands in apparent contradiction to our knowledge of statistical mechanics which tells us that the probability distribution should be the Maxwell-Boltzmann distribution, i.e. one which is exponential in \( H \). **What additional information should we bring to bear on this situation?**

We already have a hint from the Brownian motion calculation that this calculation might give the Maxwell-Boltzmann result. Let’s go back to that and see what equation we get for \( \rho \). The Einstein model for Brownian motion is

\[
\frac{d\mathbf{p}}{dt} = \ldots \eta(t) - \frac{\mathbf{p}}{\tau}
\]

where \( \ldots \) might stand for additional terms coming from Hamiltonian mechanics. I plan to study successively the effect of the two terms in this model upon the equation for \( \rho \) and then put it all together.
**The friction term \(-p/\tau\)**

We already know the effect of this term. It is a generalized velocity of the form included in equation v.7, with \(V(p,t) = -p/\tau\). We therefore know immediately what effect this term has on the equation for the probability distribution. It gives, via equation v.9

\[
\partial_t \rho(p,x,t) = -\partial_p \left[ V \rho \right] = ...+ \partial_p \left[ \frac{p}{\tau} \rho(p,x,t) \right]
\]

where \(x\) is the variable conjugate to \(p\) in a Hamiltonian formulation. We hold on to this result to use in our later analysis.

However, we cannot just look up our old result to get the effect of the other term, the stochastic kicks, \(\eta\), in the Brownian model

\[
dp/dt = ...+ \eta(t) - p/\tau
\]

As we shall see in a bit, their average first order effect is zero but their effect to second order produces a result proportional to the time that they have been in action. Our old result does not include second order effects. So we shall go back almost to the beginning to assess the effect of these kicks upon the time-dependence.
calculation of the effect of $dp/dt=......+ \eta(t)$

Recall our old calculation of $\partial_t \rho$. In this situation, we are after an understanding of the behavior of the momentum $p$. We have two ways of calculating the average of a function of momentum at time $t+\delta t$. The first comes from computing \[ \int dp \: g(p) \: \rho(p,t+\delta t). \] That same average is obtained by taking the solution at time $t+\delta t$, which is of the form $p(t+\delta t)=p(t)+\delta p$. Here, $\delta p$ is given by the effect of the stochastic term, so that

\[ \delta p = \int_t^{t+\delta t} ds \: \eta(s) \]

Then the average at time $t+\delta t$ can also be written as \[ < \int dp \: g(p) \: \rho(p,t+\delta t) >. \] Here, the average $<...>$ is an average over the possible values of the stochastic variables $\eta(s)$ for $s$ between $t$ and $t+\delta t$. If we equate these two expressions, we find

\[ \int dp \: g(p) \: \rho(p,t+\delta t) = < \int dp \: g(p) \: \rho(p,t+\delta t) >. \]

The right hand side can be rearranged by shifting the origin of integration and replacing the variable $p$ by $p-\delta p$. Then this right side becomes \[ < \int dp \: g(p) \: \rho(p-\delta p,t) >. \] and

\[ \int dp \: g(p) \: \rho(p,t+\delta t) = < \int dp \: g(p) \: \rho(p-\delta p,t) >. \]

Since $g(p)$ is arbitrary, we it follows that

\[ \rho(p,t+\delta t) = < \rho(p-\delta p,t) >. \]
calculation of the effect of $dp/dt=\ldots+\eta(t)$  

continued

$$\rho(p,t+\delta t) = <\rho(p-\delta p,t)>$$

$$\delta p = \int_t^{t+\delta t} ds \, \eta(s)$$

expand  \hspace{2em} \text{(the result is particularly simple because $\delta p$ does not depend upon $p$).}

$$\rho(p,t) + \delta t \, \partial_t \rho(p,t) = <\rho(p,t)> + <\delta p> \, \partial_p \rho(p,t) + <\delta p^2> \, (\partial_p)^2 \rho(p,t)/2$$

The first terms on each side cancel, the average of $\delta p$ is zero, and the rest gives

$$\partial_t \rho(p,t) = \left[ <\delta p^2> / (2\delta t) \right] (\partial_p)^2 \rho(p,t)$$

The average has the value:

$$[\delta p]^2 = \int_t^{t+\delta t} du \int_t^{t+\delta t} ds \, \eta(u)\eta(s) = \int_t^{t+\delta t} du \int_t^{t+\delta t} ds \, \Gamma \delta(u-s) = \Gamma \delta t$$

(recall that $<\eta(t) \eta(s)> = \Gamma \delta(t-s)$) so that we end up with the result

$$\partial_t \rho(p,t) = \ldots + (\Gamma/2) \, (\partial_p)^2 \rho(p,t)$$

This describes a diffusion in momentum space.  \hspace{2em} \text{(Notice that because it is diffusive, this result cannot be followed backward in time!)}
**Effect of Brownian motion:** toward a unique probability distribution

We put together our two different pieces of the Brownian time derivative equation and get:

$$\frac{\partial}{\partial t} \rho(p,x,t) = \ldots + \left(\frac{\Gamma}{2}\right) (\partial p)^2 \rho(p,x,t) + \partial_p \left[ \frac{p}{\tau} \rho(p,x,t) \right]$$

The ‘‘’s refer to terms which might come from usual Hamiltonian mechanics. We shall put them aside for a moment. An equation, like to one here, obtained from averaging the stochastic mechanics of a Langevin equation, is called a *Fokker-Planck equation*.

We look for a time-independent solution of this equation to see what is the equilibrium behavior. Write $\rho(p,x,t) = \exp[-Q(p,x)]$ and find

$$0 = \ldots \partial_p \left[ \left(\frac{\Gamma}{2}\right) (-\partial_p Q) + \frac{p}{\tau} \right]$$

which has the solution $Q = p^2 / (\Gamma \tau) + C(x)$, where $C(x)$ is a “constant” of integration. To get the usual Hamiltonian result, use equation v.6 to replace $\Gamma \tau$. Also, write $C(x) = U(x)/(kT)$ since that is what comes from the usual Hamiltonian mechanics. Then, $Q$ becomes $p^2/(2MkT) + U(x)/(kT)$, which is exactly the result of Hamiltonian mechanics.

Einstein’s result shows that, in order to get the Maxwell-Boltzmann equilibrium result, we have to go beyond Hamiltonian mechanics and include some stochastic behavior. *This is a surprise.*
Summary of Einstein’s dynamics

Our fullest time-dependent equation, including both Brownian motion and Hamiltonian mechanics is

\[
\partial_t \rho(p,r,t) + (\nabla_p \epsilon(p,r,t)) \cdot \nabla_r \rho(p,r,t) - (\nabla_r \epsilon(p,r,t)) \cdot \nabla_p \rho(p,r,t) = (\Gamma/2) (\nabla_p)^2 \rho(p,r,t) + \nabla_p \cdot [p/\tau \rho(p,r,t)] \quad \text{v.12}
\]

This only makes sense and has the right equilibrium behavior if the simple-particle-motion assumptions which went into the right hand side of the equation are also used on the left, specifically

\[\epsilon(p,r,t) = p^2/(2M) + U(r)\]

Equation v.12 works equally well if we use as our basic variable the density of particles in phase space, \( f(p,r,t) = N \rho(p,r,t) \). We then have

\[
\partial_t f(p,r,t) + \nabla_p \epsilon(p,r,t) \cdot \nabla_r f(p,r,t) - \nabla_r \epsilon(p,r,t) \cdot \nabla_p f(p,r,t) = (\Gamma/2) (\nabla_p)^2 f(p,r,t) + \nabla_p \cdot [p/\tau f(p,r,t)] \quad \text{v.13}
\]
The Boltzmann Equation

Boltzmann derived the Maxwell-Boltzmann distribution by using a more brute force approach than the one applied by Einstein. Like Einstein, Boltzmann looked at collisions of particles mostly described as moving independently. Therefore these particles could be well-characterized by the free particle Hamiltonian, $\frac{p^2}{2m} + U(r)$. In addition, however, Boltzmann imagined that these particles would, occasionally, come close to one another and collide, thereby substantially changing their momentum. So he started from an equation describing first the free particle motion, and second the effect of collisions. The basic variable in this approach was $f(p,r,t)$, which would then obey an equation of the form

$$\partial_t f(p,r,t) + \frac{p}{m} \cdot \nabla_r f(p,r,t) - \nabla_r U(r,t) \cdot \nabla_p f(p,r,t) = \text{effects of collisions}$$

The collisional effects are best shown in a pair of pictures. The number of particles described by $(p,r)$ will diminish because particles with momentum $p$ scatter again particles with momentum $q$, producing particles with respective momentum $p'$ and $q'$. That scattering looks like

\[\begin{array}{c}
p \\
q \\
p'
\end{array} \quad \begin{array}{c}
p' \\
q'
\end{array}\]
The scattering:

Given that there are particles available with the appropriate initial momentum, the scattering rate into a volume element of final momentum $dp' dq'$ can be written as $dp' dq' Q(p, q \rightarrow p', q')$

The probability that we could get the particles we need for the scattering produce a factor $f(p, r, t) dq f(q, r, t)$, so that the total scattering rate for this process is

$$f(p, r, t) \int dq f(q, r, t) \, dp' dq' \, Q(p, q \rightarrow p', q')$$

The process itself reduces the number described by $p, r$ at the rate shown. Conversely, there is an inverse process, and a corresponding rate of increase of $f(p, r, t)$

$$\int dq \, dp' f(p', r, t) \, dq' f(q', r, t) \, Q(p', q' \rightarrow p, q)$$
put it all together to find

\[ [\partial_t + (p/m) \cdot \nabla_r - (\nabla_r \cup (r,t)) \cdot \nabla_p] f(p,r,t) = \]

\[ - f(p,r,t) \int dq \, f(q,r,t) \, dp' \, dq' \, Q( p,q \rightarrow p',q') \]

\[ + \int dq \, dp' \, f(p',r,t) \, dq' \, f(q',r,t) \, Q( p',q' \rightarrow p,q ) \]

Since we have far too many symbols here, in the next steps we shall drop the \( r,t \) everywhere. The next step notices that each collision must include conservation of energy and of momentum. That means the Q’s must be proportional to delta functions which enforce conservation of energy and momentum. Specifically,

\[ Q( p,q \rightarrow p',q') = R( p,q \rightarrow p',q') \, \delta(p+q - p'-q') \, \delta(\epsilon(p)+\epsilon(q) - \epsilon(p')-\epsilon(q')) \]

We then find the equation

\[ [\partial_t + (p/m) \cdot \nabla_r - (\nabla_r \cup (r,t)) \cdot \nabla_p] f(p) = \]

\[ -\int\int\int dq \, dp' \, dq' \, \delta(p+q - p'-q') \, \delta(\epsilon(p)+\epsilon(q) - \epsilon(p')-\epsilon(q')) \]

\[ [Q( p,q \rightarrow p',q') \, f(p) \, f(q) - Q( p',q' \rightarrow p,q ) \, f(p') \, f(q') ] \]

Boltzmann equation

v.14
Symmetries of Boltzmann equation

One more statement is needed: This is a statement of time-reversal invariance in which we demand that the inverse process have the same probability. Specifically, the statement, called detailed balance, is

\[ Q(p,q \rightarrow p',q') = Q(p',q' \rightarrow p,q) \]  

detailed balance

This means that if we care to, we can write the Boltzmann equation as

\[ [\partial_t + (p/m) \cdot \nabla_r - (\nabla_r U) \cdot \nabla_p] f(p) = \]

\[ - \int \int \int dq \ dp' \ dq' \ \delta(p+q - p'-q') \ \delta(\epsilon(p)+\epsilon(q) - \epsilon(p')-\epsilon(q')) \]

\[ Q(p,q \rightarrow p',q') \ [f(p)\ f(q) - f(p')\ f(q')] \]

We shall need one more symmetry statement to obtain proper conservation laws, namely the statement that \( p \) and \( q \) play symmetrical roles in the scattering event.

\[ Q(p,q \rightarrow p',q') = Q(q,p \rightarrow q',p') \]

symmetrical scattering

This symmetry is appropriate because we are thinking that particles of the same kind are involved in the scattering event. If the particles were identical in the quantum sense, we would also have

\[ Q(p,q \rightarrow p',q') = Q(p,q \rightarrow q',p') \]
Detailed Balance and Local Equilibrium

\[ [\partial_t + (p/m) \cdot \nabla r - (\nabla r \cdot \nabla) \cdot \nabla p] f(p) = \]

\[- \int \int \int dq \ dp \ dq' \ \delta(p+q - p'-q') \ \delta(\epsilon(p)+\epsilon(q) - \epsilon(p')-\epsilon(q')) \]

\[ Q( p,q \rightarrow p',q') [f(p) f(q) - f(p') f(q')] \]

**local equilibrium** is the statement that the right hand side of the Boltzmann equation vanishes, specifically that

\[ f(p) f(q) = f(p') f(q') \] \quad \text{v.15} \]

so that relaxation to equilibrium is driven by the relatively slow processes controlled by the gradients on the left hand side of the equation. This provides a mechanism for the system to provide relaxation times much slower than the collision rate of a typical particle. In local equilibrium

\[ f(p,r,t) = \exp\{-\beta(r,t)[\epsilon(p,r,t)-\mu(r,t)-p \cdot v(r,t) - v(r,t)^2/(2m)]\} \]

so that the conservation laws for probability, momentum, and energy ensure that statement v.15 is satisfied. Here \( \beta(r,t), \mu(r,t), \) and \( v(r,t) \) are the parameters defining the local equilibrium state. The left hand side of the Boltzmann equation will then play a role in driving their slow relaxation to overall equilibrium.

This slide describes how the first description of the Maxwell-Boltzmann distribution was obtained.
Conservation of Particle Number

To obtain the local law for the conservation of particles, integrate the Boltzmann equation over all momentum, and look at the result term by term, starting from the left. The first term is the time derivative of the number density:

$$\partial_t n(r,t) \quad \text{with} \quad n(r,t) = \int d\mathbf{p} \ f(\mathbf{p},r,t)$$

The second term is on the left is the divergence of the particle current:

$$\nabla_r \cdot \mathbf{j}(r,t) \quad \text{with} \quad \mathbf{j}(r,t) = \int d\mathbf{p} \ f(\mathbf{p},r,t) \mathbf{p}/m$$

The third term on the left vanishes because it contains a total derivative with respect to momentum and we assume that the momentum integrands drop off fast enough at infinity so that the integral of the total derivative is zero.

When integrated over momentum, the two collision terms are exactly the same except for a sign and thus cancel with one another.

We are left with the differential form of the number conservation law

$$\partial_t n(r,t) + \nabla_r \cdot \mathbf{j}(r,t) = 0.$$
**H-Theorem**

Boltzmann proved a result called the H-theorem, which is our first representation of a low describing the non-equilibrium behavior of entropy. In fact, we have few other examples! To obtain this take the Boltzmann equation, equation v.14, and multiply by \( \ln f \). Note that

\[
(\ln f) \ d f = d [f \ln f] - d f = d[f \ln f/e].
\]

Now, integrate over all momentum. The first term on the left hand side of the Boltzmann equation becomes

\[
\partial_t h(r,t) \quad \text{with} \quad h(r,t) = \int dp \ f(p,r,t) \ln [f(p,r,t)/e]
\]

The second term is on the left is the divergence of the particle current:

\[
\nabla_r \cdot j_h(r,t) \quad \text{with} \quad j_h(r,t) = \int dp \ p/m \ f(p,r,t) \ln [f(p,r,t)/e]
\]

A brief calculation, involving an integral by parts, shows that the third term on the left vanishes because it contains a total derivative with respect to momentum and we assume that the momentum integrands drop off fast enough at infinity so that the integral of the total derivative is zero.

When integrated over momentum, the two collision terms on the right become

\[
R = -\int \int \int \int dp \ dq \ dp' \ dq' \ \delta(p+q - p' - q') \ \delta(\epsilon(p) + \epsilon(q) - \epsilon(p') - \epsilon(q'))
\]

\[
Q(\ p,q \rightarrow p',q') \ [f(p) \ f(q) - f(p') \ f(q')] \ \ln f(p)
\]

Because this result, except for the factor in blue, is symmetrical in \( p \) and \( q \), we can replace \( \ln f(p) \) by \( \ln f(q) \) or by the averages of these two, \( [\ln f(p) + \ln f(q)]/2 \) giving
\[
R = -\int \int \int \int \ dp \ dq \ dp' \ dq' \ \delta(p+q - p'\!-\!q') \ \delta(\epsilon(p) + \epsilon(q) - \epsilon(p')-\epsilon(q'))
\]

\[
Q(\ p, q \rightarrow \ p', q' \) \ [f(p) f(q) - f(p') f(q')] \ [\ln f(p)+\ln f(q)]/2
\]

Now the whole integral, except for the factor in blue, is anti-symmetrical in the replacement of unprimed variables by primed ones. For this reason we can make the replacements

\[
[\ln f(p)+\ln f(q)]/2 \rightarrow -\ln f(p')+\ln f(q')]/2 \rightarrow [\ln f(p)+\ln f(q) - \ln f(p') - \ln f(q')]/4
\]

Since \( \ln a + \ln b = \ln(ab) \) we can rewrite our entire result as

\[
R = -\int \int \int \int \ dp \ dq \ dp' \ dq' \ \delta(p+q - p'-q') \ \delta(\epsilon(p) + \epsilon(q) - \epsilon(p')-\epsilon(q'))
\]

\[
Q(\ p, q \rightarrow \ p', q' \) \ [f(p) f(q) - f(p') f(q')] \ \{\ln [f(p) f(q)]-\ln [f(p') f(q')]\}/4
\]

The entire integral is negative, except perhaps for the factor in red. However, this factor is of the form \( [X - Y] [\ln X - \ln Y] \). This factor is positive if \( X > Y \), equally positive if \( Y > X \), and only zero when \( X = Y \). In that case, we are in local equilibrium!

Put it all together, our result is that

\[
\partial_t h(r,t) + \nabla_r \cdot j_h(r,t) = R
\]

and that \( R < 0 \), except in local equilibrium when \( R = 0 \).
Put it all together, our result is that

$$\partial_t h(r,t) + \nabla_r \cdot j_h(r,t) = R$$

and that $R < 0$, except in local equilibrium when $R = 0$

$$S(t)/k = -\int h(r,t) + \text{conserved things}$$

$S$ is the entropy for a weakly coupled system and $dS/dt > 0$. 
Homework:

Assume our Brownian particle, as described by equation v.12, is charged? How can I include electric and magnetic fields in this equation? Does the system go to equilibrium in the presence of space and time-independent fields? What happens when the field depends upon time?

How can we be sure that equation conserves the total probability of finding the Brownian particle? Should it conserve the momentum or energy of that particle? What are the equations for the time dependence of the particle’s energy and momentum? What about its angular momentum?

Find the laws of conservation of energy and momentum from the Boltzmann equation, equation v.14.