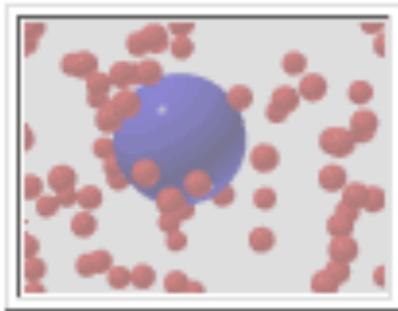# Brownian motion:

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.

The many moving tiny particles are of course **molecules of the liquid**. They were too small to see under a microscope when Brownian motion was discovered, but it was obvious they were there. You can see the molecules of liquid hitting the bigger particle in the animation on the left. (The size of the molecules has been dramatically *increased* in order to make them visible).

http://www.worsleyschool.net/science/files/brownian/motion.html

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

$$dp/dt = \ldots\ldots + \eta(t) - p/\tau$$

$p = (p_x, p_y, p_z)$ $\eta = (\eta_x, \eta_y, \eta_z)$ v.1

$\eta(t)$ is a Gaussian random variable resulting from random kicks produced by collisions. Since the kicks have random directions $\langle\eta(t)\rangle = 0$.   Different collisions are assumed to be statistically independent

$$\langle\eta_j(t)\,\eta_k(s)\rangle = \Gamma\delta(t-s)\delta_{j,k}$$ v.2

The relaxation time, τ, describes friction slowing down as the particles moves through the medium. In contrast Γ 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 τ is a friction tending to continually push our particle toward smaller speeds relative to the medium.

Calculate momentum from   dp/dt=......+ η(t)−p/τ

We have previously calculated the solution to this kind of Langevin equation for position. Now we do it for momentum.

Solution to equation v.1:

$$P(t) = \int_{-\infty}^{t} dt' \ \eta(t') \exp(-\frac{t - t'}{\tau})$$

v.3

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

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

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. Previously, we used this result without having any evidence that it was correct.

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 idea X "must be" right. If X is attractive, we hold on to that view until there is overwhelming evidence to the contrary.

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Calculate Average

$$< p_j(t)p_k(s) >= \int_{-\infty}^{t} du \int_{-\infty}^{t} dv < \eta_j(u)\eta_k(v) > \ \exp[\text{-(t-u+s-v)/τ}]$$

$$< p_j(t)p_k(s) >= \int_{-\infty}^{t} du \int_{-\infty}^{s} dv \Gamma \delta_{j,k} \delta(u-v) \exp[-(t-u)/\tau - (s-v)/\tau] \qquad \text{v.4}$$

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

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

$$= \frac{\delta_{j,k}}{2} \Gamma\tau \exp[-|t-s|/\tau] \qquad \text{v.5}$$

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.

$$\Gamma\tau = 2MkT$$

v.6

Probability distribution

$$\Gamma\tau = 2MkT$$

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

$$\rho(\mathbf{p}) = \left(\frac{\beta}{2\pi M}\right)^{3/2} \exp[-\beta p^2/(2M)] \qquad\qquad \text{v.7}$$

Einstein, A. (1905), "Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen.", *Annalen der Physik* **17**: 549–560, He actually used a more thermodynamic argument.

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

ρ(***p,r***)=*exp[-*βH(***p,r***)*]/Z,*

 where, the the simplest case the Hamiltonian is

 H(***p,r***) = *p²/(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?

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.

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Statistical and Hamiltonian Dynamics

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

$$\frac{dq_\alpha}{dt} = \frac{\partial \mathcal{H}}{\partial p_\alpha}$$

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

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

$$\mathcal{H} = \mathbf{p}^2/(2M) + U(\mathbf{r})$$

and consequently equations of motion

$$\frac{d\mathbf{p}}{dt} = -\nabla U$$

$$\frac{d\mathbf{r}}{dt} = \mathbf{p}/M$$

The statistical mechanics of such situations is given by a probability density function ρ(**p**,**r**,t) such that the probability of finding the particle in a volume element **dp dr** about **p,r** at time t is ρ(**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 motion.

Time Dependence of Dynamical systems:
A much more general problem

Instead of carrying around the variables p and q, 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

$dX_k/dt = V_k(\textbf{X}(t),t)$

to get a solution $\textbf{X}(t)$. Note that $\textbf{X}(t)$ is the solution vector while $X_k(t)$ is one component of that vector. On the other hand x is simply a vector of numbers haveing the same number of components as $\textbf{X}(t)$. I will made extensive use of a probability function $\rho(\textbf{x},t)\,d\textbf{x}$ which is the probability that the solution will be in the interval $d\textbf{x} = \prod_k dx_k$ about $\textbf{x}$.

This $\rho(\textbf{x},t)$ is a probability distribution 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 $g(\textbf{X})$ of the particle coordinates at time t, that function has an average at time t given by

$\int dx\, g(\textbf{x})\, \rho(\textbf{x},t)$. A formula that agrees with this definition is to take

$\rho(\textbf{x},t) = < \prod_k \delta(x_k - X_k(t)) > = < \delta(\textbf{x}-\textbf{X}(t)) >$

where the $< \dots >$ is an average over the probability distribution for $X(t)$. This definition looks like, and is, a tautology but it works. In particular it obeys that condition that ρ must always be positive and most always obey the completeness relation

$1 = \int dx\ \rho(\textbf{x},t) = < \int \prod_k dx_k\, \delta(x_k - X_k(t)) > = 1$ good!

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Start here

Monday	Wednesday	Friday
1 /3 class	1/5 class	1/7 class
1/10 class	1/12 class	1/14 Arnab
1/17 day off	1/19 class	1/21
1/24 class (homework 3 due)	1/26 class (4-5)	1/28 class (5)
1/31 class (5)	2/2 class (5)	2/4 class (4)
2/7 class (6)	2/9 day off	2/11 class (6)
2/14 class (6)	2/16 (6)	2/18 class (7)
2/21 class (7)	2/23 (7)	2/25 class (7)
2/28 class (8)	3/2 (8)	3/4 class(9)
3/7 (9)	3/9	no class

x

Time Dependence of $\rho(\boldsymbol{x},t)$

To calculate the time-dependence, differentiate $\rho(\boldsymbol{x},t)$ with respect to time, holding the coordinate vector, $\boldsymbol{x}$, fixed. Since $\rho(\boldsymbol{x},t)=<\prod_k \delta(x_k-X_k(t))>$, we can use the usual rules for differentiation to find

$$\partial_t\rho(\boldsymbol{x},t)=< \sum_j [\partial_t\delta(x_j-X_j(t))]\prod_{k\neq j} \delta(x_k-X_k(t)) >$$

$$=- < \sum_j \partial_t X_j(t) \, \partial_{x_j} \prod_k \delta(x_k-X_k(t))>$$

The time derivative of $X_j(t)$ is $V_j(\boldsymbol{X}(t),t)$. Thus we obtain

$$\partial_t\rho(\boldsymbol{x},t) + \sum_j \partial_{x_j} V_j(\boldsymbol{x}, t) <\prod_k \delta(x_k-X_k(t))> =0 \quad \text{or more compactly}$$

$$\partial_t\rho(\boldsymbol{x},t) + \sum_j \partial_{x_j} [V_j(\boldsymbol{x}, t) \rho(\boldsymbol{x},t)] =0 \quad \text{or more compactly yet}$$

$$\partial_t\rho + \nabla\cdot [\boldsymbol{V} \rho] =0$$

This result is of the form of a local conservation law with the jth. component of the probability current being the velocity, V_j, times the probability, ρ.

Notice how the spatial gradient appears on the far left in the local conservation law. This placement guarantees that the probability density will have a time-independent integral. Why?

Calculation Continued .....

When we expand out the derivative, our conservation law reads

$$\partial_t \rho(x,t) + \rho(x,t) \sum_j (\partial_{x_j} V_j) + \sum_j V_j \partial_{x_j} \rho(x,t) = 0 \qquad \text{v.9}$$

The last term on the left in eq. v9 is the direct result of the rate of change of each variable $X_j(t)$. That rate is simply V_j.

The second term on the left is more subtle. We call this result the dilation term. It describes the change in the size of the volume element, **dx**, produced by the changes caused by the time development. As the coordinate change, the volume element can shrink or expand and this change has to be reflected in $\partial_t \rho$ in order to keep the normalization $\int d\mathbf{x}$ $\rho = 1$.

Now we have the general result for the time development of the probability density. We next look at the Hamiltonian case, which is rather special

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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 dilation term is

$(\partial_{q_\alpha} \partial_{p_\alpha} H - \partial_{p_\alpha} \partial_{q_\alpha} H)\rho$ which, of course, vanishes

This result, called Liouville's theorem, says that the size of the volume element is independent of time. As a result the the probability density obeys a special equation, with no dilation.

$$\partial_t \rho(p,q,t) + \sum_\alpha [(\partial_{p_\alpha} H)\partial_{q_\alpha} - (\partial_{q_\alpha} H)\partial_{p_\alpha}]\rho(p,q,t) = 0 \qquad \text{v.10}$$

Compare this to the result for a function of *P* and *Q*

$$\frac{dX(P,Q)}{dt} = \sum_\alpha \ [(\partial_{P_\alpha} H)(\partial_{Q_\alpha} X) - (\partial_{Q_\alpha} H)(\partial_{P_\alpha} X)]$$

why is there a difference in notation (p,q) versus (P,Q)--∂ versus d?
why is there a difference in sign?

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Poisson Bracket

The Poisson Bracket is Defined by

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

It then follows immediately that the probability density obeys $\partial_t \rho = \{H, \rho\}$

Also, for any, $X(\boldsymbol{p}, \boldsymbol{q})$, that is a function of p's and q's, with no explicit time-dependence, the time-dependence of X is given by

$$dX/dt = \{X, H\}$$

These Poisson brackets are rather like the commutators of quantum mechanics. For example they satisfy the identities
$\{f, g\} = -\{g, f\}$
Leibnitz rule $\{fg, h\} = f\{g, h\} + \{f, h\}g$
and also Bianchi identity $\{\{f, g\}, h\} + \{\{h, f\}, g\} + \{\{g, h\}, f\} = 0$.
The same relations are true for operators in quantum theory with { and } replaced by [and]. Why are these relations important?
The bracket relations for classical time-dependence are very much like the time-dependence of operators and density matrices in quantum theory, and also of Lie derivatives. This relation between quantum mechanics and the canonical version of classical mechanics is quite surprising and turns out to be quite deep.

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Liouville's Theorem and conservation of phase space volume

This theorem is the statement that volume elements in phase space are conserved in the course of a motion. That's the consequence of the vanishing dilation term. So if you start off with a probability distribution function $\rho(p,q,0)$ at time zero and that function is non-zero in some region of phase space, of volume $\Omega(0)$, after a time, $\rho(p,q,t)$ will progress to occupy a different region of phase space of volume $\Omega(t)$. According to Liouville's theorem the volumes of the regions before and after will be unchanged, $\Omega(t) = \Omega(0)$. Imagine that the probability density was constant within the region you picked, i.e. $\rho(p,q,0)=1/\Omega(0)$. Then, by the same argument to any tiny subvolume of the original region would also have its volume preserved under the transformation, and therefore the value of $\rho(p,q,t)$ within the new region would be the same as as the one within the old. Within the new region, $\rho(p,q,t)=1/\Omega(0)$.

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Liouville's Theorem and conservation of functions of the energy

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

If   ρ(p,q,0) is any function of the Hamiltonian, e.g. ρ(p,q,0)= Z⁻¹exp[− β*H(p,q)*] then this same functional form will hold for all times, assuming that the Hamiltonian has no explicit time dependence.   ρ(*p,q,0*)=f(*H(p,q)*) implies that ρ(*p,q,t*)=f(*H(p,q)*) for any f.

Further, if ρ is any function of a time-independent *H* and of any other conserved functions of *p* and *q,* with no explicit time-dependence,   then ρ will be a solution of our equation.   Thus, not only is the Maxwell- Boltzmann distribution function a solution describing the equilibrium time-dependence of a Hamiltonian system, there are many other solutions as well.

Classical mechanics is not enough to specify a unique equilibrium probability density in a classical system.   Something else is needed in addition.

Give some examples of functions of H with and without explicit time-dependence.

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.   This is OK to use if there are no other important conserved variables, beyond the ones mentioned.   If you have a system in motion, watch out for the momentum. If you have a galaxy, watch out for angular momentum.

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. This is OK to use if there are no other important conserved variables, beyond the ones mentioned.   However, small systems with fixed energy can often have other hidden conserved things.

Any function of *H* will do, continued

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. This is OK to use if there are no other important
conserved variables, beyond the ones mentioned.   However watch out
for many different kinds of particles, each type has a conserved N.
Classical mechanics is provided with extra factors of 1/N!   in ρ for each
different kind of particle.   Particle statistics automatically does this in
quantum theory.

 For large systems, and for most purposes, all these ensembles are equivalent to one
another. Why?

However, the canonical and grand canonical ensembles are particularly convenient. They
have the property that if the Hamiltonian is a sum of independent pieces, ρ, will describe
independent probabilities for these pieces. This result simplifies both thought and
calculations.

We still need a demonstration that the canonical ensemble is a good result for a small syste.

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Say it again

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

$$\partial_t \rho(\mathbf{p}, \mathbf{r}, t) + (p/M) \cdot \nabla_r \, \rho(\mathbf{p}, \mathbf{r}, t) - (\nabla_r U) \cdot \nabla_p \, \rho(\mathbf{p}, \mathbf{r}, t) = 0$$

A time independent solution of this equation would be that ρ 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 ρ. The Einstein model for Brownian motion is

$$d\mathbf{p}/dt = \ldots\ldots + \eta(t) - \mathbf{p}/\tau$$

where ... 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 ρ and then put it all together.

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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.8, 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

$$\partial_t \rho(p,x,t) = - \partial_P [V \rho] = ...+ \partial_P [p/\tau \, \rho(p,x,t)]$$

where x is the variable conjugate to p in a Hamiltonian formulation. We hold on to this result to use in our later analysis.   (Note that the derivative ∂_p acts on everything inside the [...].)

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

$$d\mathbf{p}/dt=......+ \eta(t)-\mathbf{p}/\tau$$

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=……+ η(t)

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+δt, <g(p)>$_{t+δt}$ The first comes from computing $\int$ dp g(p) ρ(p,t+δt). That same average is obtained by taking the solution at time t+δt, which is of the form p(t+δt)=p(t) +δp.

Here, δp is given by the effect of the stochastic forcing, so that

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

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

$$<g(p)>_{t+δt} \quad = \int dp\ g(p)\ \rho(p,t+\delta t) \qquad = \quad < \int dp\ g(p+\delta p)\ \rho(p,t)>$$

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

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

Here we have subtracted the average at δt=0 in order to focus upon changes. Since g(p) is arbitrary, we it follows that

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

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calculation of the effect of dp/dt=......+ η(t)   continued

$$\rho(p,t+\delta t) - \rho(p,t) \quad = \quad < \rho(p\text{-}\delta p,t) - \rho(p,t) > \qquad\qquad \delta p = \int_{t}^{t+\delta t} ds \ \eta(s)$$

The average (<...>) in this equation is over values of η(s) for s between t and t+δt. All other averaging is included in ρ(p,t).

Now expand in δt. (the result is particularly simple because δp does not depend upon p (or q)).

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

The average of δp is zero, and the rest gives

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

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 <η(t) η(s)> =Γδ(t-s)) so that we end up with the result

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

This describes a diffusion in momentum space.
(Notice that because it is diffusive, this result cannot be followed backward in time!
Notice also that we had to go to second order in our calculation of the effect of the random kicks because the second order effect here is linear in δt and we were holding on to all linear terms.)

Effect of Brownian motion: toward a unique probability distribution

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

$$\partial_t \, \rho(p,x,t) \; = \ldots + (\Gamma/2) \; (\partial_p)^2 \, \rho(p,x,t) + \partial_p \, [p/\tau \, \rho(p,x,t)]$$

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

$$0 \; = \ldots \, \partial_p \left\{ \exp[-Q(p,x)][\, (\Gamma/2)(-\partial_p Q) + p/\tau] \right\} \qquad\qquad \text{v.12}$$

which has a 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.

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Summary of Einstein's dynamics

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

$$\partial_t \, \rho(\boldsymbol{p},\boldsymbol{r},t) + (\nabla_{\mathbf{p}} \, \epsilon(\boldsymbol{p},\boldsymbol{r},t)) \cdot \nabla_{\mathbf{r}} \, \rho(\boldsymbol{p},\boldsymbol{r},t) - (\nabla_{\mathbf{r}} \, \epsilon(\boldsymbol{p},\boldsymbol{r},t)) \cdot \nabla_{\mathbf{p}} \, \rho(\boldsymbol{p},\boldsymbol{r},t)$$
$$= (\Gamma/2) \ (\nabla_p)^2 \, \rho(\boldsymbol{p},\boldsymbol{r},t) + \nabla_p \cdot [\boldsymbol{p}/\tau \, \rho(\boldsymbol{p},\boldsymbol{r},t)] \qquad \text{v.13a}$$

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

$\epsilon(\boldsymbol{p},\boldsymbol{r},t) = p^2/(2M) + U(\boldsymbol{r})$

Equation v.13a works equally well if we use as our basic variable the density of particles in phase space, $f(\boldsymbol{p},\boldsymbol{r},t) = N\rho(\boldsymbol{p},\boldsymbol{r},t)$. We then have

$$\partial_t \, f(\boldsymbol{p},\boldsymbol{r},t) + \nabla_{\mathbf{p}} \, \epsilon(\boldsymbol{p},\boldsymbol{r},t) \cdot \nabla_{\mathbf{r}} \, f(\boldsymbol{p},\boldsymbol{r},t) - \nabla_{\mathbf{r}} \, \epsilon(\boldsymbol{p},\boldsymbol{r},t) \cdot \nabla_{\mathbf{p}} \, f(\boldsymbol{p},\boldsymbol{r},t)$$
$$= (\Gamma/2) \ (\nabla_p)^2 \, f(\boldsymbol{p},\boldsymbol{r},t) + \nabla_p \cdot [\boldsymbol{p}/\tau \, f(\boldsymbol{p},\boldsymbol{r},t)] \qquad \text{v.13b}$$

This all looks pretty. But it is based upon the $-p/\tau$ term in the eustion of motion. This term comes from experience with non-relativistic particles. If our particles were all massless ($\epsilon = pc$), we would be getting a bad answer, since the righthand side of the equation only cancels out if ρ is a Gaussian function of p. We need a better argument.

The Boltzmann Equation

Long before Einstein's work, Boltzmann had 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, $p^2/(2m) + U(\textbf{r})$. 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 then included the effect of collisions. The basic variable in this approach was $f(\textbf{p},\textbf{r},t)$, which would then obey an equation of the form

$$\partial_t\, f(\textbf{p},\textbf{r},t) + (\textbf{p}/m)\cdot\nabla_\textbf{r}\, f(\textbf{p},\textbf{r},t) - \nabla_\textbf{r}\, U(\textbf{r},t)\cdot\nabla_\textbf{p}\, f(\textbf{p},\textbf{r},t) = \text{ effects of collisions}$$

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

particles scatter out of $\textbf{p}$.

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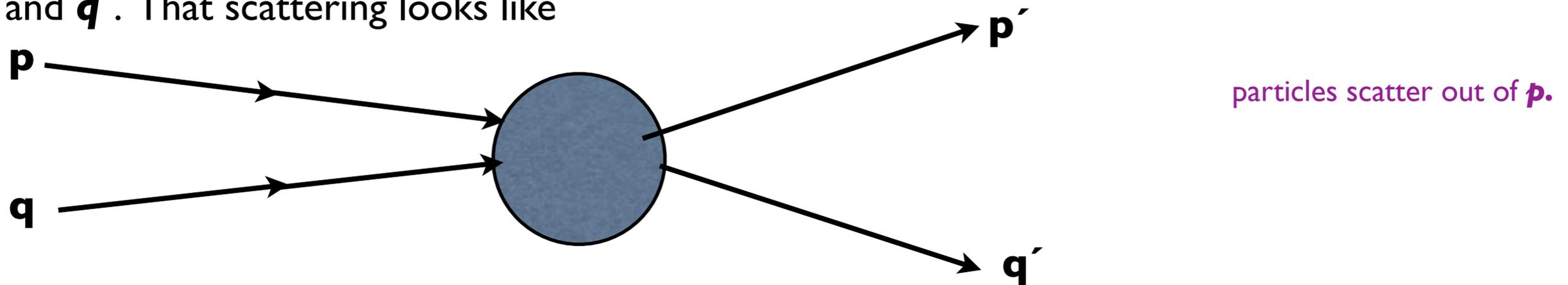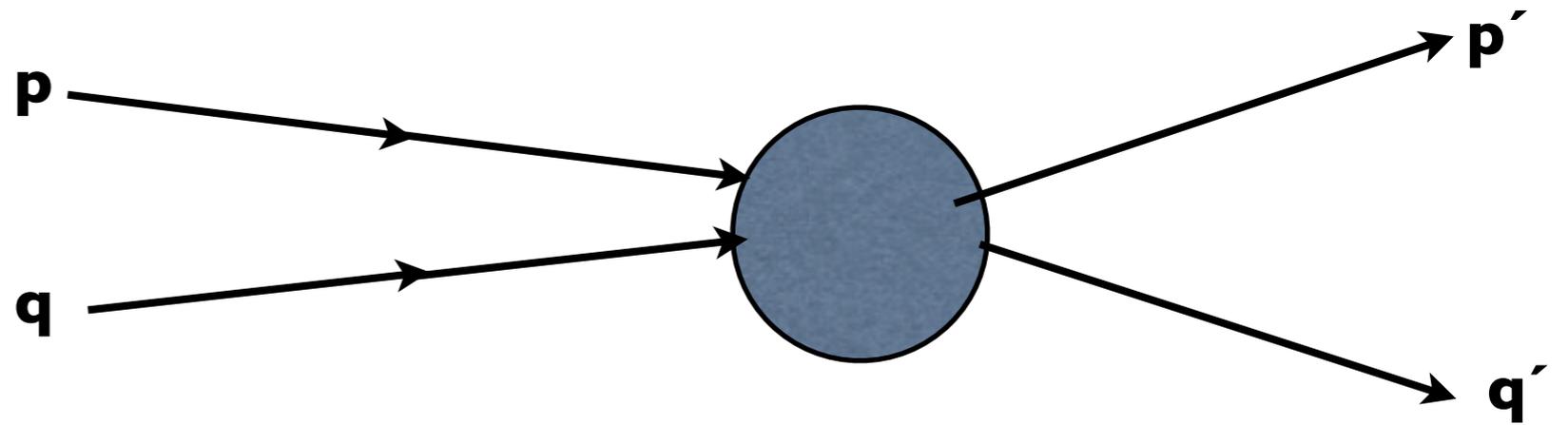
The scattering:

Given that there are particles available with the appropriate initial momentum, the scattering rate into a volume element of final momentum $d\boldsymbol{p}'\, d\boldsymbol{q}'$ can be written as $d\boldsymbol{p}'\, d\boldsymbol{q}'\ Q(\,\boldsymbol{p},\boldsymbol{q} \rightarrow \boldsymbol{p}',\boldsymbol{q}'\,)$ **particles scatter out of $\boldsymbol{p}$.**
The probability that we could get the particles we need for the scattering produce a factor

$f(\boldsymbol{p},\boldsymbol{r},t)\ d\boldsymbol{q}\, f(\boldsymbol{q},\boldsymbol{r},t\,),$ so that the total scattering rate for this process is

$f(\boldsymbol{p},\boldsymbol{r},t) \displaystyle\int d\boldsymbol{q}\, f(\boldsymbol{q},\boldsymbol{r},t\,)\, d\boldsymbol{p}'\, d\boldsymbol{q}'\ Q(\,\boldsymbol{p},\boldsymbol{q} \rightarrow \boldsymbol{p}',\boldsymbol{q}'\,)$

The process *reduces* the number described by $\boldsymbol{p},\boldsymbol{r}$.

In addition, there is an inverse process, and a corresponding rate of increase of $f(\boldsymbol{p},\boldsymbol{r},t)$:
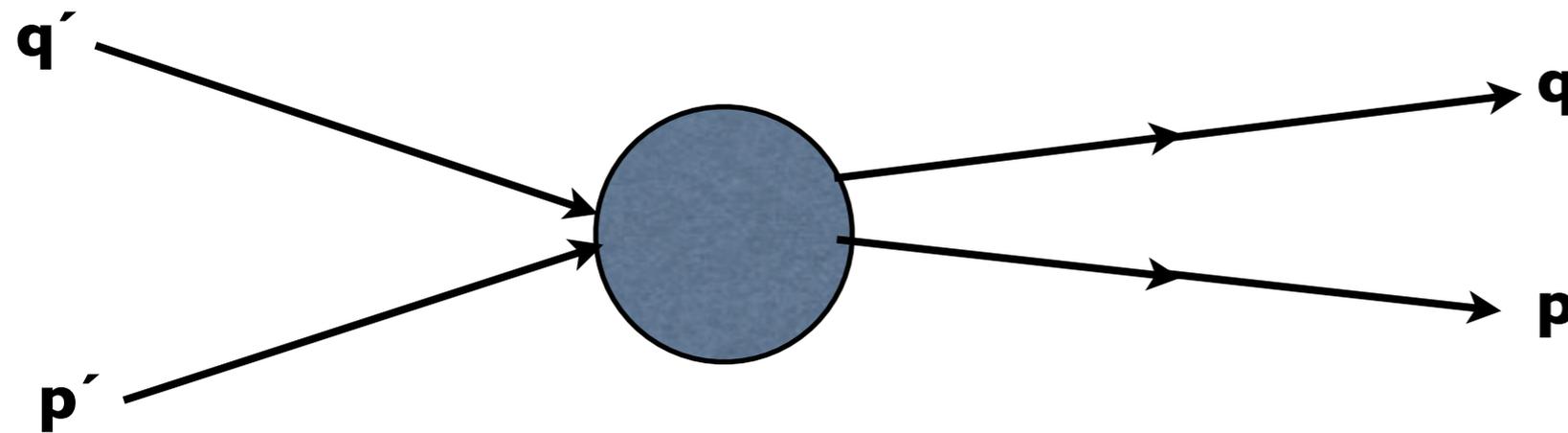
particles scatter intp $\boldsymbol{p}$.

$\displaystyle\int d\boldsymbol{q}\ d\boldsymbol{p}'\, f(\boldsymbol{p}',\boldsymbol{r},t)\ d\boldsymbol{q}'\, f(\boldsymbol{q}',\boldsymbol{r},t\,)\ Q(\,\boldsymbol{p}',\boldsymbol{q}' \rightarrow \boldsymbol{p},\boldsymbol{q}\,)$

put it all together to find

$$[\partial_t + (\boldsymbol{p}/m) \cdot \nabla_{\mathbf{r}} - (\nabla_{\mathbf{r}} \cup (\boldsymbol{r},t)) \cdot \nabla_{\mathbf{p}}] \, f(\boldsymbol{p},\boldsymbol{r},t) =$$

$$- f(\boldsymbol{p},\boldsymbol{r},t) \int d\boldsymbol{q} \, f(\boldsymbol{q},\boldsymbol{r},t) \, d\boldsymbol{p}' \, d\boldsymbol{q}' \, Q(\mathbf{p},\mathbf{q} \to \mathbf{p}',\mathbf{q}')$$

$$+ \int d\boldsymbol{q} \, d\boldsymbol{p}' \, f(\boldsymbol{p}',\boldsymbol{r},t) \, d\boldsymbol{q}' \, f(\boldsymbol{q}',\boldsymbol{r},t) \, Q(\mathbf{p}',\mathbf{q}' \to \mathbf{p},\mathbf{q})$$

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,
$$Q(\mathbf{p},\mathbf{q} \to \mathbf{p}',\mathbf{q}') = R(\mathbf{p},\mathbf{q} \to \mathbf{p}',\mathbf{q}') \, \delta(\mathbf{p}+\mathbf{q} - \mathbf{p}'-\mathbf{q}') \, \delta(\epsilon(\mathbf{p})+ \epsilon(\mathbf{q}) - \epsilon(\mathbf{p}')-\epsilon(\mathbf{q}'))$$
We then find the equation

$$[\partial_t + (\boldsymbol{p}/m) \cdot \nabla_{\mathbf{r}} - (\nabla_{\mathbf{r}} \cup) \cdot \nabla_{\mathbf{p}}] \, f(\boldsymbol{p}) =$$

$$- \iiint d\boldsymbol{q} \, d\boldsymbol{p}' \, d\boldsymbol{q}' \, \delta(\mathbf{p}+\mathbf{q} - \mathbf{p}'-\mathbf{q}') \, \delta(\epsilon(\mathbf{p})+ \epsilon(\mathbf{q}) - \epsilon(\mathbf{p}')-\epsilon(\mathbf{q}'))$$

$$[R(\mathbf{p},\mathbf{q} \to \mathbf{p}',\mathbf{q}') \, f(\boldsymbol{p}) \, f(\boldsymbol{q}) - R(\mathbf{p}',\mathbf{q}' \to \mathbf{p},\mathbf{q}) \, f(\boldsymbol{p}') \, f(\boldsymbol{q}')]$$

Boltzmann equation   v.14

Symmetries of Boltzmann equation

Some symmetry statements are needed: One of these is a statement of time-reversal invariance in which we demand that the direct and the inverse process have the same probability, assuming that the requisite particles are available for the scattering/   Specifically, this statement, called detailed balance, is

$$R(\ \mathbf{p,q} \rightarrow \mathbf{p´,q´}\ ) = R(\ \mathbf{p´,q´} \rightarrow \mathbf{p,q}\ ) \qquad \text{detailed balance}$$

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

$$[\partial_t\ + (\boldsymbol{p}/m)\cdot\nabla_{\mathbf{r}}\ - (\nabla_{\mathbf{r}}\ \mathsf{U})\cdot\nabla_{\mathbf{p}}]\ f(\boldsymbol{p}) =$$

$$-\iiint\! d\boldsymbol{q}\ \ d\boldsymbol{p´}\ d\boldsymbol{q´}\ \delta(\mathbf{p+q - p´-q´})\ \ \delta(\epsilon(\mathbf{p})+ \epsilon(\mathbf{q}) - \epsilon(\mathbf{p´})-\epsilon(\mathbf{q´}))$$

$$R(\ \mathbf{p,q} \rightarrow \mathbf{p´,q´}\ )\ [f(\boldsymbol{p})\ \ f(\boldsymbol{q}) -\ f(\boldsymbol{p´})\ \ f(\boldsymbol{q´})\ ]$$

We shall need one more symmetry statement to obtain our conservation law for energy and momentum, namely the statement that $\boldsymbol{p}$ and $\boldsymbol{q}$ play symmetrical roles in the scattering event.

$$R(\ \mathbf{p,q} \rightarrow \mathbf{p´,q´}\ ) = R(\ \mathbf{q,\ p} \rightarrow \mathbf{q´,\ p´}\ ) \qquad \text{symmetrical scattering}$$

but we do not need that now. 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

$$R(\ \mathbf{p,q} \rightarrow \mathbf{p´,q´}\ ) = R(\ \mathbf{p,q} \rightarrow \mathbf{q´,\ p´}\ ) \qquad \text{identical particles}$$

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Detailed Balance and Equilibrium

$$[\partial_t + (\boldsymbol{p}/m) \cdot \nabla_{\boldsymbol{r}} - (\nabla_{\boldsymbol{r}} \, \mathsf{U}) \cdot \nabla_{\boldsymbol{p}}] \, f(\boldsymbol{p}) =$$

$$-\iiint d\boldsymbol{q} \; d\boldsymbol{p}' \; d\boldsymbol{q}' \; \delta(\boldsymbol{p}+\boldsymbol{q} - \boldsymbol{p}'-\boldsymbol{q}') \; \delta(\epsilon(\boldsymbol{p})+ \epsilon(\boldsymbol{q}) - \epsilon(\boldsymbol{p}')-\epsilon(\boldsymbol{q}'))$$

$$\mathsf{R}(\, \boldsymbol{p},\boldsymbol{q} \rightarrow \boldsymbol{p}',\boldsymbol{q}' \,) \, [f(\boldsymbol{p}) \; f(\boldsymbol{q}) - f(\boldsymbol{p}') \; f(\boldsymbol{q}') \,]$$

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

$$f(\boldsymbol{p}) \; f(\boldsymbol{q}) = f(\boldsymbol{p}') \; f(\boldsymbol{q}')$$

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 thermal equilibrium

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

Notice that the conservation laws for probability, momentum, and energy ensure that this equation is satisfied. Except for the terms in $\boldsymbol{v}$, this is just the Maxwell Boltzmann distribution we might have expected to obtain. The chemical potential, μ, is just a different way of expressing the fact that we can increase or decrease f to produce a larger or smaller number of particles. The v-terms come from momentum conservation. They express the fact that the system may be moving past us with velocity $\boldsymbol{v}$.

This slide describes how Boltzmann obtained the Maxwell-Boltzmann distribution from a consideration of kinetic theory.

From local equilibrium to hydrodynamics

What I wrote down is the right solution of the Boltzmann equation for seeing the thermodynamic equilibrium behavior. However, the demand that the right hand side of the equation vanish gives a more general result, namely one in which the parameters in the Maxwell-Boltzmann distribution vary in space and time.

$$f(\boldsymbol{p},\boldsymbol{r},t) = \exp\{-\beta(\boldsymbol{r},t)[\epsilon(\boldsymbol{p},\boldsymbol{r},t)-\mu(\boldsymbol{r},t)-\boldsymbol{p}\cdot\boldsymbol{v}(\boldsymbol{r},t)- v(\boldsymbol{r},t)^2/(2m)]\}$$ v.15

This "solution" only makes the right hand side zero. The left hand side remains non-zero. This partial solution is described as a local equilibrium solution. Every portion of the system is brought almost to equilibrium, but has the temperature, local density, and wind velocity each vary in space and time. In fact that is precisely what happens to a gas like the air in this room or the earth's atmosphere. Collisions among the molecules happen very rapidly. As I recall every molecule collides with another with an interval between collisions of roughly 10^{-12} seconds. In a time of this order, each region of the gas approximately attains local thermodynamic equilibrium. Then slowly, much more slowly, energy diffuses through the gas equalizing the temperature in the different regions. Momentum diffuses and travels in sound waves, equalizing the local density and the local velocities. These slow transports of conserved quantities are called transport processes. As I said earlier, the conservation laws must be supplemented by constitutive equations to get partial differential equations to describe these diffusions and motions. These equations are called hydrodynamic equations. These equations are simply the results of the local forms of conservations laws.

So, the next thing we are going to do is to derive the conservations laws from the Boltzmann equation.

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:

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

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

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

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
$$\partial_t \, n(\boldsymbol{r},t) + \nabla_{\boldsymbol{r}} \cdot \boldsymbol{j}(\boldsymbol{r},t) = 0.$$

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Conservation of Particle momentum

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

$$\partial_t \, g_j(\boldsymbol{r},t) \qquad \text{with } g_j(\boldsymbol{r},t) = \int d\boldsymbol{p} \, f(\boldsymbol{p},r,t) \, p_j$$

The second term is on the left is the divergence of the momentum current, a tensor T_{jk}:

$$\sum_k \partial_{\mathbf{k}} \, T_{jk}(\,\boldsymbol{r},t) \qquad \text{with} \quad T_{jk}(\boldsymbol{r},t) = \int d\boldsymbol{p} \, f(\boldsymbol{p},r,t) p_j \, p_k/m$$

T_{jk} describes the current of the jth component of momentum in the direction k.

The third term on the left vanishes is a force density $n(\boldsymbol{r},t) \, \partial_j \cup (\,\boldsymbol{r},t)$.

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 momentum conservation law

$$\partial_t \, g_j(\boldsymbol{r},t) + \sum_k \partial_{\mathbf{k}} \, T_{jk}(\,\boldsymbol{r},t) = -n(\boldsymbol{r},t) \, \partial_j \cup (\,\boldsymbol{r},t) \ldots$$

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Constitutive Equation for T_{jk}

The stress tensor is particularly important in condensed matter physics, particle physics, and relativity. In all cases its describes how momentum is moved around. In relativistic theories it is part of a four by four matrix that describes the flow of both energy and momentum.

In the fluid context, we end up with a constitutive equation:

$T_{jk} = \delta_{j,k}\, p$ pressure comes from disordered flow of momentum

      $+\, \rho\, v_j v_k$ flow of momentum due to motion of particles

        $-\, \eta\, [\partial_j v_k + \partial_k v_i - 2\, \delta_{j,k}\, \partial \cdot v]$ dissipation term from viscosity

         $-\, \zeta\, [\, \delta_{j,k}\, \partial \cdot v]$ another dissipation term

The pressure can be calculated from statistical mechanics. The quantities η and ζ are transport coefficients, like the diffusion coefficient, λ, but these describe the flow of momentum rather than particles. These coefficient cannot be computed from statistical mechanics alone but they can be calculated from the Boltzmann equation. That calculation is done as an expansion of the solution in spatial gradients, as for example, the gradient of v. The first calculation of this kind was carried out by Maxwell in the 1870s, and then the method was improved in the 1910s, 1920s and 30s by Chapman and Enskog.   However, I shall not do that calculation now.

Instead, I shall illustrate how transport coefficients may be calculated by using a far simpler model than the one used by Boltzmann.

A toy model

The Boltzmann equation is complicated. It is a non-linear integral equation, and a partial differential equation in severn variables. That's far beyond anything taught in undergrad math courses, or most graduate ones. The derivation of hydrodynamic equations and the calculation of transport coefficients from the Boltzmann equation is hard to do, hard to understand, and hard to learn about. It might be helpful if I put together a little model which illustrates the principles of the Boltzmann equation and its use in deriving hydrodynamic equations. Besides that will illustrate the process of constructing simplified models to illustrate relatively complex ideas.

We will stick with with Boltzmann's form of the equation (see equation v.14)

$$[\partial_t + (\boldsymbol{p}/m) \cdot \nabla_{\mathbf{r}} - (\nabla_{\mathbf{r}} U(\boldsymbol{r},t)) \cdot \nabla_{\mathbf{p}}] \, f(\boldsymbol{p},\boldsymbol{r},t) = -C_{out}(\boldsymbol{p},\boldsymbol{r},t) + C_{in}(\boldsymbol{p},\boldsymbol{r},t) \qquad \text{v.16}$$

where C_{out} and C_{in} respectively are terms which describe the scattering of particles out of configurations with momentum p and into these configurations. From here on we set the forcing term involving U to zero. Our goal will be to have an equation with one conservation law, a conservation law for the total number of particles and a transport equation describing how that conservation law produces an equation for the particle density. Indeed we have already studied such an equation. The hopping model of the previous part has one conservation law

$$\frac{\partial \rho(r,t)}{\partial t} + \nabla \cdot j(r,t) = 0$$

which then gives us a diffusion equation

$$\partial_t \rho(\mathbf{r},t) = \lambda \nabla^2 \rho(\mathbf{r},t)$$

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Playing with Toys

We already know how to derive the required conservation law. Integrate equation v.16 over all momentum we then derive the conservation law for particle number from the left hand side of this equation with the density, $\rho(\boldsymbol{r},t) = \int d\boldsymbol{p}\, f(\boldsymbol{p},\boldsymbol{r},t)$ coming from the first term and the current $\boldsymbol{j}(\boldsymbol{r},t) = \int d\boldsymbol{p}\, f(\boldsymbol{p},\boldsymbol{r},t)\boldsymbol{p}/m$, coming from the second. The third term on the left integrates to zero. We then demand that the right hand side of our toy equation, v.16, not mess up this conservation law so we require

$$\int d\boldsymbol{p}\ C_{out}(\boldsymbol{p},\boldsymbol{r},t) = \int d\boldsymbol{p}\ C_{in}\,(\boldsymbol{p},\boldsymbol{r},t)$$

Now, we must set these collision terms to give us an example from which we can learn. Start by following Einstein in picking the scattering out term to give a scattering within a time τ for each and every particle. This converts into the statement

$$C_{out}(\boldsymbol{p},\boldsymbol{r},t) = f(\boldsymbol{p},\boldsymbol{r},t)/\tau$$

We have to apply the same physics to the term which takes particles from all possible directions of momentum, $\boldsymbol{q}$, and scatters them into state $\boldsymbol{p}$. Guess a simple form in which the probability of appearing in state $\boldsymbol{p}$, defined as $g(\boldsymbol{p})$ is independent of q and of the direction of $\boldsymbol{p}$. In symbols this converts into

$$C_{in}(\boldsymbol{p},\boldsymbol{r},t) = g(p) \int d\boldsymbol{q}\, f(\boldsymbol{q},\boldsymbol{r},t)/\tau \qquad \text{where} \quad \int d\boldsymbol{q}\, g(q) = 1$$

With this statement we have guarenteed that our conservation law is satisfied. Our basic equation now becomes

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Moreplay

Our basic equation is now

$$[\partial_t + (\boldsymbol{p}/m)\cdot\nabla_{\boldsymbol{r}}]\, f(\boldsymbol{p},\boldsymbol{r},t) = -f(\boldsymbol{p},\boldsymbol{r},t)/\tau + g(p)\int d\boldsymbol{q}\, f(\boldsymbol{q},\boldsymbol{r},t)/\tau \qquad\qquad \text{v.16}$$

We want to focus upon the sitation in which there is slow variation in space and time. We therefore, for the moment neglect the left hand side of the equation and find $f(\boldsymbol{p},\boldsymbol{r},t) \approx g(p)\,\rho(\boldsymbol{r},t)$. Notice that because g is rotationally invariant this lowest order solution produces no particle current so it gives no diffusion. To go to high order write

$$f(\boldsymbol{p},\boldsymbol{r},t) = g(p)\,\rho(\boldsymbol{r},t) + \delta f(\boldsymbol{p},\boldsymbol{r},t) \text{ and demand (why?) that } \int d\boldsymbol{q}\, \delta f(\boldsymbol{q},\boldsymbol{r},t) = 0. \text{ We then see}$$

$$[\partial_t + (\boldsymbol{p}/m)\cdot\nabla_{\boldsymbol{r}}][\delta f(\boldsymbol{p},\boldsymbol{r},t) + g(p)\,\rho(\boldsymbol{r},t)] = -\delta f(\boldsymbol{p},\boldsymbol{r},t)/\tau \qquad\qquad \text{v.17}$$

Notice that δf is small because space and time derivatives are small. We neglect derivatives of δf on the left hand side of equation v.17 and find the deviation from local equilibrium as

$$\delta f(\boldsymbol{p},\boldsymbol{r},t) \approx -\tau[\partial_t + (\boldsymbol{p}/m)\cdot\nabla_{\boldsymbol{r}}][g(p)\,\rho(\boldsymbol{r},t)] \qquad\qquad \text{v.18}$$

The second term on the right gives us a particle current

$$\boldsymbol{j}(\boldsymbol{r},t) = -\tau \int d\boldsymbol{p}\, g(p)\, \boldsymbol{p}\, \boldsymbol{p}/m \cdot \nabla_{\boldsymbol{r}}\, \rho(\boldsymbol{r},t) = -\lambda\, \nabla_{\boldsymbol{r}}\, \rho(\boldsymbol{r},t)$$

where the diffusion coefficient is $\lambda = \tau \int d\boldsymbol{p}\, g(p)\, p_j\, p_j/m$

Conservation laws plus slow variation in space and time gives transport equations.

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H-Theorem

Boltzmann proved a result called the H-theorem, which is our first representation of a law 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

$$\partial_t \, h(\boldsymbol{r},t) \qquad \text{with } h(\boldsymbol{r},t) = \int d\boldsymbol{p} \; f(\boldsymbol{p},r,t) \ln [f(\boldsymbol{p},r,t)/e]$$

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

$$\nabla_{\boldsymbol{r}} \cdot \boldsymbol{j_h}(\boldsymbol{r},t) \qquad \text{with } \boldsymbol{j_h}(\boldsymbol{r},t) = \int d\boldsymbol{p} \; \boldsymbol{p}/m \; f(\boldsymbol{p},r,t) \ln [f(\boldsymbol{p},r,t)/e]$$

A brief calculation, involving an integration 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

$$\mathrm{D\,H} = - \iiiint \; d\boldsymbol{p} \; d\boldsymbol{q} \; d\boldsymbol{p}' \; d\boldsymbol{q}' \; \delta(\boldsymbol{p}+\boldsymbol{q} - \boldsymbol{p}'-\boldsymbol{q}') \; \delta(\epsilon(\boldsymbol{p}) + \epsilon(\boldsymbol{q}) - \epsilon(\boldsymbol{p}')-\epsilon(\boldsymbol{q}'))$$

$$R(\; \boldsymbol{p},\boldsymbol{q} \rightarrow \boldsymbol{p}',\boldsymbol{q}'\;) \; [f(\boldsymbol{p}) \; f(\boldsymbol{q}) - f(\boldsymbol{p}') \; f(\boldsymbol{q}')\;] \; \ln f(\boldsymbol{p})$$

Because this result, except for the factor in blue, is symmetrical in p and q, we can replace ln $f(\boldsymbol{p})$ by ln $f(\boldsymbol{q})$ or by the averages of these two, [ln $f(\boldsymbol{p})$+ ln $f(\boldsymbol{q})$]/2 giving

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$$DH = -\iiint dp\, dq\, dp'\, dq'\ \delta(p+q-p'-q')\ \delta(\epsilon(p)+\epsilon(q)-\epsilon(p')-\epsilon(q'))$$

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

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

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

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

$$DH = -\iiint dp\, dq\, dp'\, dq'\ \delta(p+q-p'-q')\ \delta(\epsilon(p)+\epsilon(q)-\epsilon(p')-\epsilon(q'))$$

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

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 last case, we must be in local equilibrium!

Put it all together, our result is that

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

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

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Put it all together, our result is that

$$\partial_t\, h(\boldsymbol{r},t) + \nabla_r \cdot j_h(\boldsymbol{r},t) \quad = \mathrm{D\,H}$$

and that $\mathrm{D\,H} < 0$,
except in local equilibrium when $\mathrm{D\,H} = 0$.
Thus $-\mathrm{D\,H}$ is the rate of entropy production in the system.

$$S(t)/k_B = \;-\!\int dr\; h(\boldsymbol{r},t) + \text{conserved things}$$

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

Local Equilibrium and Hydrodynamics

Human observations are done on a scale much larger than the tiny distances the characterize the microscopic world. We don't see the collisions and energy-transfers that are the events microscopic of the microscopic world.   Instead we observe the space and time variation in the parameters defining the local equilibrium of that world. Specifically, in a fluid or the usual kind of a solid, these parameters are the local temperature, the densities of the various components, and the local velocity of the constituents.   These variations are most commonly seen in the hydrodynamic modes describing the different kinds of motion in the material. For example, in an ordinary solid the modes are heat conduction, three polarizations of sound (two transverse and one longitudinal), and the diffusion of the different constituents. In an ordinary fluid, there is a sound wave mode, heat conduction, and two components of transverse diffusion of momentum, usually described as viscous motion. These last modes are correctly predicted by a careful analysis of the effects of the conservation laws within the Boltzmann equation. There are five modes just mentioned, with sound counting as two modes because it involves two derivatives in time, corresponding to the five local equilibrium parameters and the five conserved quantities from which they are derived.

Isn't all this obvious? Not exactly. A phase transition can take us into a situation in which we find different numbers and kinds of conserved quantities, more or fewer local equilibrium parameters (usually more), and more and different kinds of hydrodynamic behavior. Ordinary fluids have one sound wave for every different wave vector; solids have three; liquid crystals have a richer zoo of behaviors. Boltzmann's equation and its consequences are just one example in a whole rich world of different phases and different kinds of behavior. These are the subjects of rich study in modern condensed matter and particle physics.

Homework:

v.1 Are there additional solutions to equation v.12, beyond the one we gave? Discuss this issue.

v.2 Assume our Brownian particle, as described by equation v.13a, 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?

v.3 How can we be sure that equation v.13a 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?

v.4 Find the laws of conservation of energy and momentum from the Boltzmann equation, equation v.14.

v.5 Draw a series of pictures or construct a little video to show the motion of a region of phase space determined by the motion of a one-dimensional harmonic oscillator.
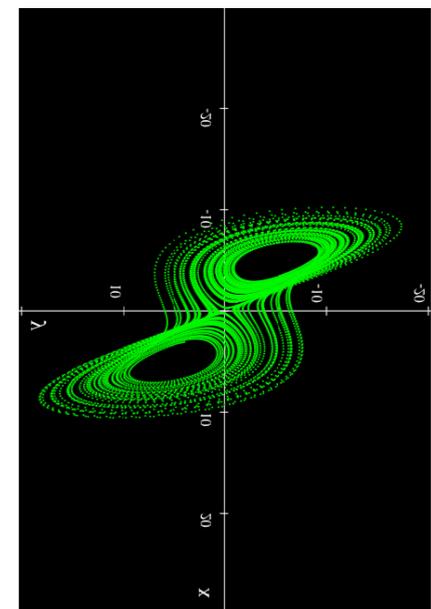
v.6 Edward Lorenz saw chaotic solutions to the equations

$dx/dt = 3 (y-x)$

$dy/dt = 26.5 x - y - xz$

$dz/dt = xy - z$

What happens to volumes in the (x,y,z) space in the time development of these equations?

v.7 One can derive a equation for sound propagation by using the local equilibrium solution, partile and momentum conservation, and then simplifying by assuming that the temperature does not vary. What is the sound velocity that you obtain in this fashion? Newton got this, incorrect, answer. The temperature is not constant during the propagation of a low-frequency sound wave.

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