Nonequilibrium Statistical Mechanics:

The Boltzmann Transport Equation

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Our starting point: equilibrium

In equilibrium statistical mechanics, by definition, our particles distributed themselves in a way as to maximize degeneracies -- whether in energy, position, etc.

From this, one can derive (energy) occupational density functions for different types of particles (e.g. fermions, bosons)

What does this tell us about the real-space location of our particles? Almost nothing.

Particle Location

Thus far in our discussions of statistical particle behavior, we have focused on describing the energy state occupational density functions of quantum particles.

Why have we not derived the space occupational density function?

Because it is a constant everywhere in the space-of-interest.

As has been said, in statistical mechanics, an isolated system in equilibrium is equi-likely to be in any of its available states. Spatially, this means that any combinations of particles can be anywhere in the isolated system (assuming a bulk material for simplicity).

But what about in nonequilibrium?

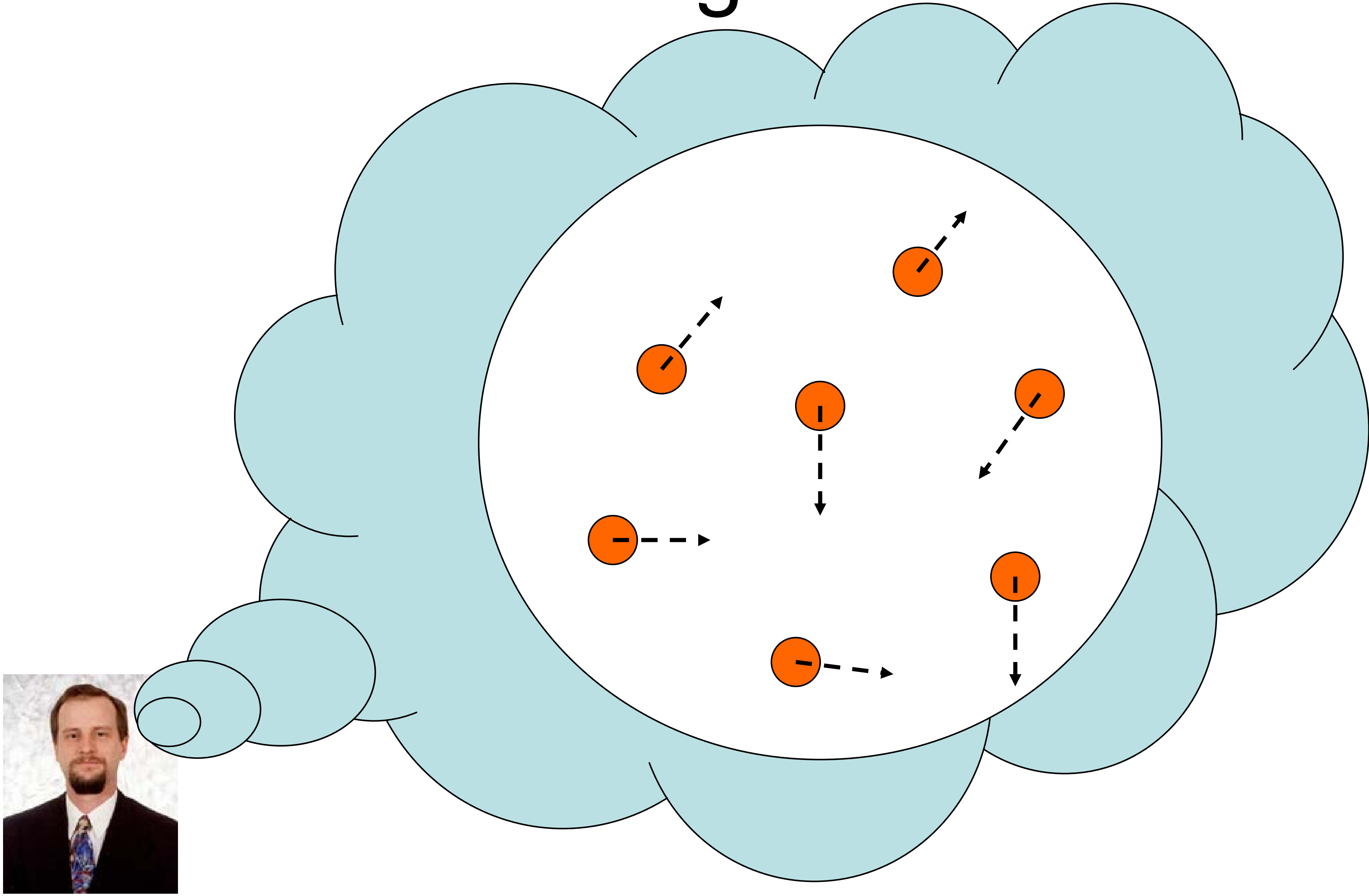
Nonequilibrium Conditions

Under nonequilibrium conditions, mechanisms exist, which promote the likelihood of particles in the system into some states and diminish the likelihood of others.

So what might these complex and destined-to-be-obscure mechanisms be?

Let’s look at an example…

Let us imagine a large balloon filled with a gas



Let's assume that…

I. There are <u>no external forces or fields</u> (e.g. gravity, fields, etc.)

II. The gas is <u>monatomic</u> and <u>uncharged</u>

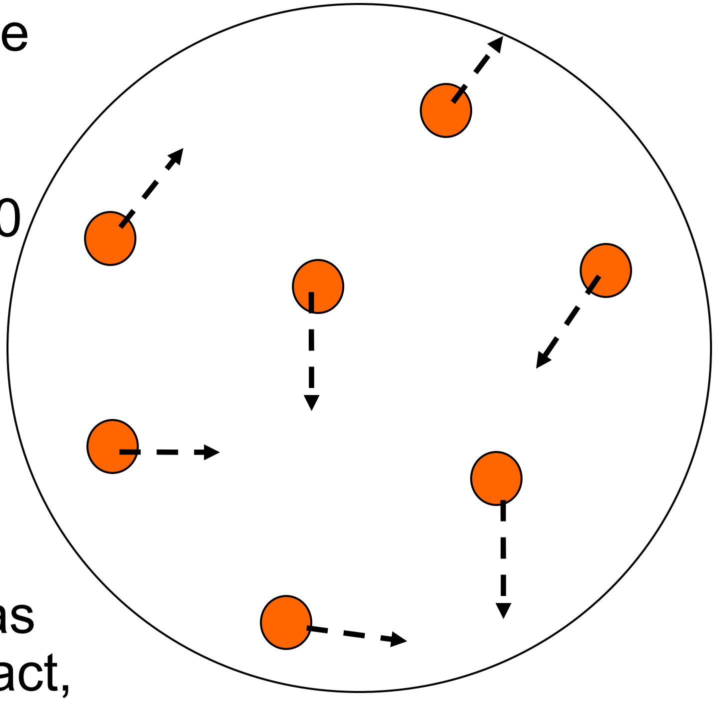
III. The gas is dilute and <u>collisions are negligible</u>

IV. The balloon is huge and we can simply <u>disregard</u> what happens when atoms come into <u>contact at the boundary</u>.

V. The systems' statistical properties are in <u>steady-state</u> e.g. the mean momentum is 0

These first 5 assumptions place our system in equilibrium.

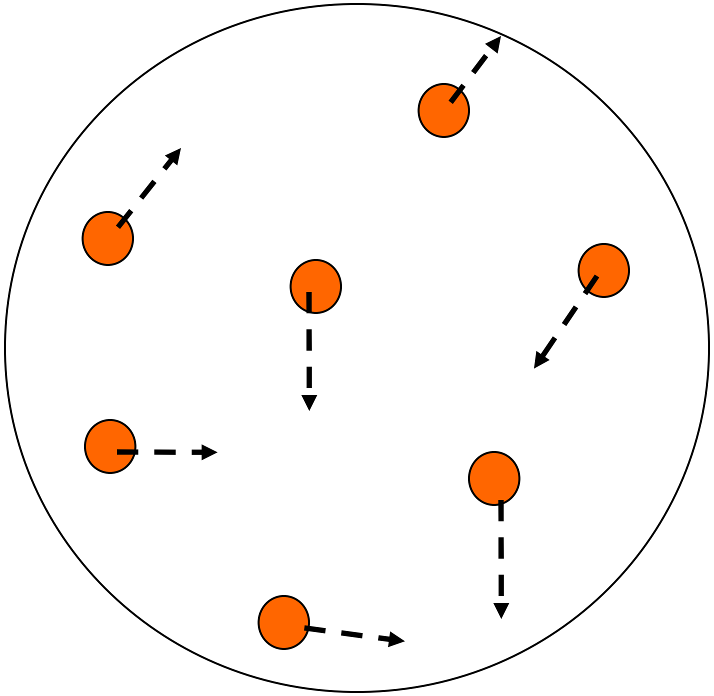
As a sixth assumption, I'll propose that the gas molecules are like people in an elevator: as far away from each other as possible (in fact, we can use circular logic to demonstrate why this is so -- but we'll get to that in a few minutes)



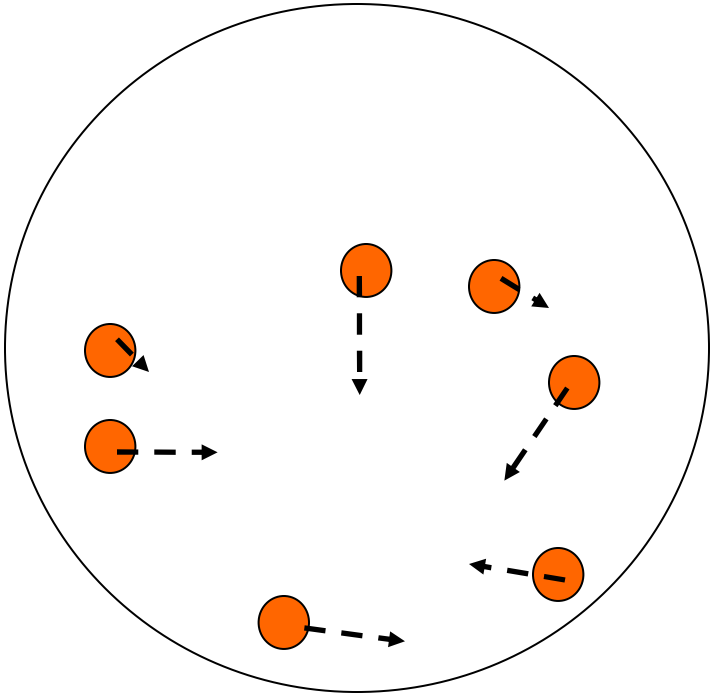
Now what if we incorporated an external force?

Let’s apply gravity -- turn on the gravity switch.

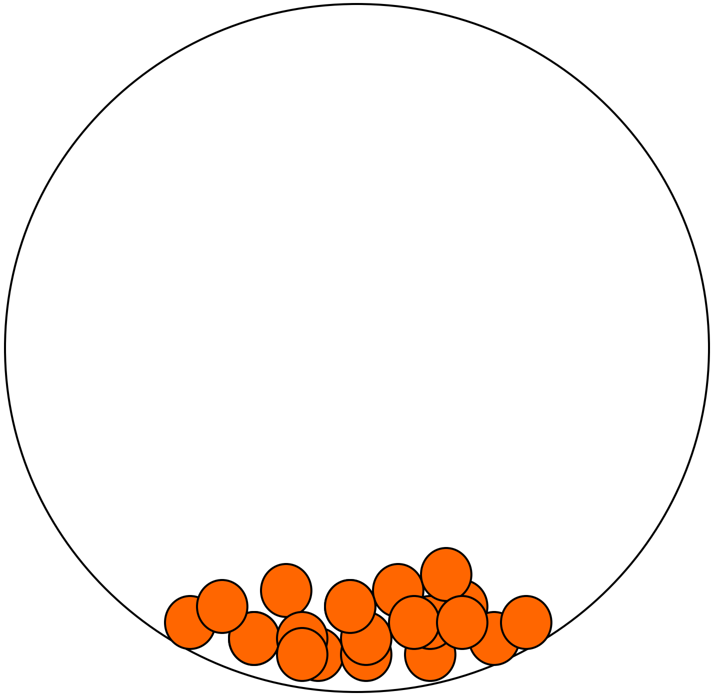
t = 0



t = some time later



Our system is now at another steady-state…

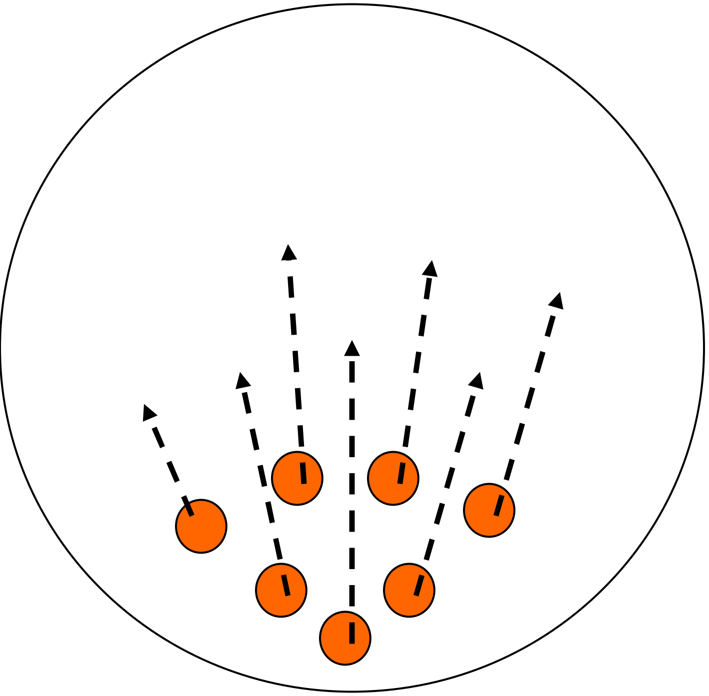


Now without pounding down the walls of our previous assumptions (e.g. negligible collisions), you can understand that the gravity [being the only force] has caused the particles to collect at the bottom of the rigid, balloon.

Now, what would happen if we flipped the gravity switch back off?

Particle Diffusion

Without the external force, the atoms will diffuse away from each other (an area of high concentration) to the other side of the balloon (area of low concentration).



After some time, one could guess that the particles will return to a state of equilibrium.

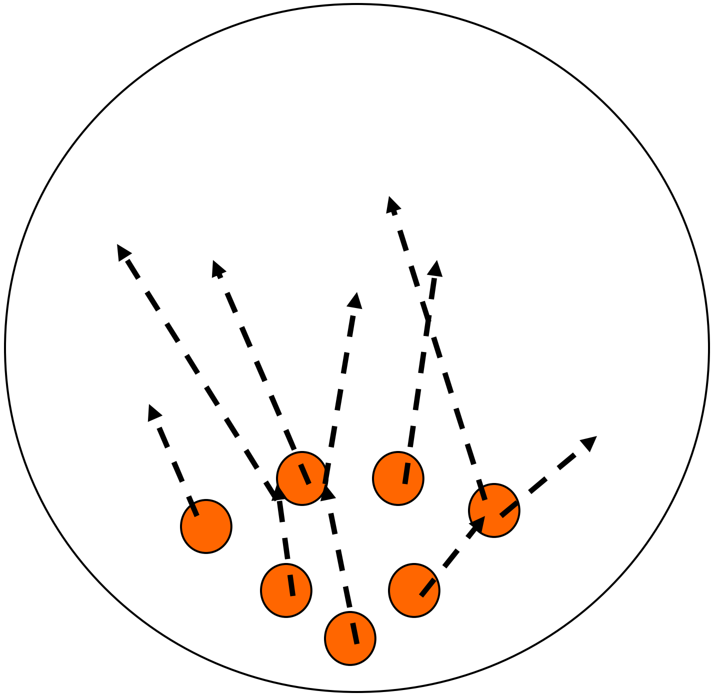
It is this diffusion, which creates an “equilibrium” in which the atoms are most likely to be as-far-from each other as possible [on average] -- circular logic.

In this scenario, this may be true, but not every system will settle at equilibrium e.g. superconductive systems.

One more mechanism: collisions

Previously, we assumed that collisions could be neglected.

Clearly in this example, the gas atoms would have at least collided with each other and the balloon as they collected at the bottom of the balloon and when they diffused away (these are not the only times atoms would have collided, but these are intuitively simple situations)



So the the mechanisms that alter state probabilities were quite intuitive and comprehensible!

Unfortunately, this doesn’t make them simple to mathematically handle.

Boltzmann's Equation

We will begin our mathematical treatment of nonequilibrium statistical mechanics by defining a probability distribution function, f(x,k,t).

In a system with no particle collisions, particle generations, or particle absorptions[*]; the probability distribution function is conserved with respect to time:

$$\frac{df(x,k,t)}{dt} = 0$$

N.B.: particle collisions and generation (or recombination) occurrences fall into an umbrella category, "scattering events".

[*]: In the uncharged gas-in-vaccuum thought experiment previously, there were only three mechanisms, but in materials such as semiconductors, the total free carriers can be adjusted through generation and recombination events

How do we know the distribution is conserved?

Let’s assume that we have a one particle system, which can only be influenced by external fields and diffusion. Let’s place this one particle within a phase-space volume $dxdydzdk_x dk_y dk_z$ at time t.

Over a span of time, dt, this one particle is influenced by an external field and/or diffusion and moves to another phase-space volume, $dx'dy'dz'dk_x'dk_y'dk_z'$

How do we know the distribution is conserved?

These two phase-space volumes can be shown (via the 6-dimensional Jacobian) to be equal to each other:

$$dV \equiv dxdydzdv_x dv_y dv_z = dx'dy'dz'dv_x'dv_y'dv_z'$$

Since the particle was not lost (absorbed) and a 2nd particle was not generated, the probability function is not fundamentally different -- it’s coordinates are just shifted (it’s just classic Newtonian mechanics):

$$f(\vec{r},\vec{k},t)dV = f(\vec{r}',\vec{k}',t')dV$$

$$t' \equiv t + dt$$

$$\vec{r}' \equiv \vec{r} + \vec{v}dt = \vec{r} + \frac{d\vec{r}}{dt}dt$$

$$\vec{k}' \equiv \vec{k} + \frac{q\vec{F}}{\hbar}dt = \vec{k} + \frac{d\vec{k}}{dt}dt$$

How do we know the distribution is conserved?

From this we can see that

$$f(\vec{r},\vec{k},t) = f(\vec{r}',\vec{k}',t')$$

$$t' \equiv t + dt$$

$$\vec{r}' \equiv \vec{r} + \vec{v}dt = \vec{r} + \frac{d\vec{r}}{dt}dt$$

$$\vec{k}' \equiv \vec{k} + \frac{q\vec{F}}{\hbar}dt = \vec{k} + \frac{d\vec{k}}{dt}dt$$

$$\longrightarrow$$

$$f(\vec{r} + \frac{d\vec{r}}{dt}dt, \vec{k} + \frac{d\vec{k}}{dt}dt, t + dt) - f(\vec{r},\vec{k},t) = 0$$

$$\therefore \frac{df}{dt} = 0$$

For a rigorous proof of this, reference:
D. Ter Haar, Elements of Statistical Mechanics (3rd),
Butterworth-Heinemann, Oxford (1995), pp 11-19.

Now to incorporate “scattering events”

As previously mentioned, “scattering events” are any events which break the conservation of the probability distribution function with respect to time such as generation, atomic collisions, and absorption.

As a mental exercise, imagine we have our 1-particle system again, and the particle is absorbed into the medium (think of a free electron recombining with a hole) -- assuming there is no possibility of another particle being created, our probability distribution is now null.

Now to incorporate "scattering events"

Including "scattering events" into our conservation of probability distribution function:

$$\frac{df}{dt}=0 \quad \Longrightarrow \quad \frac{df}{dt}=\left.\frac{\partial f}{\partial t}\right|_{\substack{\text{Scattering}\\\text{Events}}}$$

This continuity equation including scattering, is the actual Boltzmann Equation, but in this form it appears quite unhelpful

Expanding the derivative….

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial f}{\partial y}\frac{\partial y}{\partial t} + \frac{\partial f}{\partial z}\frac{\partial z}{\partial t}$$

$$+\frac{\partial f}{\partial k_x}\frac{\partial k_x}{\partial t} + \frac{\partial f}{\partial k_y}\frac{\partial k_y}{\partial t} + \frac{\partial f}{\partial k_z}\frac{\partial k_z}{\partial t} =$$

$$\frac{\partial f}{\partial t} + \vec{\nabla}_{\vec{r}} f \bullet \vec{v} + \vec{\nabla}_{\vec{k}} f \bullet \frac{\vec{F}}{\hbar} = \left.\frac{\partial f}{\partial t}\right|_{\substack{\text{Scattering}\\\text{Events}}}$$

In which ‘F’ is an external force acting on the system.

This can also be simply converted from having a k-component velocity:

$$\frac{\partial f}{\partial t} + \vec{\nabla}_{\vec{r}} f \bullet \vec{v} + \vec{\nabla}_{\vec{v}} f \bullet \frac{\vec{F}}{m} = \left.\frac{\partial f}{\partial t}\right|_{\substack{\text{Scattering}\\\text{Events}}}$$

Understanding each term

In this expression, it is fairly intuitive to point out which term is due to external forces and which is diffusion.

$$\frac{\partial f}{\partial t} + \vec{\nabla}_{\vec{r}} f \bullet \vec{v} + \vec{\nabla}_{\vec{k}} f \bullet \frac{\vec{F}}{\hbar} = \left.\frac{\partial f}{\partial t}\right|_{\substack{\text{Scattering}\\ \text{Events}}}$$

Diffusion

Force

The second left-hand term is clearly the diffusion term, because it contains a gradient with respect to space, and diffusions by their very definition are created by nonzero spatial gradients of particles (or their probability density in this expression)

The Scattering Events Term

$$\frac{\partial f}{\partial t} + \vec{\nabla}_{\vec{r}} f \bullet \vec{v} + \vec{\nabla}_{\vec{k}} f \bullet \frac{\vec{F}}{\hbar} = \left.\frac{\partial f}{\partial t}\right|_{\substack{\text{Scattering}\\ \text{Events}}}$$

The scattering term is defined in Brennan’s book as

$$\left.\frac{\partial f}{\partial t}\right|_{\substack{\text{Scattering}\\ \text{Events}}} \equiv -\int \left\{ f\left(\vec{r},\vec{k},t\right)\left[1 - f\left(\vec{r},\vec{k}',t\right)\right] S\left(\vec{k},\vec{k}'\right) - f\left(\vec{r},\vec{k}',t\right)\left[1 - f\left(\vec{r},\vec{k},t\right)\right] S\left(\vec{k}',\vec{k}\right) \right\}$$

In this expression S(k,k’) is the rate at which a particle makes a transition from state k to k’. S(k’,k) is similarly a rate, but transferring from k’ to k. f(r,k,t) is the probability of that state being occupied by another particle, and 1-f(r,k,t) is the probability of the state being empty.

You can see that a scattering event in this definition does not change a particle’s location, but rather just its k-state (momentum, which is proportional to velocity, which makes intuitive sense when one thinks of classical scattering events e.g. billiard balls)

The Boltzmann Equation incorporates several approximations*:

1. Quantum effects are negligible i.e. position and momentum can be measured simultaneously
   - ✓ As seen in the very definition of the probability distribution function
2. Collisions are instantaneous
   - ✓ Thus external fields and scattering are uncoupled
3. Collisions are all binary (occurring between 2 bodies)
4. Collisions do not accelerate particles, but merely change their direction of travel.
5. The particles are all the same
6. The force term, F, is from external fields/forces and not from atom-to-atom interactions (e.g. electric repulsion from like-charges)

Plus several others that are very obscure and overly-complicated for our surface-level understanding and needs.

*: the approximations listed here refer to the derivation of Boltzmann’s equation found in Brennan’s book. Some authors in other books make adjustments to the form of Boltzmann’s equation in order to facilitate such things as multiple atom types and quantum mechanical effects (just to name a few)

Solving Boltzmann’s Equation

Solving Boltzmann’s equation analytically can be a large challenge; thus, a huge variety of approximate solutions have been developed to analytically or numerically solve the equation in certain, specific scenarios.

One very common scenario: distribution relaxes to a steady-state. This is called the “relaxation-time approximation”.

Relaxation-time Approximation

In this approximation the integral scatter-term is replaced by a linear expression:

$$\left.\frac{\partial f}{\partial t}\right|_{\substack{\text{Scatter}\\\text{Events}}} = -\frac{f - f_{ss}}{\tau}$$

In which f_{ss} is a steady-state distribution, which out system will relax to in a characteristic time τ.

From this expression we can find our nonequilibrium distribution:

$$\left.\frac{\partial f}{\partial t}\right|_{\substack{\text{Scatter}\\\text{Events}}} = -\frac{f - f_{ss}}{\tau} \quad \Longrightarrow \quad \int_{f(0)}^{f(t)} \frac{\partial f}{f - f_{ss}} = \int_{0}^{t} -\frac{1}{\tau}\partial t$$

Relaxation-time Approximation

$$\int_{f(0)}^{f(t)} \frac{\partial f}{f - f_{ss}} = \int_0^t -\frac{1}{\tau}\partial t \quad \Longrightarrow \quad \frac{f(t) - f_{ss}}{f(0) - f_{ss}} = e^{-\frac{t}{\tau}}$$

$$\Longrightarrow \quad f(t) = \left[f(0) - f_{ss}\right]e^{-\frac{t}{\tau}} + f_{ss}$$

We can see that as time progresses, the distribution probability function approaches the steady-state value.

Understand the interesting concept that scatter is what is bringing the system to steady-state -- as in this case

$$\lim_{t\to\infty}\frac{\partial f}{\partial t} = \lim_{t\to\infty} - \frac{f(t) - f_{ss}}{\tau} = -\frac{f_{ss} - f_{ss}}{\tau} = 0$$

Side-note: Without scatter the system could sustain itself in nonequilibrium (this is the basis of superconductivity)

Reference

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