

Kinetic Theory Approaches to Large Systems

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What is Kinetic Theory?

The theory that heat was the kinetic energy of microscopic molecules was introduced by Daniel Bernoulli in 1738, but was neglected by just about everyone including himself until it was championed by Rudolph Clausius in the late 1850's. It was dubbed the *kinetic theory of heat* by Lord Kelvin in the 1860's. This was quickly shortened to *kinetic theory* when it became clear that the theory then being developed by James Clerk Maxwell and Ludwig Boltzmann explained far more than heat.

Maxwell's 1866 masterpiece unified what were three separate theories:

- 1.the theory of heat and work — later dubbed thermodynamics,
- 2.the theory of gas dynamics — which it also completed,
- 3.the theory of microscopic particles interacting by a potential.

Kinetic theory was not widely accepted. Physicists did not believe in atoms.

Boltzmann's 1872 paper gave a microscopic interpretation of the entropy. This led Boltzmann to introduce *equilibrium statistical physics* in the 1880's, which was significantly advanced by Josiah Willard Gibbs in his 1902 book.

Some of Boltzmann's arguments were adopted by Max Planck in his 1900 paper that heralded the dawn of *quantum theory*.

Most importantly, it led to Albert Einstein's dissertation on Brownian motion, which was published in 1905. This paper provided the theoretical foundation for the experiments that by 1908 convinced physicists that kinetic theory was correct — 180 years after it was introduced, over 40 years after Maxwell's masterpiece.

Now the label *kinetic theory* is applied to a wide range of theories that embrace viewpoints similar to those embraced by these earlier theories.

Measuring Heat and Pressure

Before kinetic theory heat was thought to be a massless substance called *caloric*. Before the 1600's there were no quantitative theories of heat or pressure because there was no good way to *measure* them. Quantitative physical laws that existed before then were built around measurements of length, time, and mass (weight).

Galileo Galilei championed the central role of observation, experiment, and measurement in science. He showed that objects with different masses fall at the same rate. He invented the thermoscope to measure heat (temperature) in 1592. A student of Galileo, Giuseppe Biancani, first published the details of one in 1617. In 1643 Evangelista Torricelli, disciple of Galileo, invented the mercury barometer to measure pressure.

Discovery of Gas Laws

These new measuring devices led directly to the discovery of gas laws.

The barometer led to what became known as Boyle's law — that the spring (later called pressure) of a gas is inversely proportional to the volume it occupies. This law was formulated by Richard Towneley and Henry Power in 1661, and confirmed by Robert Boyle with careful experiments in 1662.

Experiments with a thermoscope led Guillaume Amontons to conjecture in 1702 that the pressure also increased linearly with temperature. However, the thermoscope was alcohol-based, and results obtained with one were hard to reproduce.

The mercury thermometer was invented by Daniel Gabriel Fahrenheit in 1714, but almost 100 years passed before these so-called gas laws were confirmed by Joseph Louis Gay-Lussac with careful experiments in 1807.

First Kinetic Theory

In 1738 Daniel Bernoulli derived Boyle's law by assuming that a gas is composed of particles that bounce off the walls of its container. Moreover, this model showed that the pressure was proportional to the square of the speed of these particles — or equivalently, proportional to the kinetic energy of the gas particles. He observed this was consistent with the theory of Amontons if an absolute temperature is identified with this kinetic energy.

There were caloric theories that explained gas laws without assuming the existence of particles that no one had ever seen. (We will not go into these here.) Moreover, Amontons's gas law had not yet been validated by experiment. Therefore Bernoulli's theory was neglected by just about everyone, including himself.

Fluid Dynamics

In 1757 Leonhard Euler wrote three papers that created a theory of fluid dynamics governed by partial differential equations. In fact, he produced two theories — one for liquids and one for gases — called hydrodynamics and gas dynamics respectively. These greatly simplified theories based upon ordinary differential equations developed by Daniel Bernoulli in the same 1738 book (Hydrodynamica) in which the first kinetic theory appears.

Euler's theory of hydrodynamics is the theory of inviscid, incompressible fluids that we use today. He introduced the vorticity, the stream function, and the Poisson equation that relates them. He knew that internal friction (viscosity) was important, but could not figure out how to model it.

However his theory of gas dynamics was incomplete because he could not find an equation to govern temperature. He knew there had to be another equation, but could not find a foundation upon which to build it.

Back to Gas Laws and Heat

John Dalton developed atomic theory between 1803 and 1810. These atoms of chemistry were not thought of as moving in the way we think of them today. Rather, they were static ingredients the way flour and sugar are ingredients of a cake.

Following work by Amedeo Avogadro in 1811, the (universal) ideal gas law was established. In 1824 Sadi Carnot developed a theory (more laws) that connected gas laws to the mechanical work that an engine could do. This was the next big step in the development of thermodynamics.

In 1807 Joseph Fourier derived a partial differential equation that governs the flow of heat (caloric) in a solid. Moreover, he developed new ways to solve such equations — what we now call the Fourier series and Fourier transform. Because his new techniques were controversial, his paper did not get published until 1822.

Back to Fluids

Fourier's work inspired Claude-Louis Navier to introduce his viscosity term into hydrodynamics in 1823. Siméon Denis Poisson extended this theory to gas dynamics in 1829, however there still was no gas dynamics equation to govern the temperature. Navier's hydrodynamic theory (which he justified with an atomistic argument) was justified with a continuum argument first by Saint-Venant in 1843 and then by Stokes in 1845. The new governing set of equations became known as the Navier-Stokes system.

These new theories of fluids lacked the time reversal symmetry found in Euler's earlier theories, and in Newtonian mechanics of elastic collisions. This was not troubling because fluids (and solids) were thought to be a continuum, not a system of particles governed by elastic collisions.

This continuum picture of physics was at odds with the new atomic picture of chemistry.

Energy Conservation

The 1840's saw experiments (again measurement is crucial) that by 1847 convinced Hermann Helmholtz, James Prescott Joule, and others that the sum of thermal energy and mechanical energy was conserved.

Carnot's theory was reformulated by Benoit Clapeyron, Clausius, Kelvin, Helmholtz, and others to take this insight into account. By the early 1850s they had formulated the *first and second laws of thermodynamics*.

Clausius realized that if the sum of these different energies was conserved then they might be the same thing — namely, heat might be kinetic energy. He embraced kinetic theory about 1850 when he was able to develop a theory of specific heat capacities for gases based on it. However, he did not publish his theory until 1857 because atomic theories were so far out of favor.

Mean Free Path

Indeed, when Clausius did publish his atomic theory, it was criticized. One criticism went as follows. If the air was composed of atoms flying around at great speed then why is it that we do not smell the perfume of a woman who walks into the far side of a room as soon as she walks into the room?

Clausius realized that this had to be because the perfume particles had to collide with those of the air. The average distance an atom travels between collisions he dubbed the *mean-free-path*. In 1858 he published a theory that computed the mean-free-path for a gas of hard balls in terms of the size of the balls. Of course, no one knew either the mean-free-path or the size of the balls, so a test of kinetic theory was still out of reach.

Maxwell 1860

Maxwell read the mean-free-path paper of Clausius. He did not believe the atomic picture of gases was correct, but he did see that the mean-free-path idea could be applied to analyze the rings of Saturn. He published this work in 1859. He then turn his attention to showing the atomic theory of gases is wrong!

Maxwell understood that he could used the mean-free-path to compute the viscosity coefficient of a gas, which could be measured. When his 1860 theory showed that the viscosity coefficient was independent of the gas density, he thought atomic theory was dead. After all, it was well known that this was not the case for liquids. He wrote to Kelvin asking if he knew any definitive experiments for gases. Finding none, Maxwell did his own. To his surprise, the results were consistant with atomic theory. By early 1866 he was converted.

Maxwell 1866

Maxwell completely reworked his theory in 1866. He formulated a kinetic equation, which is formally equivalent to what is now called the Boltzmann equation. Indeed, it was the starting point for Boltzmann's 1872 paper.

From this kinetic equation Maxwell derived a gas dynamics system that (for the first time) included an energy equation governing the temperature. Moreover, he derived formulas for the coefficients of viscosity and thermal conductivity in terms of the microscopic dynamical laws for so-called Maxwell molecules. Euler's gas dynamics system was now complete.

Kirchoff saw Maxwell's paper and in 1868 asserted that the form of the gas dynamics system that Maxwell had derived was universal. He then linearized it and derived the first correct theory of sound.

Particle Descriptions

If the gas is composed of N identical particles (molecules), each of which is described by its momentum p_i and configuration q_i then the dynamics of the gas is governed by the ordinary differential system

$$\frac{dp_i}{dt} = -\partial_{q_i} H_N, \quad \frac{dq_i}{dt} = \partial_{p_i} H_N,$$

where the Hamiltonian $H_N = H_N(p_1, \dots, p_N, q_1, \dots, q_N)$ is the total energy. Given any initial data if we could solve this system exactly then we would know the state of the gas particles at all later times. Because N is extremely large (say 10^{23}), this might be impractical.

Moreover, we generally cannot know initial data exactly, and even if we did we generally cannot solve the system exactly. Because the dynamics of the system is chaotic, all of these errors will be rapidly amplified to the point that our solution has no fidelity.

Fluid Descriptions

Gas dynamics describes the gas in terms of its mass density $\rho(x, t)$, bulk velocity $u(x, t)$, and absolute temperature $\theta(x, t)$. The mass, momentum, and energy of the gas contained within a spatial region Ω at time t are

$$\int_{\Omega} \rho \, dx, \quad \int_{\Omega} \rho u \, dx, \quad \int_{\Omega} \left(\frac{1}{2} \rho |u|^2 + \rho \varepsilon \right) dx,$$

where the specific internal energy $\varepsilon = \varepsilon(\rho, \theta)$ is given by an equation of state. For ideal gases $\varepsilon = \varepsilon(\theta)$ where $\varepsilon'(\theta) \geq \frac{3}{2}$. For polytropic gases $\varepsilon(\theta)$ is linear. The governing system might be

$$\begin{aligned} \partial_t \rho + \nabla_x \cdot (\rho u) &= 0, \\ \partial_t(\rho u) + \nabla_x \cdot (\rho u \otimes u) + \nabla_x p &= 0, \\ \partial_t \left(\frac{1}{2} \rho |u|^2 + \rho \varepsilon \right) + \nabla_x \cdot \left(\frac{1}{2} \rho |u|^2 u + \rho \varepsilon u + p u \right) &= 0, \end{aligned}$$

where the pressure $p = p(\rho, \theta)$ is given by an equation of state. For ideal gases $p = \rho \theta$. This system neglects viscosity and thermal conductivity.

Kinetic Descriptions

To describe a gas composed of identical particles that interact locally by a central potential Maxwell introduced a mass density $F(v, x, t)$ over the velocity-position phase space. The mass of all particles whose velocity-position (v, x) lies within a phase space set A at time t is then

$$\iint_A F \, dv \, dx .$$

The mass, momentum, and internal energy densities of the gas are

$$\rho = \int F \, dv , \quad \rho u = \int v F \, dv , \quad \rho \varepsilon = \int \frac{1}{2} |v - u|^2 F \, dv .$$

The Maxwell kinetic equation for $F(v, x, t)$ is a balance law in the form

$$\partial_t \int \xi F \, dv + \nabla_x \cdot \int v \xi F \, dv = \iiint (\xi' - \xi) F_* F b \, d\omega \, dv_* \, dv ,$$

where $\xi = \xi(v)$ is an arbitrary member of a class of nice test functions. Maxwell used polynomials.

Kinetic descriptions lie in between microscopic and fluid descriptions. For more complicated molecules a kinetic theory might describe the gas by a mass density $F(p, q, t)$ in the momentum-configuration phase space. This represents a conditioned ensemble average of the empirical density

$$\sum_{i=1}^N m \delta(p - p_i) \delta(q - q_i) .$$

The governing equation might have the form

$$\partial_t F + \partial_p H \cdot \partial_q F - \partial_q H \cdot \partial_p F = \mathcal{C}(F) ,$$

where the single molecule Hamiltonian is $H = H(p, q)$ and $\mathcal{C}(F)$ models collisions. The collision operator \mathcal{C} typically respects the fact that mass, momentum, and energy are conserved by collisions. It also typically has the property that $\mathcal{C}(F) = 0$ if and only if F has a restricted form that generalizes the Maxwellian density.

If the center of mass of a molecule in state (p, q) has position $X(q)$ then its velocity will be $V(p, q) = \partial_p H(p, q) \cdot \partial_q X(q)$. Then

$$H(p, q) = \frac{1}{2}m|V(p, q)|^2 + mE(p, q),$$

where $E(p, q)$ is the nontranslational energy per unit mass of the molecule. For example, E can include the molecular rotational and vibrational energy. Then the mass, momentum, and internal energy densities of the gas are

$$\rho = \iint \delta(x - X) F \, dp \, dq, \quad \rho u = \iint \delta(x - X) V F \, dp \, dq,$$

$$\rho \varepsilon = \iint \delta(x - X) \left(\frac{1}{2}|V - u|^2 + E \right) F \, dp \, dq.$$

The pressure is given by

$$p = \iint \delta(x - X) \frac{1}{3}|V - u|^2 F \, dp \, dq.$$

This recovers the universal ideal gas law $p = \rho\theta$ when $\mathcal{C}(F) = 0$.

Boltzmann 1872

Boltzmann reformulated Maxwell's kinetic equation (by neglecting the fact that certain integrals diverge) as

$$\partial_t F + v \cdot \nabla_x F = \iint (F'_* F' - F_* F) b \, d\omega \, dv_* .$$

This piece of formal mathematics enabled him to discover his *H*-Theorem, one aspect of which is that

$$\frac{d}{dt} \iint F \log(F) \, dv \, dx \leq 0 .$$

Boltzmann identified the negative of this quantity with the thermodynamic entropy, which had been named by Clausius in 1865. In 1877 Boltzmann showed that the entropy was related to the number of microscopic states available to the system given that it is described by $F(v, x, t)$. This line of thinking led Boltzmann to lay the foundations of equilibrium statistical mechanics in 1884. Gibbs built upon this foundation in his 1902 book.

What have we seen?

1. Measurable quantities are required for a quantified theory.
2. Experiment and observation are critical.
3. Mathematical theories can connect observed laws.
4. Theories within a hierarchy of description can inform each other.

Hierarchies of quantified theories can also be used to quantify uncertainty. All of these ideas will be revisited in my talk on modeling portfolios with risky assets.

Thank you!