When does the kinetic model spectacularly fail (if ever)?

The simple kinetic models we discussed in class fail when quantum mechanics becomes important, e.g., when the details of how a gas molecule collides with another gas molecule or with molecules in the wall of the container become important.

One case this happens is the one you already thought about in the first homework assignment, when the de Broglie wavelength of the gas molecules becomes comparable to their spacing (some combination of high density and low temperature). A second case arises when the magnitude of the thermal energy $kT$ becomes comparable to or smaller than the separation $\Delta E$ between energy levels of a molecule or energy levels of a surface. (Surfaces often act like isolated quantum systems, with properties different than molecules or solids.) This usually happens at lower temperatures.

Kinetic models can be generalized to include quantum mechanics in which case they can be arbitrarily accurate. But in that case they lose their convenience for providing quick useful insights; one would have to write a complicated computer program and use a powerful computer to study a quantum mechanical kinetic model.

How can the Karo syrup unwind in exactly the same way that it wound up?

A related question was: “How do we mathematically describe the demo about the dye in corn syrup?”

A key reason for the apparent reversibility is that the diffusion constant $D$ for the dye within the Karo syrup is unusually small: a dye molecule is unable to travel far by a random walk because the syrup has long chains of sugar molecules that tangle with one another and so these long molecules can not move easily, trapping the dye molecules to close to their original positions.

As to why one can return to the original ink pattern after “unwinding” the syrup, this is a fairly simple mechanical effect of the fluid: as you turn the handle, you apply a shear stress that smears the thin cylinder of injected ink into an extremely fine concentric spiral sheet of ink that is difficult to
see by eye. As long as the diffusion constant is sufficiently small, this thin spiral of ink does not diffuse away so you can recover the ink by unwinding.

You might enjoy borrowing the mixing apparatus and trying some experiments of your own. For example, how many turns can one make before losing the ink pattern? What if you raise the temperature of the syrup, does ink diffusion increase and the effect goes away? What happens with water or other liquids instead of carp syrup? What happens if you start diluting the cargo syrup partially with water? (I would be glad to give you extra credit if you would like to explore this or pursue other thermal-physics related projects.)

A mathematical description of the syrup as you turn the crank would involve the so-called Navier-Stokes equations of fluid dynamics. These equations lie beyond the range of this course, but I can discuss them with you outside of class.

The helium or $\text{SF}_6$ doesn’t go all the way from the mouth of the person inhaling the gas to your ear. So wouldn’t it have to be the frequency and not the speed of the sound that would have to change in order for the strangeness of the noise to reach your ear?

In your introductory physics course, you hopefully learned that when a wave passes from one medium to another (say light passing from air into water, or sound passing from air into water), the frequency does not change but the wavelength does. The reason is that it is the “shaking” by the incoming wave at the interface that generates the new outgoing wave in the new medium and so the frequency of the new wave must be the same as the previous wave.

So when someone breaths $\text{He}$ gas and speaks in a funny voice, the frequency of the sound waves is always preserved as the sound waves propagate out of the helium into the surrounding denser air or even into surrounding walls.

So understanding the distortion of speech by a gas reduces to understanding what generates the initial sound frequency in the person’s mouth. The argument I gave in class was that you can model (at least roughly) a person’s throat as an organ pipe with a fixed length $L$. That organ pipe then determines the sound wavelengths $(m/n) L$ for integers $n, m \geq 1$, and so the frequency $f = c_s/\lambda = c_s/(mL/n)$ for a given speed of sound $c_s$ in a given gas.

The dependence of sound speed on temperature also explains why musicians in an orchestra who play wind instruments like a clarinet or flute
will try to warm their instrument up to room temperature before playing, otherwise their instruments will be slightly out of tune.

**Do we think of a “relaxation” time for effusion? How long does it take for the 1.0043 equilibrium to be achieved in the hypothetical boxes of U$_{235}^{235}\text{F}_6$?**

If one has a sealed box with a small hole so that gas effuses out through the hole, then there is indeed a relaxation time for effusion. This is discussed in Problem 1.22 on page 14 of Schroeder, which is essentially the same as the “cold plate in a box” problem that you solved in Assignment 2. You can show that the number of molecules $N(t)$ inside the box decays exponentially with time according to the equation

$$\frac{dN}{dt} = -\frac{N}{\tau} \Rightarrow N = N_0 e^{-t/\tau},$$

that is the number of molecules changes substantially over a time scale $\tau$ (the relaxation time) given by

$$\tau = \frac{V}{A} \left( \frac{m}{kT} \right)^{1/2},$$

where $V$ is the volume of the container, $A$ is the area of the hole, $m$ is the mass per molecule, and $T$ is the temperature of the ideal gas. (I have dropped a numerical factor of order 1 whose value is not needed for order-of-magnitude estimates.)

The derivation of effusion that I gave in lecture requires the assumption that the hole through which the gas leaks is tiny, not much bigger than a mean free path and so not much bigger than several hundred nanometers (for air at STP). If a hole is much bigger than a mean free path, separation of isotopes is no longer possible because the air acts now like a well-mixed continuous fluid that just pours out of the hole.

Because effusion is only useful with small holes and it is hard to manufacture a container with a large number of such small holes, it is impractical to sort out nuclear isotopes by effusion. Instead, people use diffusion of gases through a porous material (push the gas at high pressure through a series of ceramic plugs), the little pores in the material act like tiny effusion holes but there are now many of them) or a centrifuge, which sorts molecules radially by mass based on principles we will discuss later in the course. Porous materials and centrifuges are more efficient than effusion (much greater fluxes) but they still turn out to involve the same small enhancement ratio of about
1.004, 235 to 238. So one has to build many successive devices, in which one device enhances the ratio by 1.004 and then feeds its output to the next device, which in steady state adds another factor of 1.004 and so on.

The effusion relaxation time is not the relevant time scale. If you have a box containing a mix of gaseous uranium isotopes, the little beam of molecules effusing out of a tiny hole is already enhanced by the 1.004 factor. So the question is more “how long does it take to fill the next box with the enhanced mixture?” at which point you can open up a hole in the second box and let out a tiny beam of isotopes that is enhanced by the factor 1.004^2. I do not know the engineering details of how this is all carried out.

**How can U^{235} be better enriched? Would one solution be to mix a gas of U^{235} with an even heavier gas to promote greater effusion of U^{235}?”**

That is an intriguing idea to add a third more massive molecule but I don’t think it will work because you would face a new problem, separating the third molecule from the 235 after separating the 235 from the 238.

You can get an overview of different approaches via the Wikipedia article “Isotope separation”. My understanding is that one especially promising approach is to use lasers. A molecule like U^{235}F_6 has slightly different quantum energy levels than the molecule U^{238}F_6. By tuning a laser carefully, it is possible to excite or ionize one isotopic molecule without exciting the other kind, and then one can use electric or magnetic fields to sort the now physically different molecules.

**So what does happen in the example of a movable metal wall with He gas on one side and SF_6 on the other side, when the metal wall is heated up?**

You get to explore this for yourself in the third homework assignment.

**I am a little confused why each degree of freedom, whether it be translational, rotational, or vibrational, all have an average energy of kT/2. Why does every type of degree of freedom relate to equal energies?**

I did not give a proof of this in class and I can not say it is obvious or intuitive.

One might guess that such a result might be possible from our conclusion that \((\langle 1/2mv^2 \rangle) = (3/2)kT\), which we derived using a simple kinetic theory.
It then turns out to be true (as we will see in Section 6.3 of Schroeder) that every quadratic term that appears in the mathematical form of a molecule’s energy leads to a thermal energy of $kT/2$ for an equilibrium system. But the theorem is wrong for non-quadratic energies and such energies are typical in liquids and solids, when atoms are so close to one another that they interact in complicated non-classical way.

**Is $6(K-1)$ the formula for calculating the total number of degrees of freedom for $K$ atoms?**

This formula gives the total number of degrees of freedom (number of quadratic terms in the energy of a molecule consisting of $K$ point atoms) provided that the atoms are not collinear. For a collinear molecule, the formula is $6K - 5$.

**Where does the $3K - 6$ for vibrational motion degrees of freedom come from?**

This is a counting argument based on classical mechanics. A point atom has no spatial extent and so is not able to rotate. This means that a full description of a point atom at rest requires three numbers, the location of its center of mass. (If the atom were moving, we would need to know its location and velocity, six numbers, to get a full description.)

A set of $K$ atoms then requires $3K$ numbers to describe all the details of the atoms (at least classically and again assuming no motion of the atoms). But if the $K$ atoms are linked together by bonds to form a molecule, 3 of the $3K$ numbers can be associated with the location of the molecule’s center of mass, and 3 of the $3K$ numbers can be associated with different axes of rotation (which are all distinct if the molecule is not collinear.) There are therefore $3K - 3 - 3 = 3K - 6$ “internal” degrees of freedom that are not associated with motion or rotation of the entire molecule.

An argument using classical mechanics that I did not give to the class allows one to conclude that the $3K - 6$ internal degrees of freedom are all associated with vibrations. (One linearizes the classical potential $V(x_1, x_2, \ldots)$ about the equilibrium positions of the atoms to obtain a quadratic form.) In Physics 181 and especially in a course on physical chemistry, one learns how to calculate and identify the different vibrational modes of a molecule, and then use these to interpret the infrared spectroscopy of a molecule.
What would be the degrees of freedom of a metal? Of a liquid?

This was discussed in lecture and was discussed in Schroeder. If we can treat the molecules in a metal as point atoms, then there are 6 degrees of freedom per atom since an atom can vibrate in three different directions but not rotate itself.

Liquids are the hardest to understand in terms of the equipartition theorem since the interactions of one molecule with another via quantum mechanics involves complicated non-quadratic energies. It turns out that one can still treat the center of mass motion of liquid molecules as three degrees of freedom but it is usually not possible to identify the other degrees of freedom. You get to explore this issue in the current homework assignment when you answer Problem 1.44 on page 31 of Schroeder.

What is the reason that some of the degrees of freedom of molecules are “frozen out” at lower temperatures?

There was a closely related question: “What elements of quantum mechanics influence \( C_V \)?

We will answer this question thoroughly during the semester when we get to Chapters 6 and 7 of Schroeder. We will see that quantum mechanics gives experimentally correct expressions for the heat capacities of various substances and these expressions become consistent with the equipartition theorem for sufficiently high temperatures. When the temperature is so low that the thermal energy \( kT \) becomes comparable to or smaller than the typical spacing \( \Delta E \) between neighboring quantum levels, the degrees of freedom freeze out in ways that are precisely described by quantum mechanics.

There was some disagreement at high \( T \) for lead and aluminum in the \( C_P \) vs \( T \) graph. What is the cause of this?

Schroeder explains this in the caption to Figure 1.14 on page 30. The discrepancy arises because the plot is of the heat capacity at constant pressure, \( C_P \) and not of the heat capacity at constant volume \( C_V \). There is a small difference between these quantities as derived in Eq. (1.45) of page 29 of Schroeder. The difference \( P(\partial V/\partial T)_P \) is large for gases but small for nearly incompressible materials like solids.
Can you explain a little more why we can ignore the rotation along the axis of a diatomic molecule?

You can find a good discussion of this in the article “Specific heats and the equipartition law in introductory textbooks” by C. Gearhart, American Journal of Physics, Volume 64, pages 995-1000 (1996).

Quantum mechanics predicts that the spacing between energy levels associated with rotation about a certain axis is proportional to $1/I$ where $I$ is the moment of inertia about that axis. For rotation about the axis of symmetry in a diatomic molecule, $I$ is quite small since it arises from electrons which have a mass 2,000 times less than a nucleus. All other moments of inertia, such as rotation about an axis perpendicular to the double bond, involve motions of nuclei and so is at least 2,000 times bigger. When you plug in the values, one finds that a diatomic molecule in principle can be excited to a rotational state about its symmetry axis, but the energy to do so is so great that the molecule would disintegrate before it could start to rotate. Especially at room temperature, it is not possible to excite this rotation mode and so it is safe to say that rotation about the symmetry axis is not possible.

What exactly is a black hole?

It is a massive object whose escape speed is the speed of light so that it is impossible to escape from the black hole.

Our understanding of black holes comes mainly from Einstein’s general theory of relativity, a theory of gravity developed in 1915 and since validated many times by laboratory and astronomical experiments. (You can learn about this beautiful theory and its applications to astronomy and cosmology in Physics 222.) This theory says that space (more precisely, space-time) acts like a medium that can be distorted by the presence of masses, and the motions of masses in turn are modified by the distorted space. In Newton’s language, gravity is a force that pulls one mass toward another mass. In Einstein’s language, one mass distorts the space-time around it and the attraction between masses is the result of another mass moving through the distorted space.

At distances far from the center of the black hole (much further away than the Schwarzschild radius $\sqrt{2GM/c^2}$), the gravity is just as if an ordinary mass was present. Thus if the Sun were instantly replaced by a black hole of the same mass, all orbits of planets and comets would be exactly as before.
Analytical and numerical studies of the Einstein equations that describe space-time in the vicinity of a non-rotating black hole indicate that you should think of a black hole as a completely empty (although highly distorted) region of space except for the center of the hole, where all of the mass is concentrated. The Einstein equations predict that the mass will squeeze down to a single geometric point (called “the singularity”) but that is not possible because of quantum mechanics and since no one yet knows how to reconcile quantum mechanics with general relativity, we don’t understand what is the structure of the black hole’s center. But it will be extremely dense and small.

If you get closer to the center of the black hole than the Schwarzschild radius, you have reached a point of no return because the escape speed is now the speed of light. For a sufficiently large black hole, like the monster at the center of the Milky Way, you would actually survive intact after approaching closer than the Schwarzschild radius, and so you could look around inside the black hole for a while before, inevitably, you are utterly crushed into the tiny dense mass at the center. For a black hole formed by a star (the Schwarzschild radius would be about 3 km, tiny!), you would be torn into small pieces by the enormous gravitational gradients near the black hole, this would happen before you reach the point of no return. Google “spaghettification”.

One of the neatest features of a black hole is that they act as time machines into the future. General relativity predicts that time goes slower in strong gravitational fields. So if you were to travel by rocket from Earth to a black hole, then go into orbit just outside the Schwarzschild radius for say one day of your time, then return to Earth, you would find that millions of years will have passed. This effect has been demonstrated experimentally using high precision clocks and the Earth’s weak gravitational field. The effect is big enough to influence the satellites that provide the signals for which GPS (global positioning service) devices work, and indeed the GPS devices have built into them some formulas from Einstein’s gravity theory so as to take into account the distortion of time by gravity.

You may enjoy looking at some of the videos at the website http://apod.nasa.gov/htmltest/rjn_bht.html especially under the title “Fantasy MPEG movie to a black hole”. You can see how light from stars is bent into orbit around the black hole causing a strange sky, e.g., the same star appears in multiple places in the sky. (The simulations do not include the fact that, near the event horizon, the photons
of remote stars are blue-shifted by gravity to gamma rays and so would not only not be visible but deadly.)

We will talk about the thermodynamics of black holes several times during the semester.

**How is the mass of a black hole determined?**

The same way that the mass of any planet, star, or galaxy is determined astronomically, by following the elliptical orbit of some small-mass “satellite” around the object of interest and by using a generalized form of Kepler’s third law discovered by Isaac Newton, which relates the period $P$ of the orbit to the semi-major axis $a$ of the elliptical orbit in terms of the mass $m$ of the “satellite” and mass $M$ of the “planet” or black hole. If $m \ll M$, the light mass $m$ of the satellite disappears from the equation and then Newton’s formula lets you solve for the mass $M$ of the massive object in terms of the observables $P$ and $a$ of the satellite.

Astronomers have been able to follow the paths of stars orbiting an extremely small (solar-system size) region of space near the center of the Milky Way see this video

[www.youtube.com/watch?v=7vcSKbXnLJA](https://www.youtube.com/watch?v=7vcSKbXnLJA)

and this related image


The stars are moving so rapidly about the unseen object that only an extremely large mass, estimated to be about 4,000,000 times the mass of the Sun via Kepler’s law, could explain their rapid motion. The only known way currently to fit that much mass into a such a small region of space is if there is a black hole.

**Do you know of any good books on black holes and the explanation etc behind them? I want one that isn’t so dense like a physics textbook might be on the subject.**

Many introductory astronomy books have excellent non-technical discussions of what is a black hole and the experimental evidence for black holes and I would recommend looking there first. If you swing by my office, I will be glad to loan one of these books to you, e.g., “The Cosmic Perspective” by Jeffrey Bennett et al.

**What other gases besides xenon interact with the body in unexpected ways?**

Not sure how to answer this question, what do you mean by “unexpected”? There are many gases that have unusual neurobiological or physiological effects on people and animals, for example nitrous oxide in the brain. Xenon is a surprise because it is chemically inert.

**What are some of the engineering challenges of nuclear fusion?**

There was a related question: “How viable is energy generation through the harnessing of a fusion plasma?”

This is too complex a question to discuss here in detail but I would be glad to discuss this in person. There are three difficult goals in fusion: to maintain a time-varying magnetic field that holds a 10-meter-wide 500,000,000 K plasma in place for minutes at a time, to breed new tritium fuel by allowing neutrons created by fusion reactions to strike liquid lithium flowing through the fusion device, and building concrete and steel structures that can withstand the intense blast of neutrons without failing mechanically. The last two steps are barely started, much progress has been made on the first step of magnetic confinement.

It is really difficult to say whether fusion will ever become a competitive energy source. Various people predict that the human race will start running out of oil in about 50 years. Switching to the easiest alternative, coal, would cause a big increase in CO\textsubscript{2} emission and pollutants. There is not enough fission fuel (uranium) worldwide to last more than about 80 years and so far no one sees how to scale up sunlight, wind power, and geothermal enough to replace oil, coal, and nuclear plants. So one hundred years from now, the world may be in such a mess that fusion plasmas may be one of the few long-term attractive solutions.

Note: fusion devices basically use seawater for their fuel (actually the deuterium in the seawater) and the oceans are so big that this corresponds to an energy supply of tens of thousands of years. The main waste product is helium gas which is completely harmless environmentally. So this is a highly attractive technology to pursue. Unfortunately, it is extremely complicated to design and build, mainly because electrical currents flowing in the plasma
generate its own magnetic field that interferes with the magnetic field trying to confine the plasma, causing a “hole” in the magnetic bottle to open up.