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The quantum mechanics of viscosity

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Although a liquid's viscosity depends strongly on temperature and pressure, its minimum value is fixed by fundamental physical constants.

In the 1970s, physicist and Nobel laureate Edward Purcell noticed that no liquid exists with a viscosity much lower than that of water. In the first paragraph of his essay "Life at low Reynolds number," he writes, "Viscosities have a big range *but they stop at the same place*. I don't understand that."

By stopping "at the same place," Purcell meant that liquid viscosities never drop below a certain value. And he says in the first footnote of the essay that Victor Weisskopf had explained the phenomenon to him. To date, however, no one has ever found a published account of the explanation. Even so, Weisskopf published his own essay "About liquids" around the time Purcell published his. That paper starts with a sobering story of the challenges that theoretical physicists face when they try to deduce the states of matter using only quantum mechanics. They can predict the existence of gases and solids, but not liquids.

The upshot is that liquids are difficult—a point hammered home in textbooks. Lev Landau and Evgeny Lifshitz's *Statistical Physics*, for instance, repeatedly asserts that the thermodynamic properties and temperature dependences of a liquid simply cannot be calculated in analytic form applicable to all liquids. The reason is a combination of strong molecular interactions and the absence of small oscillations that simplify the theory of solids. That complication is embodied in the famous "no small parameter" problem: Liquids have neither the weak interactions of a gas nor the small atomic displacements of a solid. Despite the difficulty, we have developed our own theory of liquid thermodynamics, based on excitations in liquids, which is currently undergoing detailed tests.

Viscosity minimum

Meanwhile, we can ask whether theorists understand viscosity well enough to answer Purcell's question of why all viscosities stop at the same place. Viscosity η denotes a liquid's resistance to a shear force and governs important properties such as diffusion and dissipation. In a dilute gas-like fluid, η is set by molecules moving at distances up to the mean free path L and transferring momentum during collisions: Specifically, $\eta = \rho v L / 3$, where ρ and v are the density and average velocity of molecules, respectively.

That equation predicts that the viscosity of a gas increases with temperature, because molecular velocity increases with temperature. That prediction is counterintuitive because fluids usually thin when they are heated. Unlike gases, dense liquids

have a viscosity set by their molecules vibrating around quasi-equilibrium positions before jumping to neighboring sites. The frequency of those jumps increases with temperature, and viscosity consequently decreases with temperature: $\eta = \eta_0 \exp(U/k_B T)$, where U is the activation energy.

The increase of viscosity at high temperature and its decrease at low temperature imply that it has a minimum. That minimum arises from the crossover between two different viscosity regimes: a gas-like regime, where the kinetic energy of higher-temperature particles provides a larger momentum transfer, and hence larger η , and a liquid-like regime, where lower temperature decreases the frequency of site-jumping particles and slows down the liquid flow, also resulting in larger η .

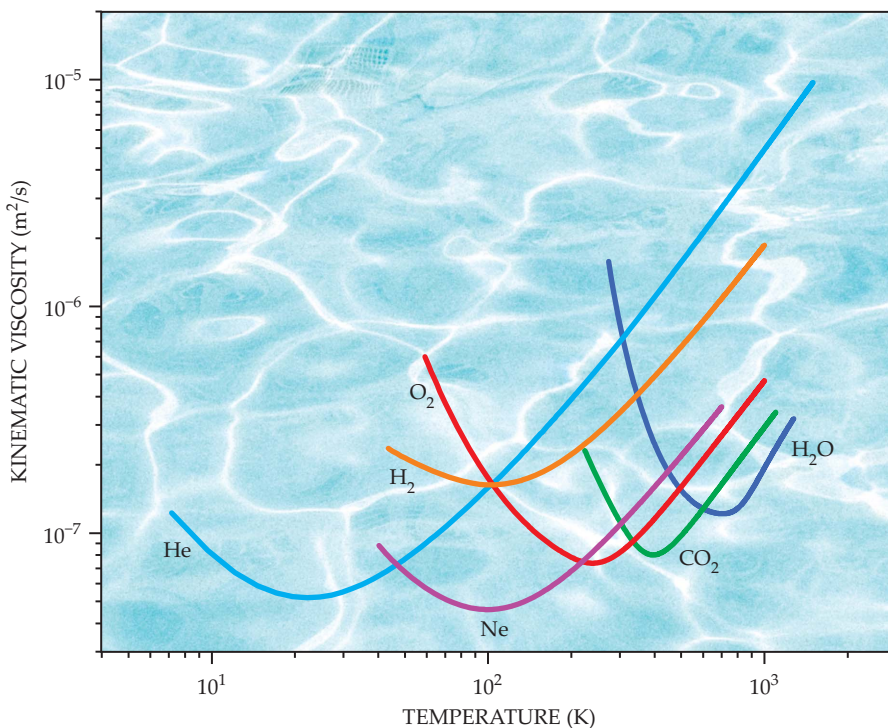
It is convenient to look at that crossover above the critical point where it is smooth and no liquid-gas phase transition intervenes. Think in terms of kinematic viscosity $\nu = \eta/\rho$, which describes the properties of liquid flow. The figure on page 67 shows experimental values of several supercritical fluids. Kinematic viscosities clearly have minima, and one can understand them as the crossover states between gas-like and liquid-like behavior.

The viscosity minima provide the first clue to the Purcell question: Viscosities stop decreasing, of course, when they hit their minima. But can each minimum itself get arbitrarily close to zero? (Note that we do not discuss superfluidity in this Quick Study.) Why are the minima of η hard to move up or down and somehow close to the viscosity of water at ambient conditions?

Scientists could answer that question if they could calculate the viscosity at its minimum. But that's complicated, as Landau and Lifshitz discuss in their book. Molecular interactions are strong and system specific. Calculating viscosity parameters even in simple liquids is difficult using only theory and no input from modeling. And for molecular liquids, such as water, it's nearly impossible.

A revealing approximation

Fortunately, the minimum of viscosity at the crossover is a special point where viscosity can, in fact, be evaluated, if only approximately. The minimum values ν_{\min} are related to just two basic properties of a condensed-matter system $\nu_{\min} = \omega_D a^2 / 2\pi$, where a is the interatomic separation and ω_D is the system's Debye frequency. The two parameters can, in turn, be related to the radius of the hydrogen atom and a characteristic



EXPERIMENTAL KINEMATIC VISCOSITIES

of noble and molecular liquids. Each one exhibits a minimum. Viscosities of helium, hydrogen, oxygen, neon, carbon dioxide, and water are plotted at 20 MPa, 50 MPa, 30 MPa, 50 MPa, 30 MPa, and 100 MPa, respectively. (Source: NIST, <https://webbook.nist.gov/chemistry/fluid/>)

The fundamental physical constants \hbar , m_e , and m_p are of general importance. Together with the electron charge and speed of light, they form dimensionless constants that determine whether the universe is biofriendly. That's because they affect the formation of stars and the synthesis of heavier elements, including carbon, oxygen, and so on, which can then form molecular structures essential to life.

Fundamental constants and water

The fundamental constants are friendly to life at a higher level too: Biological processes, such as what happens in cells,

bonding strength set by the Rydberg energy. Then ν_{\min} becomes

$$\nu_{\min} = \frac{1}{4\pi} \frac{\hbar}{\sqrt{m_e m}}, \quad (1)$$

where m_e is the mass of an electron and m is the mass of the molecule.

Two fundamental constants \hbar and m_e appear in that equation. The minimal viscosity turns out to be quantum! That may seem surprising and at odds with our concept of high-temperature liquids as classical systems. But equation 1 reminds us that the nature of interactions in condensed matter is quantum mechanical, with \hbar affecting both the Bohr radius and Rydberg energy.

The fundamental constants help keep ν_{\min} from moving up or down much. And because ν_{\min} is inversely proportional to the square root of the molecule's mass, the viscosities themselves are not universal—although that does not change ν_{\min} much. For different liquids, such as those plotted in the figure, equation 1 predicts that ν_{\min} should fall in the range $(0.3\text{--}1.5) \times 10^{-7} \text{ m}^2/\text{s}$. That range is reassuringly close to experimental values.

Therefore, the answer to the Purcell question is that viscosities stop decreasing because they have minima, and those minima are fixed by fundamental constants. Interestingly, the same happens to an unrelated liquid property, thermal diffusivity, which governs how well liquids transfer heat. That variable also exhibits minima given by equation 1. It does so because thermal diffusivity depends on the same two parameters as ν_{\min} , a and ω_D .

As shown in equation 2, when m is set equal to the proton mass m_p , equation 1 gives rise to a universal quantity ν_f , the fundamental kinematic viscosity:

$$\nu_f = \frac{1}{4\pi} \frac{\hbar}{\sqrt{m_e m_p}} \approx 10^{-7} \text{ m}^2/\text{s}. \quad (2)$$

rely heavily on water. Were Planck's constant to take on a different value, for instance, water viscosity would change too—both its kinematic viscosity ν , which is relevant to water flow, and its dynamic viscosity η , which sets internal friction and diffusion. If the viscosity minimum were to increase because of a higher value of \hbar , for instance, water would become more viscous, and biological processes would not be the same. Life might not exist in its current form or even at all.

One might hope that cells could still survive in such a universe by finding a hotter place where overly viscous water becomes thinned. That would not help, though. Planck's constant sets the minimum below which viscosity cannot fall, regardless of temperature. Water and life are indeed well attuned to the degree of quantumness of the physical world.

One can hope that Purcell would have been happy with the answer to his question. Unless he already heard it from Weisskopf in the 1970s.

Additional resources

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