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What separates a liquid from a gas?

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Standard ways to distinguish between the two phases don't apply at high pressure and high temperature. But a look at a medium's microscopic behavior makes it possible to discriminate between liquid and gas everywhere on a phase diagram.

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Along with solids, liquids and gases are the most common aggregate states of matter. It doesn't take a physicist to distinguish among them and, in particular, to tell the difference between a liquid and a gas; it's enough to point to partially filled and empty glasses such as those shown in figure 1. And yet an attempt to introduce a rigorous physical distinction between the two phases raises subtle issues. In this Quick Study we discuss some of those issues and describe the microscopic behavior that determines whether a substance is in the liquid or gaseous state.

At first glance, it seems that numerous quantitative distinctions separate gases from liquids. To name just two, gas densities and viscosities are many times smaller than those of liquids. Those and other distinctions, however, depend strongly on temperature and pressure, and the quantitative distinctions cease to hold near the critical point, the abrupt terminus of the line separating liquid and gas. Indeed, as illustrated in figure 2a, the system can be continuously changed from liquid to gas along a phase-space path that goes around the critical point, but quantitative properties would not reveal just where the change from one phase to the other takes place. For that reason textbooks may report that distinguishing between liquid and gas beyond the critical point is impossible. We propose that it is possible, but the distinction must be based on qualitative grounds.

Useful but not rigorous distinctions

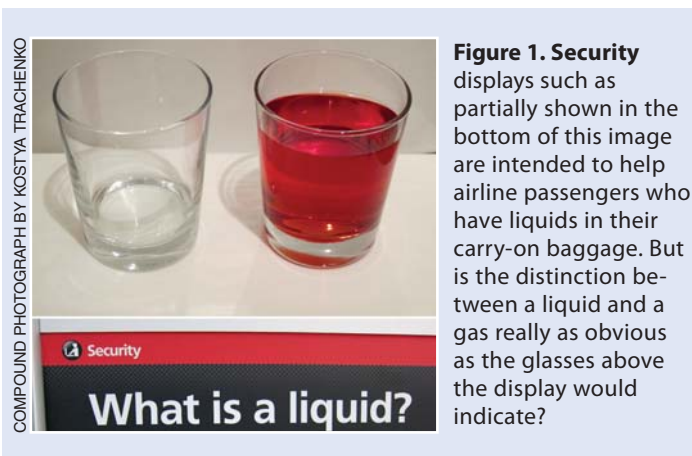
Two discussions, often found in textbooks, of what distinguishes a liquid from a gas do point to legitimate differences. But neither provides insight as to how the system changes from liquid to gas as it is brought along a phase-diagram path that goes around the critical point. Moreover, we have general objections to both approaches.

One description is that a gas fills all the volume

available to it but a liquid doesn't. Our main objection to that formulation is that it is inherently macroscopic. A proper distinction, in our view, should appeal to microscopic properties of the medium. Indeed, you can't even ask whether water or another liquid will fill an available volume unless *external* parameters—the temperature and pressure—are also specified.

A second feature often cited is that in the liquid phase, particles attract, or cohere. That distinction does point to internal properties of a medium. And indeed, it's not difficult to do convincing experiments showing that when water is at atmospheric pressure and room temperature, its molecules attract. In reality, though, the notion of cohesion is not straightforward. To rigorously establish that the particles in a system are attracting, it is necessary to remove all external forces and demonstrate that at zero pressure the system will have a finite volume. (Noninteracting ideal gases, of course, expand indefinitely as the pressure is brought to zero.) But that's a program that often can't be carried out, even in principle. When you reduce the pressure on a liquid, the system eventually crosses the liquid-gas phase transition line. With great care, however, you can maintain the system in a metastable state even while crossing that line. The shaded region in figure 2b shows the portion of phase space in which such metastable states can exist. A part of the shaded region extends to zero pressure, and so, in some cases, one can rigorously check that system particles do attract. Note, though, that a section of the region is bounded at nonzero pressure by a so-called spinodal curve. Lowering pressure and crossing the spinodal will vaporize the metastable system.

In brief, textbook descriptions often provide useful ways to distinguish between liquid and gas. But we seek a distinction that is microscopic, can be applied at any pressure and temperature, is implementable in practice, and illuminates what happens to a system as it transits from liquid to gas via excursions around the critical point. Perhaps ironically, our program for distinguishing between the two follows other



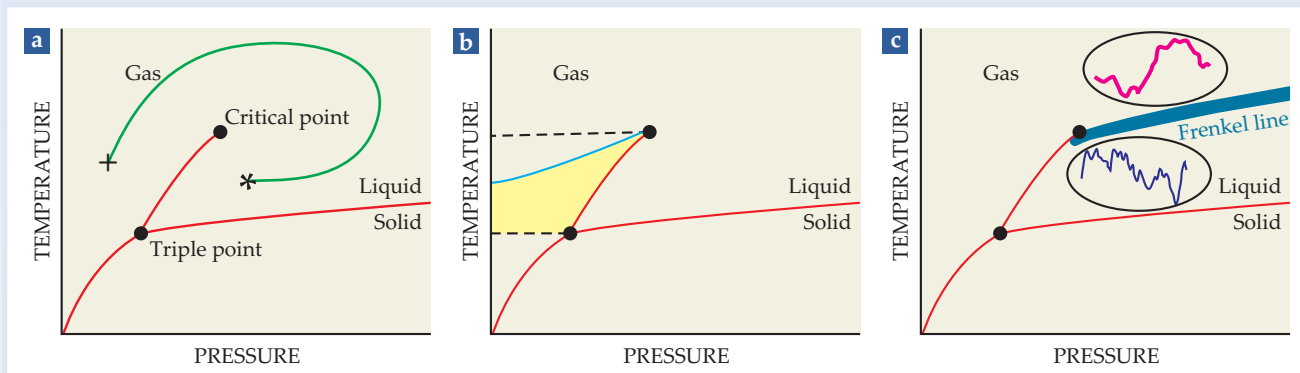


Figure 2. Phase diagrams relate states of matter to temperature and pressure. **(a)** The line of equilibrium between a liquid and a gas starts from the triple point and ends at the critical point. If a phase-space excursion from the state indicated by the star to the state indicated by the plus crosses that line, then the system will undergo a phase transition. But for excursions around the critical point such as the green curve, you'd be hard pressed to say where the system changes from liquid to gas. **(b)** A liquid can exist in a metastable state for the portion of the phase-space diagram shaded in yellow. The bounding turquoise curve is called a spinodal. **(c)** The Frenkel line separates systems with liquid-like and gas-like properties. The two inset plots show particle position as a function of time. The particle motion in the liquid below the line combines both small-amplitude vibrational motion as in a solid and large-amplitude, ballistic-collisional motion as in a gas. As illustrated above the Frenkel line, particle motion in a gas is purely ballistic-collisional.

experimental and theoretical work focused on the region of the phase diagram beyond the critical point—the very region where conventional wisdom held that the phases could not be meaningfully distinguished.

The Frenkel line

The earlier studies explored the idea that the distinction between liquid and gas could be extended past the critical point by extrapolating the line specifying the maxima of second derivatives of thermodynamic potentials such as heat capacity. In doing so, they posed intriguing questions about how far beyond the critical point the extrapolation can be made and how well it works overall.

In our approach, we zero in on the qualitative difference between the atomic trajectories in gases and liquids. Gas particles move in almost straight lines until they collide with other particles or container walls and change course. In liquids, atomic motion has two components: a solid-like, quasi-harmonic vibrational motion about equilibrium locations and diffusive jumps between neighboring equilibrium positions. As the temperature increases or the pressure decreases, a particle spends less time vibrating and more time diffusing. Eventually, the solid-like oscillating component of motion disappears; all that remains is the ballistic-collisional motion. That disappearance, a qualitative change in particle dynamics, corresponds to the transition of the substance from the liquid to the gas.

In truth, identifying a one-dimensional line on the phase diagram where the change from liquid to gas occurs is not quite possible; rather, the qualitative change occurs over a narrow band that we call the Frenkel line, after Yakov Frenkel, author of the 1946 monograph *Kinetic Theory of Liquids*. The Frenkel line is illustrated in figure 2c. It exists at arbitrarily high pressure and temperature and, moreover, is present even in systems in which the liquid-gas transition and the critical point are absent altogether.

When a system is brought across the Frenkel line, many of its key properties are altered. But those changes lack the sharp, thermodynamically anomalous character of the changes in a system traversing the liquid-gas phase transition line. Consider, for example, the ability of liquids to flow, which is associated with their zero shear rigidity and distinguishes liquids from

solids. Liquids, however, actually have zero rigidity only at small frequency; if a shear stress is applied at high enough frequency, a liquid will support that stress. But above the Frenkel line, the system simply cannot sustain rigidity at any frequency—it behaves like a gas. The loss of rigidity is accompanied by a reduction of the constant-volume specific heat to $2k_B$ per particle (k_B is Boltzmann's constant); that reduction corresponds to the potential energy of shear modes becoming zero.

Furthermore, viscosity, the speed of sound, and thermal conductivity all decrease with increasing temperature below the Frenkel line, as in liquids, but increase with temperature sufficiently above the line, as in gases. The behavior of the diffusion constant crosses over from exponential temperature dependence below the Frenkel line, as in liquids, to power-law dependence above the line, as in gases. And crossing the Frenkel line also results in the disappearance of so-called high-frequency fast sound and roton minima, both characteristic features of liquids.

Considerations of particle dynamics do more than help distinguish liquids from gases. They also shed light on why liquids are so difficult to describe theoretically. The dynamics suggest that solids and gases are pure states of matter in the sense that dynamics in solids are purely oscillatory and dynamics in gases are purely ballistic and collisional. Physically, the different behaviors arise because in solids the kinetic energy of particles is much smaller than the energy barriers between various potential minima and in gases it is the other way around. The dynamics of a liquid, on the other hand, involves both oscillations and ballistic motions, and the relative contributions of the two types of motion gradually change in response to external parameters. To a large degree, it is this mixed dynamical state that has been responsible for the difficulty in constructing a theory of liquids.

Additional resources

- ▶ J.-L. Barrat, J.-P. Hansen, *Basic Concepts for Simple and Complex Liquids*, Cambridge U. Press, New York (2003).
- ▶ G. G. Simeoni et al., "The Widom line as the crossover between liquid-like and gas-like behaviour in supercritical fluids," *Nat. Phys.* **6**, 503 (2010).
- ▶ V. V. Brazhkin et al., "Two liquid states of matter: A dynamic line on a phase diagram," *Phys. Rev. E* **85**, 031203 (2012).