A Simple Model that Predicts the Liquid-Vapor Phase Transition

Randy S

Abstract   When water is heated, it undergoes a sudden transition from liquid to vapor at a specific temperature. Why does this happen? Two water molecules tend to attract each other when they are close enough to each other, but there is a limit to how close they can get because each water molecule has a non-zero volume (roughly speaking). This article uses these two simple inputs to deduce the existence of a liquid/vapor phase transition, which is characterized by a sudden change in density when the temperature reaches a special value.

Contents

1

1   Introduction

A fluid (either liquid or vapor) can be loosely defined as a substance that assumes the shape of its container. If it settles to the bottom of the container, we call it a liquid. If it expands to fill the container, we call it a vapor (or gas).

Those differences between liquid and vapor phases are mainly a consequence of their different densities: under ordinary conditions, liquid water is $\sim 10^5$ times more dense than water vapor. The higher-density phase (liquid) is approximately incompressible because the molecules are already packed relatively close together. The lower-density phase (vapor) is very compressible because the molecules are relatively far away from each other. That's why the density of the atmosphere decreases gradually with increasing altitude, whereas the density of the ocean changes relatively little from the bottom to the surface.

The boiling phenomenon is a sudden transition from liquid to vapor at a specific temperature.[1] The fact that this occurs so suddenly is part of why we tend to think of liquid and vapor as distinct phases. However, when the pressure is high enough, the sudden transition disappears (section 16): the density changes smoothly as a function of temperature, with no liquid/vapor transition at any temperature.[2,3]

These observations suggest that the essence of the liquid/vapor phase transition is the sudden change in density when a particular temperature is crossed, so if we can reproduce this phenomenon using a simple model, then we can use that simple model to understand the essence of why liquids boil. Many different real fluids exhibit a liquid/vapor phase transition, so the existence of such a phase transition must be relatively insensitive to most of the microscopic details.[4] That gives us hope that we might be able to reproduce this phenomenon using a simple model, and this article shows that we really can.

---

[1]The opposite transition, from vapor to liquid, is called condensation.

[2]To learn more about this, the keywords are **critical point**, in the context of thermodynamics.

[3]Transitions to other phases, like solid and plasma phases, are not considered in this article.

[4]Different fluids boil at different temperatures, so the *quantitative* properties of the boiling phenomena apparently *do* depend on specific molecular properties; but our goal here is only to understand the general reason for the phase transition, not the quantitative details for any specific substance.

2   Simplifications

The real boiling phenomenon involves several complications, most of which are not essential for understanding why the phase transition must occur. The goal in this article is to explain why the phase transition must occur, without any inessential complications.

One complication is that real boiling occurs inhomogeneously, through the formation of bubbles. The model used here assumes that any changes in density, including any sudden changes, occur evenly throughout the whole fluid.

Another complication comes from allowing the vapor from the boiling fluid to mix with the ambient air. To eliminate this complication, this article uses a model with an impermeable but movable partition separating the fluid of interest from the ambient air. The fluid of interest, which I'll just called the **fluid**, is on one side of the partition. On the other side of the partition is an ideal gas, which I'll call **air**. The whole system will be in a closed container, as depicted here:
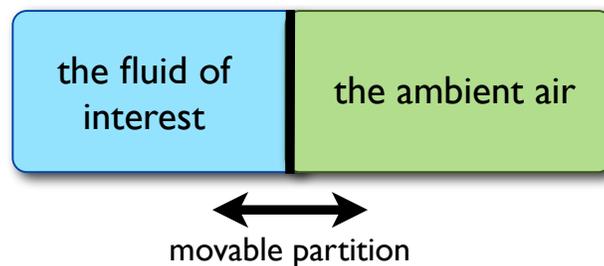
Another complication is the tendency of the liquid to settle to the bottom of its container. In this article, gravity is neglected, so there is no "bottom." When the fluid is in its liquid phase, the pressure exerted by the air keeps the partition pressed firmly against the liquid, with no empty space. When the fluid boils, the pressure exerted by the resulting vapor pushes the partition back, compressing the air on the other side until a new equilibrium position is reached. Again, the key difference between the liquid and vapor phases is their difference in density: the fluid occupies a larger volume when in the vapor phase than it does when in the liquid phase.

3 Preview

A cupfull of water contains an enormous number of molecules. Tracking the motion of all of these molecules is not feasible, but the enormity of the number of molecules allows us to use **statistical mechanics** (article 66313), which is much easier. This article uses statistical mechanics to explain why the liquid/vapor phase transition occurs, using a simple model for the fluid and an even simpler model for the air. Specifically:

- For the fluid, this article uses a **van der Waals fluid**. In this model, each molecule of the fluid tends to attract its neighbors, up to a limit at which the neighbors are not allowed to come any closer. In other words, each molecule likes company, as long as that company doesn't get into its personal space.

- For the air, this article uses the **ideal gas** model. This means that each air molecule will be oblivious to its neighbors, neither attracting them nor excluding them from its personal space.

The liquid/vapor phase transition occurs in the fluid, with the air serving as a reservoir that can exchange energy and volume (but not molecules) with the fluid.

A state of the combined system, specified in complete microscopic detail, is called a **microstate**. The combined system has a fixed total volume, and we will consider what happens when we smoothly change its total energy. For any given total energy, we can count the number $\Omega(\nu)$ of microstates that are consistent with any given value ν of the fluid's volume – that is, with any given position of the partition. Some values of ν account for a larger number of microstates than others. For most combinations of the total volume and total energy, the overwhelming majority of the microstates are all concentrated near one value of ν. The graph of the $\Omega(\nu)$ then has a single peak at this one value of ν, and this peak is very narrow and much taller than the rest of the graph. Statistical mechanics then predicts that the partition remains at that one position, as long as we don't change the system's total energy or total vlume.

However, for certain combinations of the total energy and total volume, the graph of $\Omega(\nu)$ has *two* very narrow peaks of equal height. By smoothly varying the total energy, we can change which of these two peaks is the highest one. Because of the enormity of the numbers involved, a very slight change in the total energy is enough to change which one of these two peaks is overwhelmingly higher than the other. Statistical mechanics then predicts that the observed value of ν will jump from one of these values to the other. This sudden change in volume – which entails a sudden change in density – is the essence of the liquid/vapor phase transition. This article doesn't try to reproduce the details of the boiling or condensation *processes*, like bubble formation or droplet formation, but it does explain why a sudden change in density must occur.

In practice, we normally control the combined system's temperature instead of its total energy, but the conclusion is the same: for a special value of the temperature, $\Omega(\nu)$ is concentrated in two peaks of equal height, and the slightest deviation from this special temperature makes one of the two values of ν overwhelmingly more likely than the other. This is why liquids boil.

4   The ideal gas

Article 66313 introduced the basic idea of statistical mechanics, which derives a system's thermodynamic properties from a knowledge of the entropy $S(E,V) \propto \log \Omega(E,V)$, where $\Omega(E,V)$ the number of mutually orthogonal states of the system with total energy $\leq E$ and volume V. (The dependence of Ω on other macroscopic parameters can also be considered, but this article focuses on E and V.)

For an **ideal gas**, the function $\Omega(E,V)$ is[5] (article 23206)

$$\Omega(E,V) \propto E^{ND/2}V^N, \tag{1}$$

where N is the number of molecules, and D is the number of dimensions of space (normally $D = 3$). This is what we'll use for the air on one side of the partition.

If the fluid on the other side of the partition were also an ideal gas, then no phase transition would occur. To get a phase transition, we need to consider a slightly more realistic model. We can still treat the air as an ideal gas, but we'll use something different for the fluid, as described in the next section.

---

[5]The proportionality factor depends on N but not on E or V.

5   The van der Waals fluid

For the fluid, we'll use

$$\Omega(E, V) \propto \left(E + \frac{aN^2}{V} \right)^{DN/2} \cdot (V - bN)^N, \tag{2}$$

where a, b are constants characterizing the fluid. Equation (1) is the special case $a = b = 0$. More generally, equation (2) describes a **van der Waals fluid**. This (slightly) more realistic than equation (1), in two respects:

- The parameter $b > 0$ accounts for volume of each molecule's "personal space," inside which other molecules are not permitted.

- The parameter $a > 0$ accounts for an attractive interaction between molecules that are outside each other's personal space. The factor of V in the denominator accounts for the attraction being stronger when the molecules are closer together.

Section 6 describes this intuition in more detail. Empirically, in cases where (2) is a good approximation, the constant b is roughly the volume of one molecule (a few angstroms in diameter), and a typical value of the constant a is[6]

$$a \sim b \times (100 \text{ Kelvin}).$$

The variables E, V are subject to the constraints

$$E + \frac{aN^2}{V} > 0 \qquad\qquad V - bN > 0,$$

so that both factors on the right-hand side of (2) are positive for all N, D.

---

[6]Page 178 in Reif (1965).

6   Intuition behind equation (2)

The ideal gas model ignores interactions between molecules, so the total energy E is the same as the total kinetic energy K. The derivation in article 23206 actually showed that

$$\Omega(E,V) \propto K^{ND/2}V^N, \tag{3}$$

where K is the total *kinetic* energy, independently of any assumptions about the relationship between E and K. The factor V^N comes from the idea that each of the N molecules can occupy any location in the volume V. In reality, a molecule has a finite size; each molecule takes up some space, making this space unavailable to the other molecules. This reduces the number of ways that the molecules can be distributed, so the factor V^N is an overestimate. To make the model a little more realistic, we can replace the factor V^N with $(V - bN)^N$, where b is a positive constant. The constant b may be roughly interpreted as the volume that is used up by an individual molecule, so that the $V - bN$ represents the remaining space. After this replacement, equation (3) becomes

$$\Omega(E,V) \propto K^{DN/2} \cdot (V - bN)^N. \tag{4}$$

Now assume some kind of attractive force between molecules. To be specific, suppose that the average energy per molecule is related to the average kinetic energy per molecule like this:

$$\frac{E}{N} = \frac{K}{N} - \frac{a}{V/N}, \tag{5}$$

where a is some positive constant. The term inversely proportional to V/N, the average volume per molecule, says that the energy decreases when the molecules come closer together. This is the hallmark of an attractive force. Using equation (5) in (4) gives the result (2).

7   The van der Waals equation of state

Equation (2) gives this expression for the entropy:[7]

$$S(E, V) \equiv \log \Omega(E, V)$$
$$= \text{constant} + \frac{ND}{2} \log \left(E + \frac{aN^2}{V} \right) + N \log(V - bN). \qquad (6)$$

In statistical mechanics, temperature T and pressure p are defined by (article 66313)

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} \qquad\qquad \frac{p}{T} \equiv \frac{\partial S}{\partial V}. \qquad (7)$$

Use equation (6) in the definitions (7) to get

$$\frac{p}{T} = \frac{N}{V - bN} - \frac{a}{(V/N)^2} \frac{1}{T},$$

which can be rearranged to get

$$\left(p + \frac{a}{v^2} \right) (v - b) = T \qquad (8)$$

where $v \equiv V/N$ is the average volume per molecule. This is called the **van der Waals equation of state**, which is why I'm using the name "van der Waals" for the model defined by (6).

     By the way, equations (5), (6), and (7) imply $T = (2/D)K/N$, so the temprature is proportional to the average kinetic energy per molecule.

---

[7]I'm using units in which Boltzmann's constant equals 1.

8   The combined system

Now the model that was previewed in sections 2-3 will be described mathematically, using the ingredients introduced in sections 4-5. Notation:

	combined	fluid	air
energy	E	ϵ	$E - \epsilon$
volume	V	ν	$V - \nu$
number of molecules	N	n	$N - n$

For given values of $E, V, \epsilon\,\nu$, the number of microstates of the combined system is

$$\Omega(E, V, \epsilon, \nu) = \Omega_{\text{fluid}}(\epsilon, \nu)\,\Omega_{\text{air}}(E - \epsilon,\, V - \nu), \tag{9}$$

where the functions on the right-hand side are defined by

$$\Omega_{\text{fluid}}(\epsilon, \nu) \propto \left(\epsilon + \frac{an^2}{\nu} \right)^{Dn/2} \cdot (\nu - bn)^n \tag{10}$$

$$\Omega_{\text{air}}(E - \epsilon, V - \nu) \propto (E - \epsilon)^{D(N-n)/2}(V - \nu)^{N-n}. \tag{11}$$

Equation (10) is the van der Waals model (2), and equation (11) is the ideal gas model (1). The allowed ranges of ϵ and ν are

$$bn < \nu < V \qquad\qquad -an^2/\nu < \epsilon < E, \tag{12}$$

so all of the factors on the right-hand sides of (10)-(11) are positive.

For each allowed combination of V and E, we want to determine the values of ϵ and ν that maximize the number (9) of microstates. As previewed in section 3, we can use this information to explain why liquids boil, using the principles of statistical mechanics that were introduced in article 66313.

9   How the model will be used

The total energy E and total volume V are prescribed by an external agent, but ϵ and ν are free to vary on their own. The partition prevents the two subsystems (fluid and air) from exchanging molecules with each other, but it allows them to exchange energy with each other, and it is freely movable so that they can also exchange volume with each other. For given values of E and V, equation (9) counts the number of microstates as a function of ϵ and ν. The calculations in the following sections lead to these results:

- For most values of E and V, the overwhelming majority of the microstates are concentrated very close to a single point in the ϵ-ν plane, so the graph of this function of ϵ, ν has a very narrow peak that is much higher than the rest of the surface.

- For some values of V, a special value of E exists for which the surface has *two* narrow peaks of equal height, at two different points in the ϵ-ν plane.

- Slightly above or below that special value of E, one of these two peaks is *much* taller than the other. Below that special value of E, the smaller-ν peak dominates. Above that special value of E, the larger-ν peak dominates. The shape of the surface (9) changes smoothly as E is increased, but the honor of being the high*est* peak jumps discontinuously from one to the other.

Statistical mechanics then predicts a sudden change in the observed values of ν and ϵ. The sudden change in volume ν implies a sudden change in the fluid's density, which is the essence of the boiling phenomenon.[8,9]

---

[8]The corresponding change in ϵ is related to something called the **latent heat of vaporization**.

[9]In this model, the density of the air also changes, because the system's total volume is fixed. However, the change in the air's density is negligible when $N - n \ggg n$, which is an appropriate condition to consider. (Think of a small pot of boiling water in contact with a much larger atmosphere.)

10   Finding the peaks

We want to find the points in the ϵ-ν plane that maximize the quantity (9), which is the same as maximizing the log of (9). At such a point, the partial derivatives must be zero:

$$\frac{\partial}{\partial \epsilon} \log \Omega(E, V, \epsilon, \nu) = 0 \qquad \frac{\partial}{\partial \nu} \log \Omega(E, V, \epsilon, \nu) = 0. \tag{13}$$

We can solve equations (13) using a two-step process:

- First solve the first equation for ϵ, which gives ϵ as a function of ν. This defines a curve C in the ϵ-ν plane, and the maxima of Ω are on this curve.

- Next, substitute this expression for ϵ back into (9) to get the number of microstates along the curve C, parameterized by ν. Finding the maxima of this function of ν gives us the maxima of the original function Ω.

The first of equations (13) gives

$$\frac{n}{\epsilon + an^2/\nu} = \frac{N - n}{E - \epsilon}, \tag{14}$$

which can be rearranged to get[10]

$$\epsilon + \frac{an^2}{\nu} = \frac{n}{N} \left(E + \frac{an^2}{\nu} \right). \tag{15}$$

This defines a curve C in the ϵ-ν plane. Use equations (14) and (15) in (9) to get this expression for the height of the surface (9) along the curve C:

$$\Omega_C(\nu) \propto \left(\nu - bn \right)^n \left(V - \nu \right)^{N-n} \left(E + \frac{an^2}{\nu} \right)^{ND/2}. \tag{16}$$

The proportionality factor depends on N, n but not on E, V, ϵ, ν. The next step is to find the maxima of this function.

---

[10]This shows that any value of ϵ that satisfies (13) is automatically in the allowed range (12).

Use the abbreviations

$$r \equiv n/N \qquad\qquad \alpha \equiv EV/(an^2)$$
$$\delta \equiv D/2 \qquad\qquad \beta \equiv bn/V \qquad\qquad (17)$$

The function (16) may be written as

$$\Omega_C(\nu) \propto \Big(\omega(\nu/V) \Big)^N$$

with a proportionality factor that depends on V but not on E, and

$$\omega(u) \equiv \Big(u - \beta \Big)^r \Big(1 - u \Big)^{1-r} \left(\alpha + \frac{1}{u} \right)^\delta . \qquad (18)$$

We want to find the maxima of this function $\omega(u)$, which is equivalent to finding the maxima of $\log \omega(u)$. At a maximum, the derivative must be zero. Equation (18) gives this expression for the derivative:

$$\frac{d}{du} \log \omega = \frac{r}{u - \beta} - \frac{1 - r}{1 - u} - \frac{\delta}{\alpha u^2 + u}. \qquad (19)$$

All three denominators are positive (recall the inequalities (12)), so requiring (19) to be zero leads to a cubic equation for $u \equiv \nu/V$:

$$\alpha u^3 = c_2 u^2 - c_1 u + \beta \delta \qquad\qquad \beta < u < 1 \qquad (20)$$

with

$$c_2 = (\delta - 1) + \big(r + (1 - r)\beta \big)\alpha$$
$$c_1 = (\delta - r) - (\delta + 1 - r)\beta.$$

Equation (20) can be solved explicitly, but that's messy. The next section describes a more intuitive way of analyzing equation (20).

14

11   Graphic solution

Define a new independent variable x by

$$u = \frac{c_2}{\alpha}x,$$

and substitute this into (20). Move the quadratic term to the left-hand side and divide by the coefficient of the x^3 term to get

$$x^3 - x^2 = A(B - x) \tag{21}$$

with

$$A \equiv \frac{\alpha c_1}{c_2^2} \qquad B \equiv \frac{\alpha\beta\delta}{c_1 c_2}.$$

We want to know when equation (21) has three distinct real-valued solutions, which corresponds to (16) having two distinct peaks (with a local minimum between the two peaks). We can study this by graphing both sides of equation (21) on the same axes. Values of x where the two graphs intersect each other are values of x that satisfy equation (21). Figure 1 shows an example for which equation (21) has three solutions.

For what values of A and B does equation (21) have three real solutions? Here are a few simple observations:

- If $B = 0$ and $0 < A < 1/4$, then it has three real solutions.

- If $B = 0$ and $A > 1/4$, then it cannot have three real solutions.

- If $AB > 1/27$, then it cannot have three real solutions.

- For any given value of AB with $0 < AB < 1/27$, positive values of A exist for which it has three real solutions.

The next section sketches proofs of these statements. Beware that even if three real solutions of (21) exist, they might not all be in the range allowed by $\beta < u < 1$.
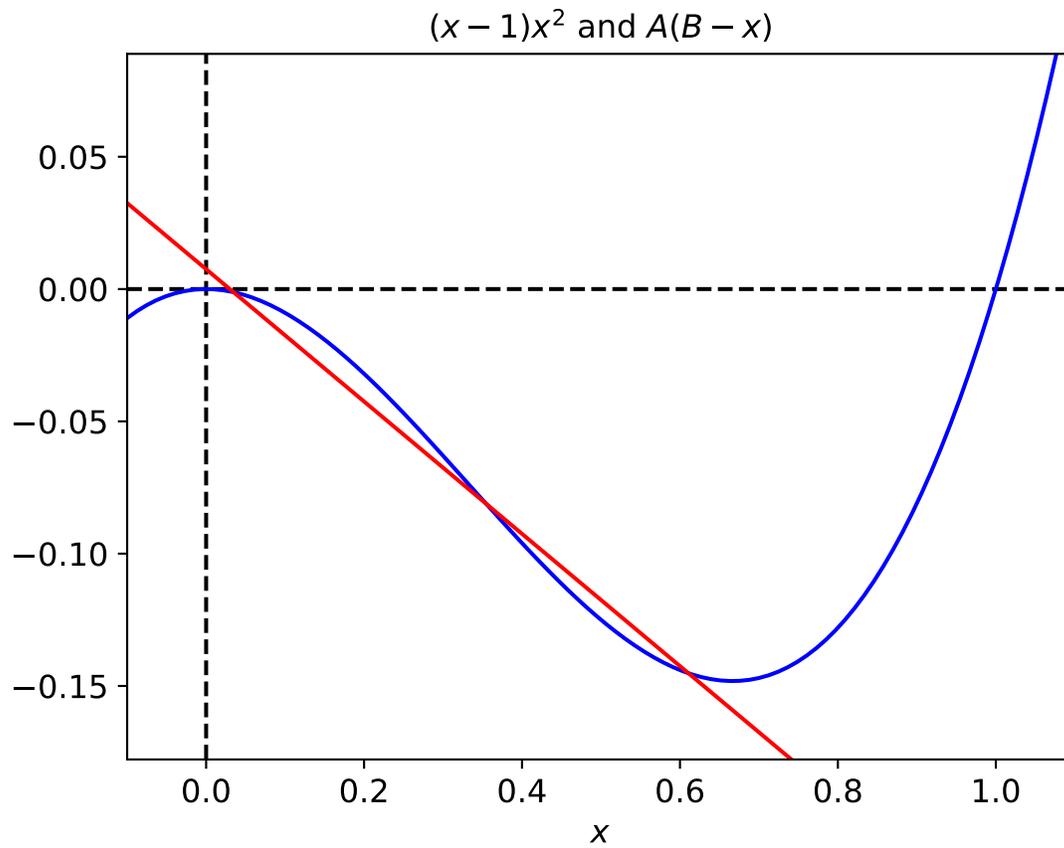
Figure 1 – The blue curve is the left-hand side of equation (21). The red line is the right-hand side with $A = 0.25$ and $B = 0.03$. The two curves intersect each other at three points, which are the values of x that satisfy equation (21).

12 Proofs for section 11

This section outlines how to deduce the observations listed at the end of section 11.

Choose a value of AB, which is the value of the right-hand side of (21) at $x = 0$. The quantity A is the magnitude of the slope of the line defined by the right-hand side of (21). Keeping that value of AB fixed, suppose that A can be chosen so that (21) has three real solutions. Then, by increasing or decreasing the value of A, we can make the line tangent to the graph of the left-hand side of (21). With this in mind, consider two cases:

- If $B = 0$ (so that $AB = 0$), then the only two values of A that make the line tangent to the left-hand side of (21) are $A = 0$ and $A = 1/4$. This establishes the first two observations at the end of section 11.

- Now consider the straight line tangent to the curve $y(x) = x^3 - x^2$ at any given point $x = x_0$. Straightforward calculation tells us where that line intersects the y-axis, and more straightforward calculation tells us that $1/27$ is the threshold between points on the y-axis that are and aren't intersected by at least one of those tangent lines.[11] This establishes the other two observations at the end of section 11.

---

[11]Here are the straightforward calculations. At any given point $x = x_0$, the equation for the line tangent to $y(x)$ is $y_L(x) = y(x_0) + (x - x_0)y'(x_0)$ where y' is the derivative of y. This line intercepts the y-axis at $y_L(0) = x_0^2 - 2x_0^3$. Maximizing this with respect to x_0 shows that the maximum occurs for $x_0 = 1/3$, which gives $y_L(0) = 1/27$ as the highest point on the y-axis that is intercepted by any of the tangent lines.

13   Example with two equal maxima

The example in figure 1 was made by choosing the values of A and B, but evaluating (18) requires knowing the values of r, α, β, which are not uniquely determined by A, B. The pictures below show an example with $r = 0.1$, $\alpha \approx 596.8$, $\beta = 0.005$, and $\delta = 3/2$. which gives $A \approx 0.2096$ and $B \approx 0.0513$. The first picture shows the two sides of equation (21), which intersect each other three times, and the second picture shows the log of the quantity (18), which has two peaks of equal height.
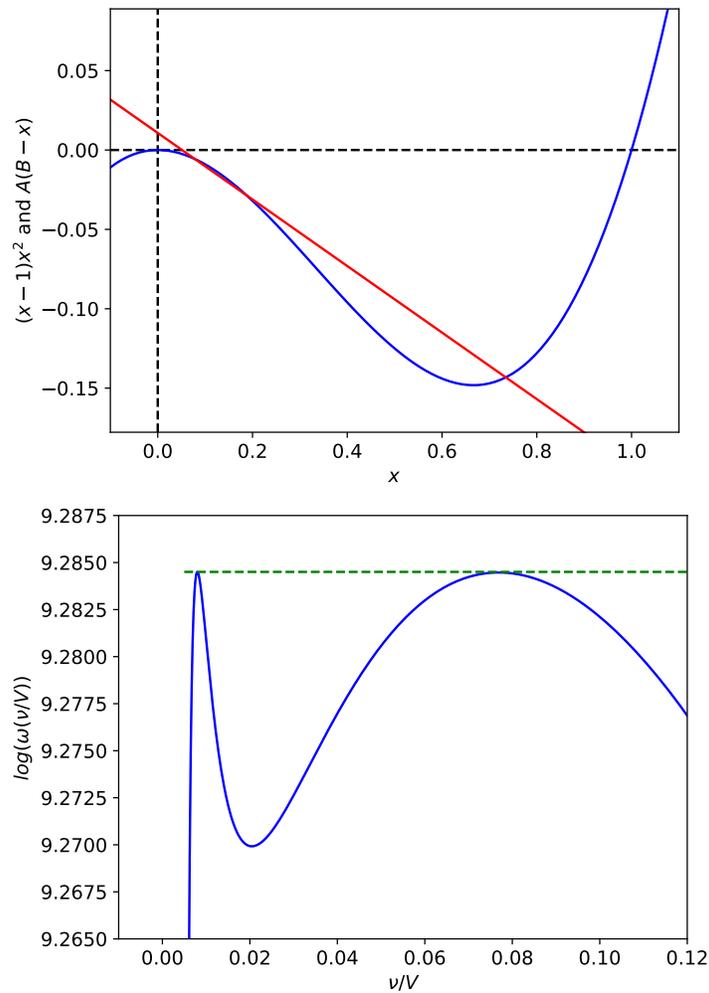
14   Realistic values

The model only has two parameters a, b characterizing the interactions between molecules. That's not enough to characterize the diversity of real molecules, so we shouldn't expect the model's predictions to be quantitatively accurate for real fluids, but we can still ask whether the model exhibits a liquid/vapor phase transition for any semi-realistic values of the model's inputs. Let's try these round values:

- $D = 3$

- $V = 1$ meter^3

- $N = 10^{25}$, which is in the right neighborhood for nitrogen gas at atmospheric pressure for the given V at a temperature consistent with the boiling point of water.

- $n = 10^{22}$, which says that the number of fluid molecules (n) is a small fraction of the total number of fluid + air molecules (N), so that the air can act as a reservoir capable of exchanging plenty of energy with the fluid.

- $b = (10^{-10}$ meter$)^3$, which is in the right neighborhood for the volume of a single molecule.

Using these values, our strategy will be to look for a value of $\alpha \equiv EV/(an^2)$ at which the quantity (18) has two peaks of equal height, which is the hallmark of the liquid/vapor phase transition. Using the values suggested above gives

$$r = 10^{-3} \qquad\qquad c_1 \approx \delta = 3/2$$
$$\beta = 10^{-8} \qquad\qquad c_2 \approx 1/2 + r\alpha.$$

This implies $B \approx \beta/(r + 1/2\alpha) < \beta/r = 10^{-5}$, which is close to zero, so the observations listed at the end of section 11 suggest that A should be somewhere in the range $0 < A < 1/4$. To relate this to α, write

$$c_2 = P + Q\alpha$$

with

$$P \equiv \delta - 1 = 1/2 \qquad\qquad Q \equiv r + (1-r)\beta \approx 10^{-3} \qquad (22)$$

so that

$$A = \frac{\alpha c_1}{(P + Q\alpha)^2}.$$

Given a value of A, the corresponding values of α are the solutions of the quadratic equation $(P + Q\alpha)^2 A = c_1\alpha$. In particular, taking $A \to 0$ corresponds to taking either $\alpha \to 0$ or $\alpha \to \infty$, and taking $A = 1/4$ corresponds to taking either

$$\alpha \approx \frac{1}{24} \qquad \text{or} \qquad \alpha \approx \frac{4c_1}{Q^2} \approx 6 \times 10^6.$$

Looking in the range $0 < A < 1/4$ therefore corresponds to looking in the ranges

$$0 < \alpha \lesssim \frac{1}{24} \qquad\qquad 6 \times 10^6 \lesssim \alpha < \infty.$$

Values of α in the smaller range may admit three solutions of equation (20), but not within the allowed range of values of $u \equiv \nu/V$, so we should consider values of α in the larger range instead. Figure 2 shows the result for $\alpha \approx 1.0608 \times 10^{10}$, which gives two peaks of equal height. The first peak is so narrow that it looks like a vertical line in that figure, so figure 3 presents the same information in a different way – with $\log(\nu/V)$ on the horizontal axis instead of ν/V – to clarify the structure.

Section 15 explains the significance of this result.
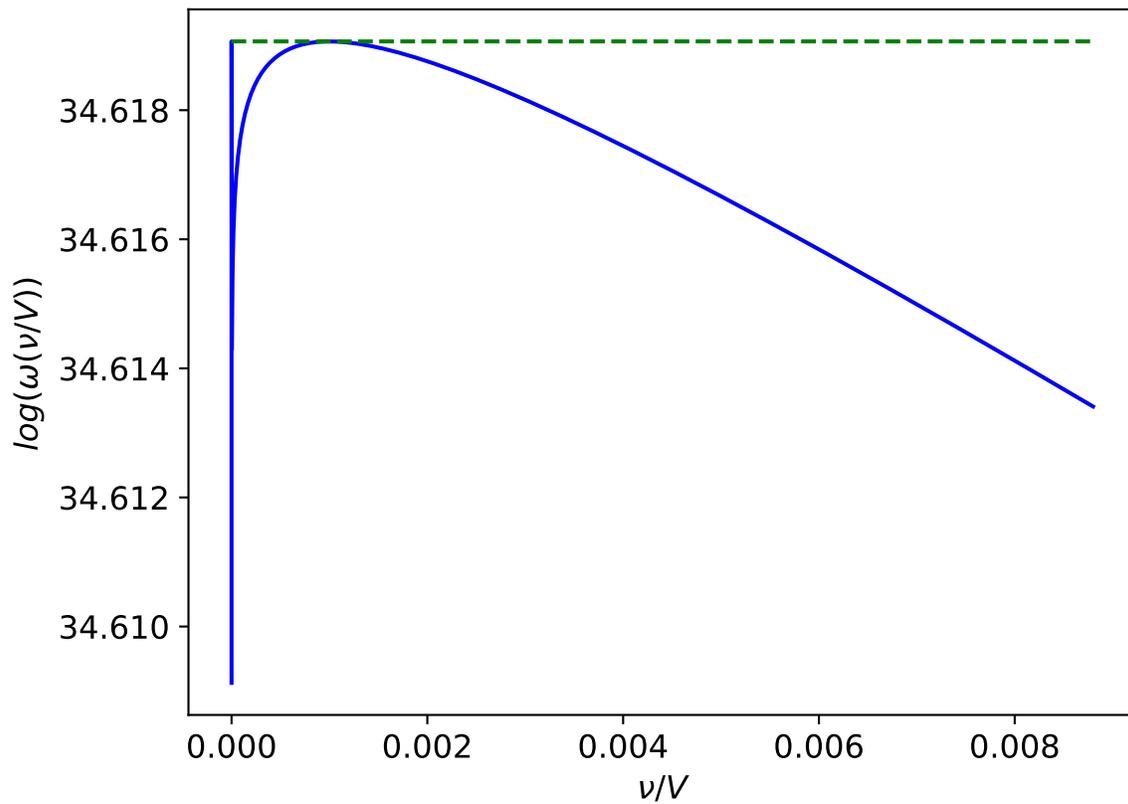
Figure 2 – Graph of (18) for $r = 0.001$, $\alpha \approx 1.0608 \times 10^{10}$, $\beta = 10^{-8}$, and $\delta = 3/2$. Figure 3 presents the same information in a different way to clarify the structure.
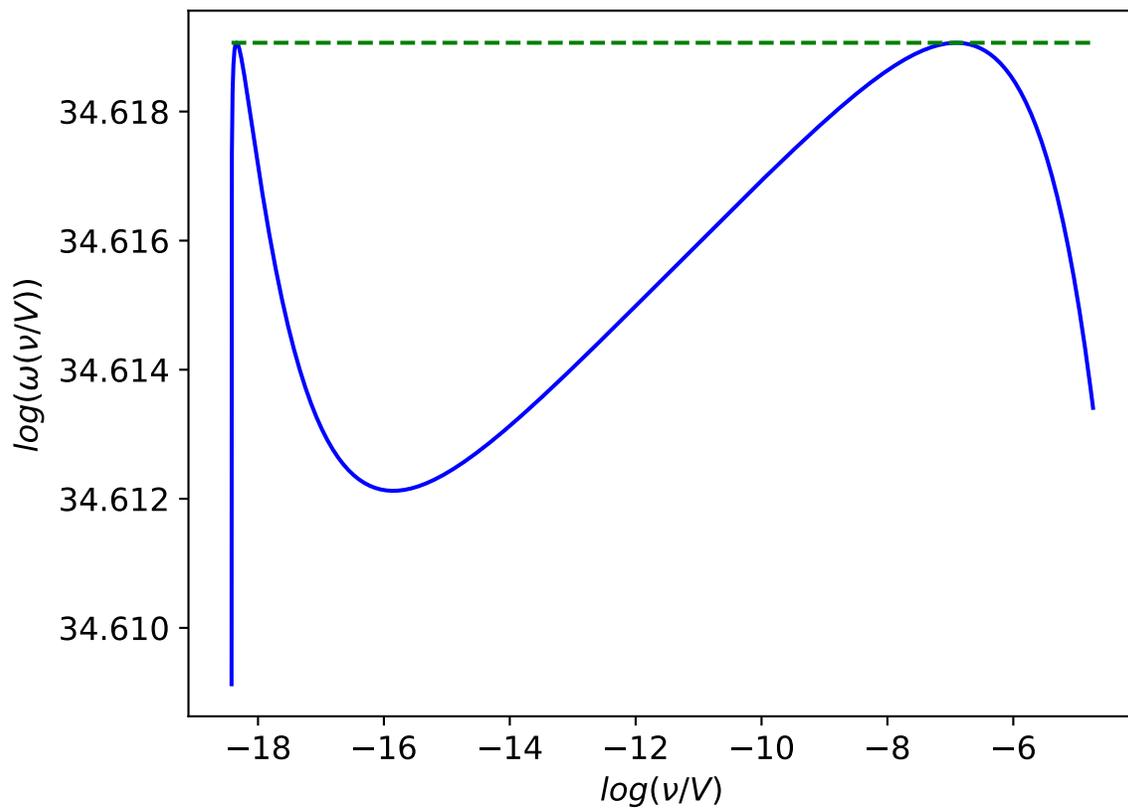
Figure 3 – The same as figure 2, but with the horizontal axis changed to $\log(\nu/V)$ instead of ν/V, which has the effect of "zooming in" more on smaller values of ν/V to clarify the structure.

15   Why liquids boil

Using semi-realistic values for the model's inputs, section 14 showed that the energy E can be tuned to a special value E_{boil} where the quantity defined in (16) has two peaks of equal height. These two peaks occur at

$$\log(\nu/V) \approx -18 \;\Rightarrow\; \nu \approx 10^{-8}\,V$$
$$\log(\nu/V) \approx -7 \;\;\Rightarrow\; \nu \approx 10^{-3}\,V.$$

where ν is the volume of the fluid and V is the total volume of the combined fluid + air system. These two values of ν correspond to a high-density state ("liquid") and a low-density state ("vapor"), respectively. The ratio of these densities is $\approx 10^{-5}$, which is realistic.[12]

Changing the total energy E changes the relative heights of the two peaks. When $E < E_{\text{boil}}$, the liquid peak higher than the vapor peak. When $E > E_{\text{boil}}$, the vapor peak higher than the liquid peak. In terms of the quantity ω defined in equation (18), a $\pm 0.1\%$ change in E changes the peak-height ratio by only $\sim 10^{-5}$. That might seem insignificant, but remember that the quantity (16), which counts the number of microstates, is proportional to ω^N with $N = 10^{25}$ in this example, so the highest peak in (16) is highest *by far* whenever E deviates even slightly from E_{boil}. To quantify this, use

$$(1 + 10^{-5})^N \sim 10^{4 \times 10^{19}}$$

to see that a $\pm 0.1\%$ change in E changes the ratio of the numbers of microstates associated with the two peaks by an *enormous* factor. The peaks in the function ω^N are likewise *extremely* narrow compared to the peaks in ω, so practically all of the microstates are consistent with whichever value of ν hosts the highest peak. Altogether, this is why the density of a fluid changes abruptly when the total energy reaches a special value. In other words, this is why liquids boil.

---

[12]Under normal conditions, the density of liquid water is ≈ 1000 kg/m^3, and the density of water vapor is ≈ 0.01 kg/m^3, consistent with the ratio $\approx 10^{-5}$.

16   Things this article didn't address

This article focused on explaining why liquids boil, using a simple model that reproduces the essence of the phenomenon. To conclude, I'll acknowledge a few interesting things that this article didn't address:

- This article used a specific model for the air on the other side of the partition. In fact, most details of the air model don't really matter. Just about any compressible heat reservoir should work.

- For simplicity, this article parameterized the analysis in terms of the system's total energy. The analysis could be recast in terms of the system's temperature instead, which is how we normally parameterize things in practice.

- This article focused on the discrete change in ν at the boiling point, but it didn't address the significance of the corresponding discrete change in ϵ, which turns out to be related to something called the **latent heat of vaporization**.

- This article didn't try to estimate the temperature at which the liquid boils. To estimate the temperature, we would need to choose a specific value for the parameter a in (5), based on some other criterion like giving the correct latent heat of vaporation. Of course, we shouldn't expect the simple model used here to match real fluids in perfect quantitative detail.

- This article didn't address the **critical point**, even though its existence is correctly predicted by the same model. Thanks to the critical point, if the pressure is high enough, then boiling does not occur at any temperature. We can pass smoothly from the liquid phase to the vapor phase without any discrete phase transition (no boiling), by following a path that goes around the critical point in pressure-temperature space. Many real fluids, including water, have such a critical point. This corroborates the idea that a sudden change in the fluid's density really is the essence of the boiling phenomenon.

17 References

Reif, 1965. *Fundamentals of Statistical and Thermal Physics.* McGraw-Hill

18 References in this series

Article **23206** (https://cphysics.org/article/23206):
"The Entropy of an Ideal Gas" (version 2022-10-23)

Article **66313** (https://cphysics.org/article/66313):
"The Concept of Entropy as the Foundation for Statistical Mechanics" (version 2024-05-21)