Why a Phase Transition Temperature Remains Constant

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Abstract

A common misconception about phase transitions is that latent heat is used exclusively to break intermolecular bonds, leaving the kinetic energy and therefore the temperature unchanged. In reality, the release of molecules from fixed positions involves changes in kinetic energy. So why does the temperature remain constant? This paradox arises from a more fundamental misunderstanding of temperature itself. Contrary to conventional textbook definitions, our study suggests that temperature is not a direct measure of a system's kinetic energy, but is instead more fundamentally linked to its radiative energy. Since radiative energy is emitted by potential energy components, such as intermolecular bonds, temperature is more closely tied to potential energy than previously recognized. This perspective is supported by infrared thermometers, which measure temperature based on radiated energy, not molecular motion. Further evidence comes from discrepancies in the specific heat of ideal gases: predictions based on the kinetic theory of gases consistently fall short of observed values, with the deficit corresponding to the number and type of molecular bonds. This implies that the unaccounted specific heat arises from increases in potential energy rather than kinetic energy. Accordingly, the constancy of temperature during a phase transition is not due to fixed kinetic energy, but to an upper limit on the system's potential energy, determined by the strength of intermolecular bonds. These bonds, like springs, store increasing amounts of energy as they are stretched with rising temperatures. A phase transition occurs when the bonds reach their maximum extension and begin to rupture, driven by *transimpacts*—impacts caused by atomic electron transitions. The energy threshold of these transimpacts defines the maximum potential energy the system can sustain, which in turn determines its radiative output and thus fixes the temperature during the phase change.

Introduction

It is a common observation that phase transitions occur at constant temperatures. For instance, under standard pressure, ice transitions to water at a fixed temperature of 0 °C, while water boils at 100 °C. Conventional textbook explanations suggest that the energy of latent heat in a phase transition is used to break bonds between molecules, resulting in no net increase in the particle's kinetic energy and, consequently, no change in temperature. This explanation implicitly assumes that temperature represents the average kinetic energy of the particles.

However, during a phase transition like the melting of ice to water, molecules are liberated from their fixed positions within hydrogen bonds, leading to an increase in their kinetic energy. If temperature accurately reflected the average kinetic energy of a system, it would be expected to rise during the transition. So why does the temperature not change?

This question highlights a misconception that temperature represents kinetic energy, as discussed in the study "Can Temperature Represent Kinetic Energy?"[1] Additionally, certain phase transitions, such as the helium superfluid transition[2] and the phase transition of sodium acetate trihydrate, do not maintain a fixed temperature. Our study indicates that temperature does not directly quantify the average kinetic energy of a system; rather, it measures dynamic energy, which is the dynamic fraction of internal energy primarily related to the system's radiative and potential energy. With these insights, we can clarify and correct common misconceptions about phase transitions and the true nature of temperature during these processes.

Transimpact

To comprehend the nature of phase transitions, we need to understand the concept of transimpact, an interaction between particles due to a side effect of atomic electron transitions.[3-4] Electrostatic attraction is typically induced between atoms/molecules nearby. When their distance becomes too small, the electron repulsion increases rapidly. The repulsion and attraction strike a balance at a certain spacing, known as the Van der Waals distance. This balance is often disrupted during an atomic electron transition. When absorbing energy, an electron excites and jumps to a higher orbital, typically in a few nanoseconds or less.[5-6] The volume of the host atom expands as the electron cloud takes up a larger space, reducing the distance to adjacent atoms. The sudden reduction in the distance between them breaks the established balance and typically increases the repulsion between them, pushing them apart, as illustrated in Figure 1. Transimpacts are explosive, like a burst of popcorn. The impact exerts a significant force on adjacent particles and pushes them apart, causing or intensifying particle vibrations.

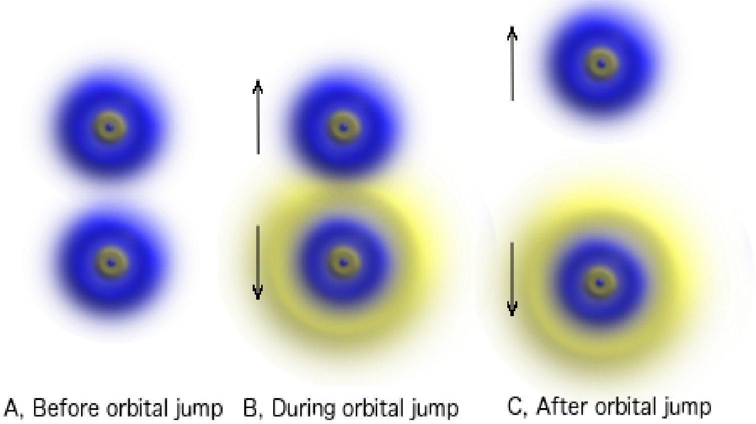


Figure 1: Transimpact due to an atomic electron transition.

Because atomic electron transitions occur routinely at the microscopic level, **transimpacts** are a common type of interaction that influences many physical processes, particularly thermodynamics. For example, the long-debated behavior of Crookes radiometers [7–8] can be naturally explained using transimpact theory.[4] When illuminated, the black side of a radiometer vane absorbs light more efficiently than the white side, resulting in a greater number of transimpacts that push nearby air molecules away. This creates an imbalance in momentum transfer across the vane surfaces, causing the vanes to rotate.

Unlike conventional explanations, transimpact theory uniquely predicts a **maximum initial acceleration** of the vanes. Since atomic electron transitions and the resulting transimpacts occur almost instantaneously upon light exposure, the driving force reaches its peak at the onset. As the vanes begin to rotate, aerodynamic resistance increases, gradually counteracting the driving force. This leads to a reduction in net acceleration, and eventually, the rotation speed stabilizes.

These predictions are in good agreement with experimental observations and provide a compelling mechanistic explanation.

Brownian motion is typically attributed to the random motion of fluid molecules.[9–10] However, estimates indicate that to accelerate a pollen grain to a speed of 300×10^{-9} m/s, a water molecule would need to hit the pollen at a speed greater than 10% of the speed of light, which is unattainable for water molecules.[3] On the other hand, the impact of transimpacts is much more intense than the movement of water molecules and should provide sufficient momentum to drive small particles in Brownian motion. Transimpacts also play a crucial role in phase transitions, which will be detailed in this study.

Furthermore, transimpacts play a central role in mediating the transformation among the three dynamic forms of energy within a system: radiative energy, potential energy, and kinetic energy. Collectively, these forms constitute the system's *dynamic energy*. The random motion of molecules arises from and is sustained by transimpacts, which enable the transfer of kinetic energy between particles. Moreover, transimpacts facilitate the conversion of radiative energy and potential energy—stored in orbital electrons or chemical bonds—into kinetic energy, thereby driving the system's overall energetic dynamics.

Impactrans

On the other hand, kinetic energy within a system cannot accumulate indefinitely through transimpacts; there must be a mechanism for converting this energy into other forms, such as potential and radiative energy. This mechanism is known as **impactrans**. When particles, such as atoms or molecules, move or vibrate, they interact with neighboring particles via electrostatic forces, effectively "knocking" nearby electrons into different orbitals. This interaction accelerates electrons, often resulting in the emission of radiative energy. Additionally, electrons may undergo orbital transitions that alter their potential energy, which can also be released in radiative form. In essence, impactrans enables the conversion of kinetic energy into both radiative and potential energy, thereby maintaining energetic balance within the system.

The conversion of kinetic energy into potential and radiative energy is evident in many everyday phenomena. A common example is the dent formed on a surface after being struck by a hammer. The deformation arises from alterations in the atomic bond structure. Some bonds are compressed, others are stretched, absorbing the hammer's kinetic energy as potential energy. Some change in the potential energy of the impacted bonds is also released as radiative heat, a process commonly experienced as impact heat, which frequently occurs during collisions. Although this interaction appears to occur at the macroscopic level, it is fundamentally governed by microscopic forces. In most cases, the molecules of the hammer do not come into direct contact with the surface molecules; rather, they interact through electrostatic forces. At its core, this impact can be understood as a collective impactrans process involving a vast number of particles.

Another example is the generation of static charges through rubbing. A surface is usually not as smooth as it appears; at a microscopic scale, it resembles the rough surface of a file. When two objects move relative to each other, their surface molecules collide via electrostatic forces. This impact can cause some electrons to be displaced or even dislodged. Static charges are the buildup of dislodged electrons. Frictional heat is another outcome of transimpacts. You feel warmth when rubbing your palms together. The hand motion displaces the electrons in surface molecules, raising their potential energy. Thus, the kinetic energy of the motion is converted to potential energy. When these electrons return to lower levels, the stored energy is released as radiative heat energy.

In more extreme scenarios, where two objects collide, electrons can be dislodged from molecules, resulting in observable sparks. Similarly, in a cloud chamber,[11] a high-speed particle interacts with the gaseous mixture. The collisions can be so intense that they knock electrons off gas molecules. The unpaired charges induce attraction between these molecules to form bonds, resulting in surface tension and triggering condensation. As a result, a visible trail of tiny droplets along the particle's trajectory enables physicists to study the behavior and properties of the particle.

Transimpact and *impactrans* are fundamental mechanisms through which a system exchanges dynamic energy among its various forms: potential, radiative, and kinetic. These interactions facilitate energy transfer both within the system and between the system and its surroundings, playing a key role in maintaining thermodynamic equilibrium. One manifestation of these interactions is reflected in the **Zeroth law of thermodynamics**, which establishes the basis for dynamic equilibrium between systems.

Components of Dynamic Energy

Through **transimpacts** and **impactranses**, the three forms of energy, potential, radiative, and kinetic, continuously transform into one another, forming the dynamic energy of a system. Accordingly, the dynamic energy T can be expressed as the sum of potential energy U, kinetic energy K, and radiative energy R:

$$T = U + K + R \tag{1}$$

Potential energy is stored in orbital electrons and the bonds between charged particles. Kinetic energy is carried by particles through their motion or vibration. Radiative energy, which can propagate through a vacuum, interacts with particles and facilitates energy exchange. These distinct forms of energy arise from various types of interactions, primarily electrostatic in nature. Three main types of electrostatic forces influence the dynamic energy of a system: (1) interactions between electrons and their host atoms, (2) intermolecular forces between molecules, and (3) intramolecular or chemical bonds between atoms within a molecule.

When an electron absorbs energy from its surroundings, such as radiation, it is excited to a higher orbital. The absorbed energy is held by the electron in two forms: potential energy (U_e) due to increased distance from the nucleus and kinetic energy (K_e) in orbital motion. Therefore, the electron orbital energy is the sum of these two forms:

$$T_e = U_e + K_e \tag{2}$$

When an electron transitions to a higher orbital, the volume of its host atom expands, increasing electrostatic repulsion with neighboring atoms. This repulsion pushes adjacent atoms apart, extending the bond distance and storing a portion of the absorbed energy as potential energy in the bond, denoted by U_m. Additionally, the orbital transition induces and amplifies vibrations in nearby atoms, raising their kinetic energy, represented by K_m. Together, these components constitute the molecule's internal energy, commonly referred to as chemical energy, which is typically measured in terms of enthalpy. Thus, molecular internal energy is the sum of potential and kinetic contributions:

$$T_m = U_m + K_m \tag{3}$$

Finally, both potential and kinetic energy are also stored in interactions between molecules. At high temperatures, the distance between molecules in solid or liquid increases, similar to the expansion of molecular bonds, leading to a rise in the potential energy of intermolecular bonds, denoted by U_i, as well as an increase in kinetic energy from intensified particle vibrations, represented by K_i. Therefore, the total intermolecular energy is:

$$T_i = U_i + K_i \tag{4}$$

The potential energy U_i of intermolecular bonds plays the primary role during phase transitions. In a gas system, molecules are liberated and less affected by intermolecular bonds. Therefore, U_i is negligible, while K_i becomes more pronounced, which is the primary concern in the kinetic theory of gases. The influx of specific heat increases K_i, as well as some other constituents of energy. In particular, U_m picks up the majority of specific heat miscounted in the kinetic theory, as demonstrated in the next section, while other components are relatively less significant. The energy that characterizes the thermodynamic attributes, particularly the temperature, of a system is the total energy of all these components, in addition to the radiative energy. Thus, the total potential energy in Equation 1 is the sum of the potential energy related to the three interactions:

$$U = U_e + U_m + U_i \tag{5}$$

The total kinetic energy of a system includes the kinetic energy of the motion and vibration of all the particles:

$$K = K_e + K_m + K_i \tag{6}$$

When energy is added to a system, the energy in each of the components rises through transimpacts and impactrans. However, the change rates vary among different components. The change in the radiative and potential energy plays the leading role, while the kinetic energy typically trails. Over time, these components should attain an equilibrium, representing a stable ratio of energy among different components.

Discrepancy between Temperature and Kinetic Energy

Specific heat capacity is defined as the amount of energy required to raise the temperature of a unit mass of a substance by one degree. If temperature were determined solely by a system's kinetic energy, then changes in temperature and kinetic energy could be directly used to calculate specific heat. According to kinetic theory, temperature is related to the average molecular speed in ideal gases, at least within the assumed optimal ranges of temperature and pressure:[12-14]

$$v = \sqrt{\frac{3k_B T}{m}} \tag{7}$$

Here, m denotes the mass of a gas molecule, T is the absolute temperature, k_B represents the Boltzmann constant,[15] and v is the predicted average speed of the gas molecules. Consequently, the average kinetic energy due to the motion of a gas molecule in an ideal gas can be derived from the kinetic theory as follows:

(8) $$K = \frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

This suggests the kinetic energy of a gas molecule is proportional to the absolute temperature in the system. This equation expresses the common belief that temperature represents the average kinetic energy of the particles in a system. So, the total kinetic energy per mole of gas molecules is:

(9) $$K_m = KN_A = \frac{3}{2}k_B N_A T = \frac{3}{2}RT$$

Here, N_A denotes the Avogadro number and R represents the molar gas constant. The molar-specific heat capacity is defined as the amount of energy required to raise the temperature of one mole of a substance by one degree:

(10) $$C_m = \frac{K_m}{T} = \frac{3}{2}R$$

Thus, kinetic theory predicts that the molar-specific heat capacity should be constant and identical for all ideal gases. This prediction aligns remarkably well with experimental data for monatomic gases, achieving an accuracy of over 99%. However, the theory fails to accurately predict the specific heat of gases composed of polyatomic molecules. In these cases, the predicted values are consistently lower than those observed experimentally, and the discrepancy increases with molecular complexity. For example, the predicted specific heat of octane is only about 7% of the measured value, reflecting a prediction error of approximately 93%.

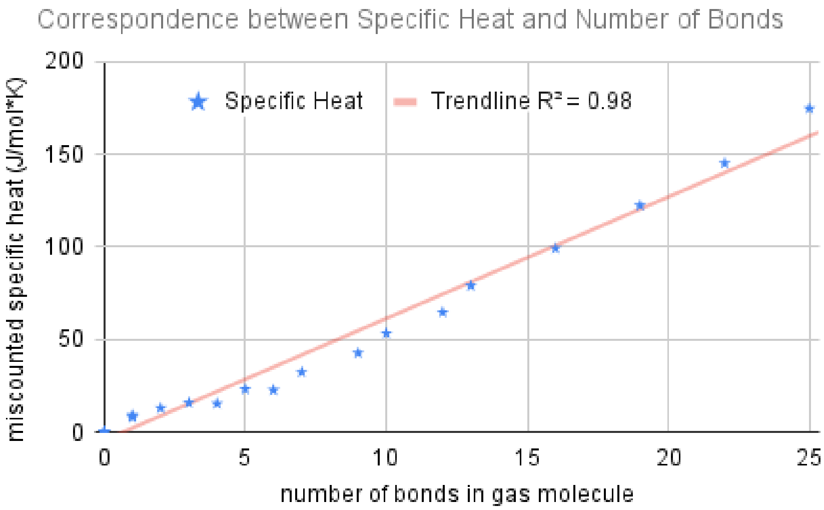


Figure 2: Correspondence between unaccounted molar-specific heat in the kinetic theory and the number of bonds. The miscounted molar-specific heat is the measurement offsetting the value predicted by the kinetic theory in Equation 10. The slope of the fitted trendline is about 6.56 with an R^2 of 0.98.

To investigate the source of the missing energy in specific heat predictions, experiments were conducted to measure the specific heat of various ideal gases with differing molecular complexities. Analysis of the results reveals a strong correlation between the discrepancy in specific heat and the number of bonds within the molecules, as shown in Figure 2. This suggests that the unaccounted energy primarily contributes to an increase in the potential energy of these bonds.

Bonds act like springs, storing energy when stretched. When work is done to increase the bond distance between atoms or molecules, that energy is retained as potential energy in the extended bond.

Based on the analysis of dynamic energy components in the previous section, the intermolecular potential energy U_i becomes negligible in gases, as intermolecular bonds are already broken. The strong correlation between specific heat and the number of molecular bonds suggests that the missing specific heat primarily contributes to an increase in molecular potential energy U_m, indicating that temperature is not solely determined by kinetic energy.

Temperature Measuring Radiative Energy and Reflecting Potential Energy

Many thermometers, particularly infrared thermometers, actually detect radiative energy. The behavior of ideal radiative emission is described by Planck's law, which relates the spectral distribution of radiation to temperature.[16-18] When Planck's law is integrated over all frequencies, it yields the total power P emitted by a perfect blackbody, which is proportional to the fourth power of its absolute temperature T, as expressed by the Stefan–Boltzmann law:[19-20]

$$(11) \qquad P = pT^4$$

Here, p is the Stefan-Boltzmann constant. By reorganizing this equation, the temperature can be expressed in terms of the power emission of a target body:

$$(12) \qquad T = \sqrt[4]{\frac{P}{p}}$$

This relationship indicates that temperature can be inferred from the radiation emitted by a system, forming the theoretical basis for temperature measurement devices. Infrared thermometers, for instance, determine temperature by detecting the intensity of radiation emitted by a target object, without requiring direct contact.

Another direct consequence of Planck's radiation law is Wien's displacement law, which states that the peak wavelength of emitted radiation shifts inversely with temperature. In other words, as the temperature increases, the peak of the radiation curve moves to shorter wavelengths:

$$(13) \qquad \lambda = \frac{b}{T}$$

Here, λ represents the peak wavelength of the radiation curve, and b is Wien's displacement constant. This relationship is derived by finding the peak wavelength of Planck's radiation curve, specifically, by taking its derivative for wavelength and solving for the maximum. Rearranging the resulting equation allows the temperature to be expressed in terms of the peak radiation wavelength:

$$(14) \qquad T = \frac{b}{\lambda}$$

This relationship enables temperature to be determined by measuring the peak wavelength of radiation emitted by a target system. Wien's displacement law is reflected in everyday observations. For example, an experienced baker can estimate the temperature of an oven by observing the color of the flame. The Sun’s surface temperature is approximately 5,778 K, and according to Wien’s law, its peak emission occurs near 500 nm, within the visible spectrum. This illustrates how temperature is fundamentally linked to the radiative energy emitted by a source.

It is important to note that radiative energy is emitted by the potential components within a system. As a result, temperature is closely linked to potential energy. This relationship helps explain the strong correlation observed in the previous section between the missing specific heat and the number of bonds in gas molecules. Through transimpacts and impactranses, different forms of dynamic energy, kinetic, potential, and radiative, continuously transform into one another. Therefore, kinetic energy is not isolated from other forms of dynamic energy, except during phase transitions, when temperature is temporarily decoupled from the changes in kinetic energy.

The Cause of Phase Transition

Another common misconception is that phase transitions are driven by the increasing intensity of molecular vibrations at high temperatures. However, our study suggests that phase transitions are not caused by molecular vibrations, but by *transimpacts*. It is essential to recognize that molecular vibrations are a result of transimpacts, not their cause. Transimpacts are inherently more energetic than molecular vibrations, as vibrational energy is transmitted through these interactions. In reality, bonds are typically broken by transimpacts *before* vibrational energy reaches a comparable intensity. Phase transitions arise from the interplay of three key forces in a system: pressure, bond forces that hold molecules together, and transimpacts that break those bonds.

The intensity of transimpacts and the relative strength of these forces within a system vary with the energy level across different states of matter. In general, as temperature increases, indicating a higher level of radiation and dynamic energy, the average intensity of transimpacts also rises. Simultaneously, bond strength tends to weaken as the increased dynamic energy leads to greater intermolecular distances. At lower temperatures, transimpact forces remain weaker than the combined retaining forces of pressure and intermolecular bonds, allowing the system to maintain structural cohesion, governed by the following relationship:

$$(15) \qquad T(t, d) < S(d) + P$$

Here, *T* denotes the average transimpact force, *S* represents the bond force, *P* stands for pressure, *t* indicates temperature, and *d* denotes bond distance, which itself varies with temperature. Expression (15) describes the relationship among these three forces in the solid state, where molecules are held in fixed relative positions at low temperatures. As the temperature increases, additional energy is stored in the bonds as they are extended. However, stretched bonds become weaker. At the same time, the intensity of transimpacts rises with increasing temperature. Eventually, the temperature reaches a point where the transimpact force becomes strong enough to counterbalance and overcome the combined retaining forces (*S* + *P*):

$$(16) \qquad T(t, d) = S(d) + P$$

This establishes an upper-temperature limit for the solid state of matter. As additional energy is introduced into the system, the solid-state bonds can no longer restrain the molecules against the growing intensity of transimpacts. A phase transition occurs when these bonds are broken and molecules are released from their fixed positions. During this transition, latent heat is absorbed to break the bonds and increase the kinetic energy of the now-free molecules. This transition may involve a direct mutation from rigid solid bonds to more flexible liquid bonds. In the liquid state, molecules are constrained by the retaining forces given below:

(17) $T(t,d) < L(d) + P$

Here, *L* denotes the liquid bond force. This cohesive force allows molecules to move relative to one another while remaining bound together, giving rise to the liquid's viscosity. As more energy is added to the liquid, the bond potential increases due to the expansion of intermolecular distances. When these distances grow sufficiently large, the liquid bond force weakens to the point where the transimpact force becomes comparable to the total retaining forces:

(18) $T(t,d) = L(d) + P$

This balance between transimpacts and retaining forces defines the liquid-to-gas phase transition. At this point, additional energy further weakens the liquid bonds until they can no longer withstand the increasing intensity of transimpacts, resulting in vaporization. In the gaseous phase, although intermolecular bonds are broken, the electrostatic attraction between electrons and their host nuclei remains strong enough to keep the electrons bound within atoms:

(19) $A(t,r) < C(r) + P$

Here, *A* denotes the atomic transition force, which depends on the energy absorbed by the electron; *C* represents the Coulomb attractive force between the electron and the host nucleus; and *r* is the electron's orbital radius, which also varies with temperature *t*. At low temperatures, when *A* is small, electrons may transition between different orbitals but remain confined within their host atoms. These low-energy transitions modify the electron's potential energy as the orbital radius changes, much like how bond potential energy varies with bond length. As more energy is introduced into the system, electrons are excited to higher orbitals, increasing their potential energy. At the same time, the Coulomb attraction weakens with increasing orbital radius, eventually reaching a point where the atomic transition force balances the combined retaining forces of Coulomb attraction and external pressure:

(20) $A(t,r) = C(r) + P$

This balance defines the threshold for the gas-to-plasma transition. As more energy is supplied, the bond between electrons and their host nuclei can be broken, freeing the electrons from their atoms or molecules and resulting in the formation of plasma. Unlike previous phase transitions, this process is driven not by transimpacts but directly by atomic electron transitions.

Equation 16 describes the balance of forces during the solid-to-fluid phase transition. Since the bond distance *d* in Equation 16 is a function of temperature *t*, the equation effectively represents a relationship between pressure *P* and temperature *t*. This defines a curve in the *P*-*t* plane, corresponding to the phase boundary in a phase diagram. By rearranging Equation 16 to express *P* as a function of *t*, it yields the pressure required for a given melting temperature. The set of these (*P*, *t*) coordinates traces the phase boundary curve shown by the green and red lines in Figure 3. Likewise, Equation 18 defines the liquid–gas transition boundary, represented by the blue curve, and Equation 20 defines the gas–plasma transition boundary, illustrated by the purple curve.

In fluids, the pressure term *P* in Equation 18 plays a significant role in the transition between liquid and gaseous phases. Fluid molecules are confined together by pressure, increasing the chance of molecule interactions and facilitating the induction of elastic liquid bonds between them, creating high viscosities. Thus, the transition boundary is typically flatter, as illustrated by the blue curve in Figure 3, indicating it is more sensitive to pressure changes.

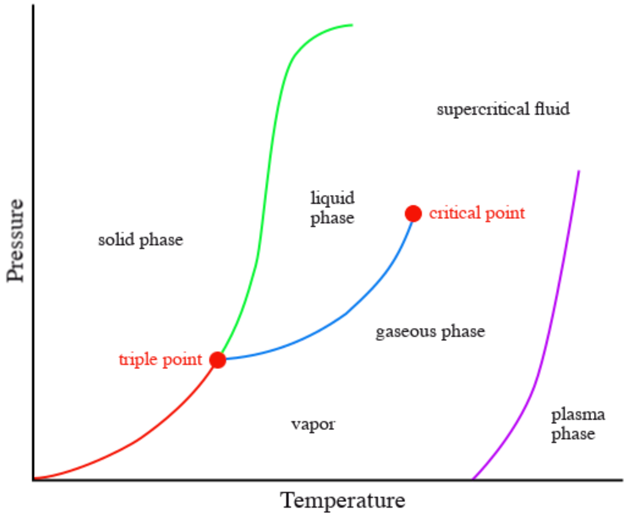


Figure 3: Typical phase diagram. The red curve illustrates the sublimation temperature, the blue curve the boiling point, the green curve the melting point, and the purple curve the ionizing point, showing how most substances vary with pressure.

In general, the pressure term *P* in all phase transition equations acts as an additional retaining force, supplementing molecular bonds to keep molecules together. For example, water boils below 100 °C at high altitudes, such as in Tibet, due to the lower atmospheric pressure. As pressure varies, the corresponding phase transition points shift, shaping the trend of the transition curves. The flatter the transition curve, the more sensitive the phase change is to pressure. This is evident in the blue curve representing the liquid–gas transition.

It is important to note that Equations 16, 18, and 20 reflect a balance between the retaining forces (such as pressure and bonding) and the disrupting force of transimpacts. This balance is typically achieved as bonds weaken at elevated temperatures. However, individual transimpacts of exceptionally high intensity can overcome even relatively strong bonds at lower temperatures, ejecting molecules from the surface and resulting in phenomena such as sublimation or evaporation. A similar mechanism applies to the photoelectric effect,[21] in which high-energy photons eject electrons from a material, even at low temperatures, without triggering a plasma phase transition. Accordingly, these transitions can be classified as either bond-limited or impact-driven, as summarized in Table 1.

	Solid to Liquid	Liquid to Gas	Gas to Plasma
Bond-Limited Transition (High Temperature)	Melting	Boiling	Ionization
Impact-Driven Transition (Low Temperature)	Sublimation	Evaporation	Photoelectric Effect

Table 1: Comparison between bond-limited and impact-driven transitions

In other words, bond-limited transitions are standard phase changes that occur at high, and typically well-defined, temperatures, when bonds are stretched to their maximum extent and can no longer retain structural cohesion. In contrast, impact-driven transitions result from exceptionally high-intensity transimpacts that overcome relatively strong bonding forces. These transitions typically occur at temperatures below the normal phase transition point.

Essentially, phase transitions are primarily driven by transimpacts as bonds weaken at higher energy levels. Adding energy to a system increases the potential energy of bonds, causing them to lengthen and lose strength. Simultaneously, the intensity of transimpacts rises, eventually softening bonds during solid-to-liquid transitions or breaking them completely during gas-to-plasma transitions. A similar mechanism also governs ionization.

Phase Transition at Constant Temperature

Here are the general trends observed in a system between phase transitions as energy is added. As energy is absorbed, electrons jump to higher orbitals, causing atoms to move farther apart and increasing both bond distances and potential energy. This weakens the bonds while simultaneously increasing the intensity of transimpacts. The temperature rises, reflecting the level of radiation closely linked to the bonds that emit it. Meanwhile, the system's kinetic energy also increases in response to the growing transimpact intensity.

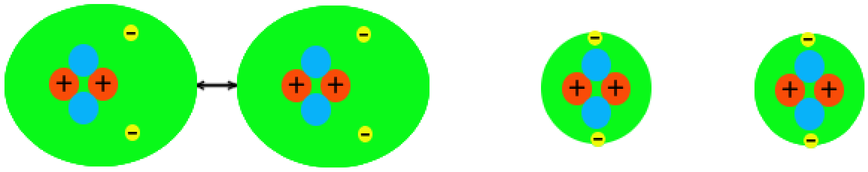
The temperature during a phase transition remains constant primarily because of the maximum limit on bond extension. In solids and liquids, as energy is added, the intermolecular potential energy (U_i) increases, causing bond lengths to stretch. As the bond distance grows, the bond strength weakens. Eventually, the bonds become too fragile to withstand the increasing intensity of transimpacts and break, initiating the phase transition. In other words, the increase in potential energy U_i is limited by the transimpact level defined by Equations 16 and 18. Once this threshold is reached, bonds break, and U_i can no longer increase beyond that level. This restriction on potential energy also limits its radiative emission, which is reflected in the temperature, tied to these limits, causing the temperature to remain constant during the phase transition.

During a phase transition, latent heat is used both to break bonds and to increase the kinetic energy of freed molecules. Therefore, the kinetic energy of particles indeed rises during phase transitions, contrary to the assumption that it remains unchanged. However, these changes in kinetic energy do not affect the system's emission level and thus are not reflected in temperature. Similarly, breaking bonds does not alter the emission level; emission changes only when the potential energy components, the bonds, vary. Since the system's overall emission level is limited by the potential energy U_i, which reaches its maximum during a phase transition, the temperature, being a reflection of this emission level, is effectively anchored to a fixed potential and radiative level.

Phase Transition at Variable Temperature

Not all phase transitions occur at a fixed temperature. When the energy required to change the temperature competes with the energy needed to break bonds, the transition temperature can remain constant during a quasi-static process. Otherwise, the transition temperature will vary. For example, when ice melts into water, energy is needed both to raise the temperature and to break bonds. These competing energy demands keep the transition temperature constant. In contrast, during the helium superfluid transition, energy must be removed to lower the temperature, while breaking the bonds between helium molecules also consumes energy and contributes to the temperature decrease. Since these processes do not compete for energy, the transition temperature is not fixed and instead decreases throughout the superfluid transition.[2]

The bonds between helium molecules are formed due to the attraction of the London dispersion force, as illustrated in Figure 4A. At high temperatures, the excited electrons in high orbitals are more susceptible to perturbations, resulting in stronger London dispersion forces. However, at low temperatures, helium electrons retreat to lower orbitals and are tightly attracted to their nuclei, reducing electron perturbations and weakening the London dispersion force.[22] When the temperature drops sufficiently, the dispersion forces become so weak that the interactions between molecules become negligible. Consequently, the attractions between molecules disappear, and bonds are broken, as shown in Figure 4B. In the absence of these attractions, the helium molecules can move freely, resulting in a fluid with zero viscosity, the unique property of superfluidity.[23] Essentially, a superfluid is not a conventional fluid but a collection of free molecules.



A, London Dispersion Force

B, Helium Superfluid Molecules

Figure 4: Superfluid–a collection of molecules without attraction. A) Bonds are formed between helium molecules at high temperatures due to London dispersion. B) The bonds disappear at low temperatures, as electrons retreat to lower orbitals, weakening the London dispersion.

As energy is removed from a helium liquid, the temperature decreases, and the bonds between liquid molecules will eventually start to break due to the weakening and disruption of London dispersion. Breaking bonds needs energy, which lowers the liquid temperature further. So, the system cannot remain at a fixed temperature during the transition. The temperature range of the helium superfluid transition can be roughly identified by analyzing the curve of helium-specific heat, as shown in Figure 5.

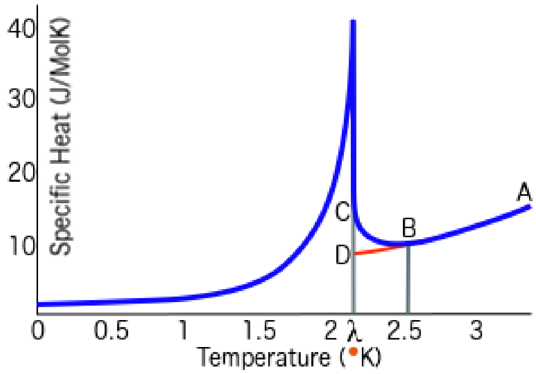


Figure 5: Identifying the temperature range of the helium-4 superfluid transition. The blue curve depicts the specific heat of helium-4 as a function of temperature. The change in curvature between points B and C suggests that the transition begins before the λ-point at approximately 2.17 K.

The helium superfluid transition, which concludes around 2.17 K at the λ-point, is visually indicated in experiments by the abrupt cessation of boiling. The formation of bubbles needs surface tension to enclose helium vapor, signifying the presence of intermolecular bonds. Therefore, the disappearance of bubbles indicates the absence of these bonds or intermolecular attractions.

For a homogeneous liquid, the specific heat decreases smoothly from point A as energy is removed from the helium liquid. The specific heat curve is expected to follow a similar downward trend from A to B and D, as shown by the extension of the red curve in Figure 5. However, the trend changes at point B. The significant upward curvature from B to C indicates a much higher specific heat, suggesting a major phase change in the liquid.

The significantly high specific heat to the left of the λ-point indicates that molecules in the superfluid phase possess a higher specific heat compared to those in the liquid phase. Thus, the increase in specific heat to the right of the λ-point suggests the presence of superfluid molecules, indicating that the transition starts before the λ-point when the trend begins to change. Therefore, the onset temperature of the superfluid transition should be at least from point B, if not higher. The temperature range for the helium-4 superfluid transition is roughly between point B and the λ-point. The upper bound of this range is not well defined due to the less sensitive curvature change at the initial transition.

Phase Transition beyond Transition Point

Phase transition at a constant temperature typically occurs in quasi-processes, which gives enough time for the anchor effect to fully propagate throughout the system. However, during a rapid transition, the temperature may not be fixed even though the bond mutation works against the transition. This is usually observable during a transition beyond the transition point.

This type of transition is utilized in a portable heating product called a sodium acetate heating pad. The product consists of a plastic bag containing a supersaturated solution of sodium acetate in water and a stainless steel disc, as shown in Figure 6. Once the disc is flexed, the sodium acetate in the solution starts to crystallize. The bond energy releases so quickly that it causes the pad to warm up, and therefore, it can be used as a heating pad in cold weather, which is the intended functionality of the product. The heating pad is reusable, as the sodium acetate crystals will melt when the pad is submerged in hot water.

Figure 6: Sodium acetate heating pad.

Sodium acetate (CH_3COONa) is the sodium salt of acetic acid. Sodium acetate trihydrate crystals melt around 58-58.4 °C.[24] Submerged in hot water, the sodium acetate crystals melt normally inside a container bag. As it cools down slowly, the sodium acetate solution gradually passes the freezing point and becomes supersaturated at room temperature without crystallizing. The crystallization can be activated by clicking the disc in the solution. Clicking the disc creates an impactrans, knocking electrons off their normal orbitals and triggering the formation of bonds, thereby starting the reaction chain of crystallization.

Here are some of the notable observations. Firstly, the phase transition or bond formation is triggered by an impactrans, while the impact of normal molecule vibration is not intense enough to activate the crystallization process. Secondly, during the crystallization process, molecules are locked by bonds into fixed positions, and their kinetic energy is reduced. However, the temperature of the pad still rises. This is another piece of evidence supporting the idea that temperature is not directly related to kinetic energy, but rather to radiative and potential energy. Finally, if this were a quasi-process to give enough time for the released heat to dissipate slowly, the transition could still maintain a constant temperature.

Many examples of phase transitions occurring beyond the transition point can be observed in daily life. For instance, placing a bottle of water in a refrigerator can cool it below the freezing point without forming ice. However, ice may form when the bottle is shaken, triggering the phase transition. This is similar to activating a sodium acetate heat pad by clicking the disc, which initiates crystallization.

In contrast to the supercooling experiments above, heat a glass of water in a microwave above its boiling point. The superheated water may not boil while inside the microwave. However, as soon as the glass is picked up, the water may start boiling, triggered by the disturbance from the movement.

Conclusions

Misconceptions about constant temperature during phase transitions often arise from a fundamental misunderstanding of what temperature represents. Rather than directly indicating the average kinetic energy of particles, temperature primarily reflects a system's average radiative emission level, which is more closely associated with its potential energy. The constant temperature observed during many phase transitions is due to an anchoring effect imposed by the maximum potential energy that intermolecular bonds can sustain. These transitions are influenced by the interaction of three key factors: transimpacts, pressure, and intermolecular bonding. Transimpacts work to break the bonds, while pressure and intermolecular bonds work to hold the molecules together. The potential energy of the bonds is limited by the highest transimpact intensity they can withstand, thereby stabilizing the system's temperature during a phase transition. However, not all phase transitions occur at a fixed temperature, further challenging the notion that constant temperature during such changes can be attributed solely to unchanging kinetic energy.

Revision History

- 10/21/2023: Initial Post on Stanford site
- 11/01/2025: Published on Zenodo
- 12/17/2025: Adding Links to Summaries of Related Articles

Links to Summaries of Related Articles

- https://cs.stanford.edu/people/zjl/abstract.html, PDF
- https://sites.google.com/view/zjl/abstracts, PDF
- https://xenon.stanford.edu/~zjl/abstract.html, PDF
- https://doi.org/10.5281/zenodo.17967154, PDF

Further Literature

- Misconceptions in Thermodynamics (PDF: DOI) (中文: DOI)
- The Mechanism Driving Crookes Radiometers (PDF: DOI) (中文: DOI)
- The Cause of Brownian Motion (PDF: DOI) (中文: DOI)
- Can Temperature Represent Average Kinetic Energy? (PDF: DOI) (中文: DOI)
- The Nature of Absolute Zero Temperature (PDF: DOI) (中文: DOI)
- The Triangle of Energy Transformation (PDF: DOI) (中文: DOI)
- Is Thermal Expansion Due to Particle Vibration? (PDF: DOI) (中文: DOI)
- Superfluids Are Not Fluids (PDF: DOI) (中文: DOI)
- Why a Phase Transition Temperature Remains Constant (PDF: DOI) (中文: DOI)
- What Causes Friction to Produce Heat? (PDF: DOI) (中文: DOI)
- The Easiest Way to Grasp Entropy (PDF: DOI) (中文: DOI)
- Entropy Can Decrease (PDF: DOI) (中文: DOI)
- The Restoration Principle (PDF: DOI) (中文: DOI)
- Is There a Sea of Free Electrons in Metals? (PDF: DOI) (中文: DOI)
- Electron Tunnel (PDF: DOI) (中文: DOI)
- Unified Theory of Low and High-Temperature Superconductivity (PDF: DOI) (中文: DOI)
- LK-99 Limitations and Significances (PDF: DOI) (中文: DOI)
- Superconductor Origin of Earth's Magnetic Field (PDF: DOI) (中文: DOI)
- Fundamental Problems about Mass (PDF: DOI) (中文: DOI)
- The Evolution from the Law of Gravitation to General Relativity (PDF: DOI) (中文: DOI)
- The Simplest Derivation of $E = mc^2$ (PDF: DOI) (中文: DOI)
- How to Understand Relativity (PDF: DOI) (中文: DOI)
- Mathematics Is Not Science (PDF: DOI) (中文: DOI)
- Tidal Energy Is Not Renewable (PDF: DOI) (中文: DOI)
- AI Contamination (PDF) (中文)
- DeepSeek pk ChatGPT (PDF) (中文)

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