Is Thermal Expansion Due to Particle Vibration?

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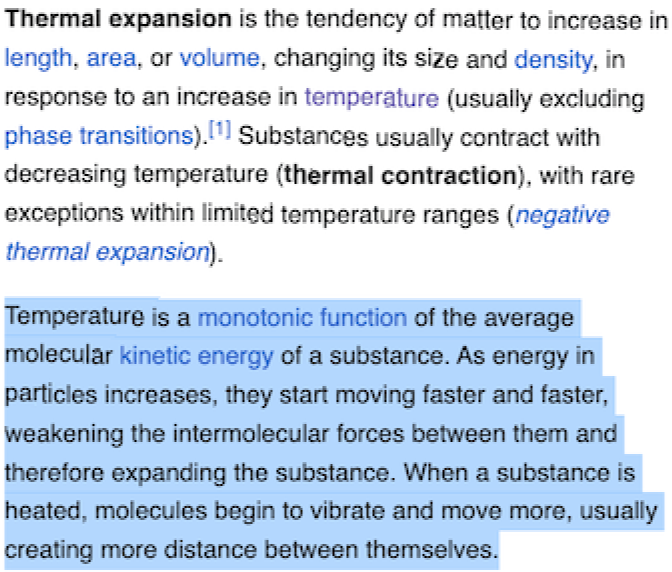
Abstract

Contrary to the common belief that thermal expansion results from increased particle vibration, our study suggests it is primarily driven by the expansion of bond space between particles to accommodate greater potential energy. If vibration alone caused expansion, then a substance's volume should increase monotonically with temperature, since vibrations typically intensify with heat. However, this is contradicted by the fact that many substances exhibit thermal contraction as temperature rises. Bonds behave like springs, storing energy by stretching against attractive forces. When a substance absorbs heat, electrons are excited to higher orbitals, storing energy as increased potential energy. Similarly, bond stretching reflects an energy-driven increase in potential energy. This is evident in the specific heat of gases, particularly polyatomic gases, where specific heat correlates with the number of internal bonds, indicating that added energy primarily elevates bond potential rather than kinetic motion. These observations suggest that thermal expansion arises from the need for more space to store additional energy, not merely from particle vibration. Bond expansion can occur as increased intermolecular distances, intramolecular bond stretching, or larger electron orbitals. All contribute to volume changes at higher temperatures. Crucially, the structure formed by bonds determines a substance's volume. This also explains thermal contraction in cases where bonding leads to more compact structures, such as hydrogen bonding near 4 °C in water.

Introduction

Thermal expansion is the tendency of matter to change its shape, area, volume, and density in response to a change in temperature without a phase transition.[1] A classical textbook misleadingly attributes the expansion to the vibration of particles in substances, presuming that molecules at high temperatures vibrate more and need more space between them. Wikipedia provides a similar definition, as shown in Figure 0.

The vibration theory rests on three key assumptions: (1) temperature corresponds to kinetic energy, (2) kinetic energy arises from molecular vibration, and (3) molecular vibration requires more space. If all these assumptions held, a substance's volume should increase monotonically with rising temperature, since molecular vibrations intensify with heat. There should be no exceptions to this trend. However, this theory is challenged by the observation of thermal contraction in many substances as temperature increases.[2-3] For instance, water reaches its minimum volume at 4 °C and expands as the temperature decreases—behavior that contradicts the expectations of the vibration theory and highlights flaws in its underlying logic.



Thermal expansion is the tendency of matter to increase in length, area, or volume, changing its size and density, in response to an increase in temperature (usually excluding phase transitions).[1] Substances usually contract with decreasing temperature (**thermal contraction**), with rare exceptions within limited temperature ranges (*negative thermal expansion*).

Temperature is a monotonic function of the average molecular kinetic energy of a substance. As energy in particles increases, they start moving faster and faster, weakening the intermolecular forces between them and therefore expanding the substance. When a substance is heated, molecules begin to vibrate and move more, usually creating more distance between themselves.

Figure 0: Screenshot of Wikipedia's definition of *thermal expansion* as it appeared on October 22, 2025.

An intuitive argument against the vibration theory can be made by analogy. In a solid, molecules are bound within a crystal lattice or molecular network, much like trees are rooted in a forest. Molecular vibration is akin to trees swaying in the wind—their movement causes only slight shifts at the forest's edges. If thermal expansion were solely due to vibration, then a railway track should show only minimal extension at its ends, regardless of its total length. In reality, however, thermal expansion occurs uniformly along the entire length of the track, indicating that the effect is cumulative and not confined to boundary displacement. This challenges the idea that vibration alone accounts for the observed expansion.

The fundamental flaw in the vibration theory lies in its underlying assumptions, at least two of which are demonstrably inaccurate. First, the notion that temperature directly represents kinetic energy is a misconception. As discussed in the study *"Can Temperature Represent Kinetic Energy?"*, temperature does not directly quantify a system's average kinetic energy.[4] Instead, it reflects dynamic energy—the dynamic component of internal energy—that is primarily associated with changes in potential energy. Second, thermal expansion is more accurately attributed to structural changes in the bonding between molecules rather than to molecular vibrations. This alternative explanation forms the basis of the new theory proposed in this study.

Discrepancy between Temperature and Kinetic Energy

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. 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. 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:[5-7]

$$(1) \qquad v = \sqrt{\frac{3k_B T}{m}}$$

Here, m denotes the mass of a gas molecule, T is the absolute temperature, k_B represents the Boltzmann constant,[8] 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:

$$K = \frac{1}{2}mv^2 = \frac{3}{2}k_B T \tag{2}$$

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:

$$K_m = KN_A = \frac{3}{2}k_B N_A T = \frac{3}{2}RT \tag{3}$$

Here, N_A denotes Avogadro's number, and R is the molar gas constant. If all of the specific heat were used solely to increase the kinetic energy of a gas, the specific heat capacity could be predicted based on kinetic theory. By definition, the molar-specific heat capacity is the amount of energy required to raise the temperature of one mole of a substance by one degree. Therefore, under this assumption, the molar-specific heat capacity of a gas can be derived from Equation 3 as follows:

$$C_m = \frac{K_m}{T} = \frac{3}{2}R \tag{4}$$

According to kinetic theory, the molar-specific heat capacity of an ideal gas should be constant and identical across all ideal gases. This prediction aligns exceptionally well with experimental results for monatomic gases, with accuracies exceeding 99%. However, the theory fails to accurately account for the specific heat of gases composed of polyatomic molecules. In such cases, the predicted values are consistently lower than those observed experimentally, and the discrepancy grows with molecular complexity. For instance, the predicted specific heat of octane is only about 7% of the measured value, corresponding to a prediction error of approximately 93%.

To investigate the source of the missing energy in specific heat predictions, experiments were conducted to measure the specific heat capacities of various ideal gases with differing molecular complexities. Analysis of the results reveals a strong correlation between the discrepancy in predicted and measured specific heat and the number of bonds within the gas molecules, as illustrated in Figure 1. This finding suggests that the unaccounted energy is primarily allocated to increase potential energy within molecular bonds. These bonds behave like springs, storing energy when stretched. When work is done to increase the bond distance between atoms or molecules, the energy is retained as potential energy within the extended bond.

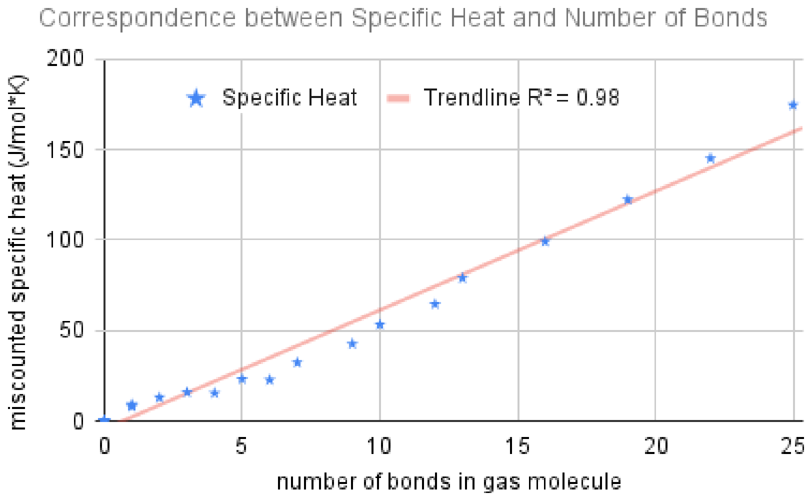


Figure 1: Correlation between the unaccounted molar-specific heat and the number of molecular bonds. The unaccounted specific heat refers to the difference between the experimentally measured values and those predicted by kinetic theory, as given by Equation 4. The fitted trendline shows a slope of approximately 6.56, with a coefficient of determination (R^2) of 0.98, indicating a strong linear relationship.

This observation leads to two key implications: first, temperature is not solely a measure of kinetic energy; and second, it is more fundamentally linked to the potential energy within a system. These insights call for a reassessment of the conventional understanding of temperature and a deeper exploration of the concept of dynamic energy.

Representation of Temperature

Temperature is commonly regarded as a measure of a system's thermal energy and, by extension, as an indicator of the average kinetic energy of its particles. However, the preceding observations suggest that this conventional view may be incomplete or even inaccurate. A fundamental disconnect exists between temperature and kinetic energy. Many thermometers, particularly infrared thermometers, do not measure kinetic energy directly; instead, they detect radiative energy. The behavior of ideal radiative emission is governed by Planck's law, which relates the spectral distribution of radiation to temperature.[9-11] When Planck's law is integrated over all frequencies, it yields the total power P emitted by a perfect blackbody. This power is proportional to the fourth power of the absolute temperature, as described by the Stefan–Boltzmann law:[12-13]

$$(5)\qquad P = pT^4$$

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:

$$(6)\qquad T = \sqrt[4]{\frac{P}{p}}$$

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 temperature increases, the peak of the radiation curve moves to shorter wavelengths:

$$(7) \qquad \lambda = \frac{b}{T}$$

Here, λ represents the peak wavelength of the radiation curve, and b is Wien's displacement constant. This relationship can also be 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:

$$(8) \qquad T = \frac{b}{\lambda}$$

This relationship allows temperature to be determined by measuring the peak wavelength of radiation emitted by a system. Wien's displacement law, which describes this inverse relationship between temperature and peak emission wavelength, is evident in everyday observations. For instance, an experienced baker can tell oven temperature from observing the color of the flame. Similarly, the Sun's surface temperature, approximately 5,778 K, corresponds to a peak emission near 500 nm, which lies within the visible spectrum. These examples illustrate how temperature is fundamentally linked to the radiative energy emitted by a source.

Radiation is closely linked to the potential energy within a system. When a body undergoes acceleration, changes in its associated force fields can result in the emission of energy in the form of waves.[14-15] For example, when a charged particle accelerates, such as during an electron's transition between orbitals, it emits energy as radiation, including visible light. In essence, radiative energy originates from the transformation of potential energy stored in chemical bonds or orbital electrons. This perspective helps explain the observed discrepancy between temperature and specific heat in gas systems. It suggests that temperature is more closely correlated with the system's radiation level and its internal potential energy than with kinetic energy alone.

Origin of Kinetic Energy

The origin of kinetic energy, such as that observed in particle vibrations, raises a deeper, often overlooked question: why and how do particles vibrate in the first place? To date, there has been little research directly addressing this fundamental issue. However, this question is explored in a study investigating the mechanism behind Crookes radiometers.[16] According to that work, kinetic energy arises from a process known as *transimpact*—a side effect of atomic electron transitions.

Coulomb attraction typically arises between atoms or molecules nearby. However, when they come too close, electron-electron repulsion increases sharply. A balance between these opposing forces is achieved at a characteristic spacing known as the van der Waals distance. This equilibrium is often disrupted during atomic electron transitions. When an electron absorbs energy and becomes excited, it jumps to a higher orbital, typically within a few nanoseconds or less.[17-18] As the electron cloud expands, the volume of the host atom increases, thereby reducing the distance to adjacent atoms. This sudden decrease in spacing disturbs the existing force balance, usually resulting in a surge in repulsive forces that push the atoms apart. This phenomenon, illustrated in Figure 2, is referred to as *transimpact*.

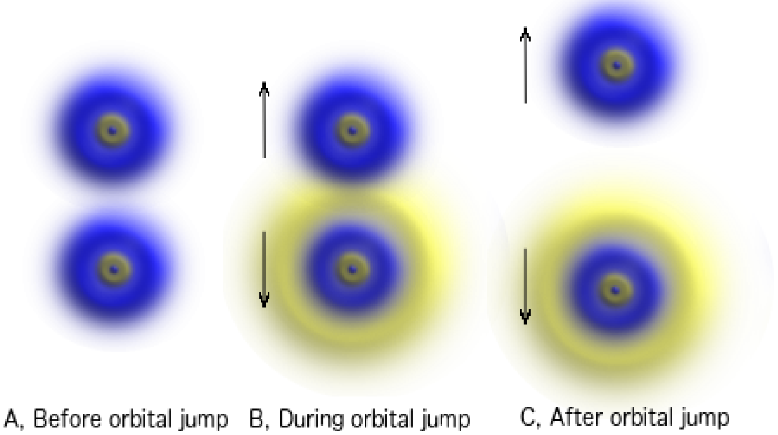


Figure 2: Transimpact due to atomic electron transition.

Transimpacts are explosive events, akin to the sudden burst of popcorn. The resulting momentum imparts significant kinetic energy to neighboring particles, propelling them apart and initiating or enhancing their motion. Atomic electron transitions are routine processes at the microscopic level, occurring continuously in all matter. As a result, transimpacts are widespread interactions that play a fundamental role in many areas of physics, particularly in thermodynamics. They also underlie various observable phenomena, including Brownian motion,[19-21] phase transitions,[22] and the operation of the Crookes radiometer.[23-27] Thus, the kinetic energy of microscopic particles ultimately originates from radiative energy and reflects changes in potential energy.

While transimpacts allow kinetic energy to accumulate within a system, this accumulation does not continue indefinitely. There must be a mechanism by which kinetic energy is converted into other forms of energy—a process referred to as *impactrans*.[16] In this process, the motion or vibration of particles (such as molecules, atoms, or subatomic particles) leads to collisions with neighboring particles via electrostatic interactions. These interactions can "knock" electrons into different orbitals, or even eject them, thereby altering the particles' potential energy. Additionally, the accelerated motion of electrons during these impacts results in the emission of electromagnetic radiation. Through *impactrans*, kinetic energy is thus transformed into both potential and radiative energy.

The transformation of kinetic energy into radiative energy can be observed in a variety of everyday phenomena. For instance, frictional heat is a manifestation of *impactrans*: when you rub your palms together, the warmth you feel results from kinetic energy being converted into radiation. Similarly, the heating observed at the base of a pump tube is also attributed to the effects of *impactrans*. In the case of static electricity, rubbing a plastic rod against fur dislodges electrons from atoms, building up an electric charge—another example of kinetic interactions leading to changes in potential energy.

Definition of Dynamic Energy

Thermal energy, often referred to as heat energy, is traditionally defined as the total kinetic energy of a substance’s particles, encompassing their translational, rotational, and vibrational motion. Temperature is typically understood as a measure of this thermal energy, and by extension, as an indicator of the average kinetic energy of the particles within a system. However, the preceding observations suggest that these conventional definitions may be incomplete or fundamentally flawed, overlooking significant contributions from potential energy and radiative processes.

Based on our study, potential energy, radiative energy, and kinetic energy are not isolated components but are continuously transformed into one another. Together, they form the dynamic portion of a system’s internal energy. While all three influence temperature, it is primarily affected by radiative and potential energy. Kinetic energy contributes indirectly, as it is positively correlated with the other energy forms. To capture this relationship, we define *dynamic energy* as the sum of these three interrelated components:

(9) $$T = R + U + K$$

Here, *T* represents a system’s *dynamic energy*, composed of radiative energy (*R*), potential energy (*U*), and kinetic energy (*K*). These components are termed *dynamic* because their continuous interconversion drives the system’s evolution. Grouping them under the concept of dynamic energy emphasizes their inherently interactive and fluctuating nature. This energetic interplay underpins a wide range of physical and chemical processes, including thermal expansion.

The Cause of Thermal Expansion

Since temperature reflects a system’s dynamic energy, an increase in temperature corresponds to a rise in dynamic energy. Among the three forms of dynamic energy, potential, kinetic, and radiative, both the potential and kinetic components may influence a substance’s volume. As previously discussed, the influence of kinetic energy on volume should be monotonic, leading only to expansion, which cannot account for the phenomenon of thermal contraction. In contrast, structural changes driven by variations in potential energy provide a more plausible explanation, as they can account for both expansion and contraction. At higher energy levels, the extension of interatomic or intermolecular bonds explains typical thermal expansion. Conversely, certain bond structures can reorganize into more compact configurations, enabling thermal contraction under specific conditions.

Under this understanding, the thermal expansion ratio can be estimated based on the observed correlation between temperature and the number of molecular bonds, as shown in Figure 1. Equation 4 provides the molar-specific heat derived from kinetic theory, representing the portion of energy allocated to increasing the kinetic energy of particles. Since each bond can store a portion of the absorbed energy, and given the strong correlation between specific heat and bond count, it is reasonable to assume that all bonds have a similar energy storage capacity. Based on this assumption, an empirical expression for molar-specific heat can be formulated:

(10) $$C_m = \frac{3}{2}R + cB$$

Here, *B* represents the number of bonds in the gas molecules, and *c* denotes the average energy storage capacity per bond. Based on the data for the selected gases shown in Figure 1, each bond stores approximately 6.56 J/mol*K of energy. The first term in the equation accounts for the contribution of kinetic energy in a gas system. In liquids and solids, however, this kinetic contribution is generally much smaller and can be effectively incorporated into the energy stored by intermolecular bonds, which increases the total number of bonds *B*. As a result, Equation 10 can be simplified for liquids and solids as follows:

$$(11) \qquad C_m = cB$$

According to the definition of specific heat, this equation can be rewritten as:

$$(12) \qquad \frac{\Delta E}{\Delta T} = C_m = cB$$

Note that this represents the specific heat for one mole of molecules. The extension of each bond contributes to both linear and volumetric thermal expansion. Accordingly, the equation suggests that thermal expansion is proportional to the number of bonds, scaled by a coefficient factor. This expansion corresponds to the work performed by the specific energy against the ambient pressure *P* over an area *A* and an increment *ΔL* and is expressed as:

$$(13) \qquad \Delta E = PA\Delta L$$

All these contributing factors can be incorporated into the linear and volumetric thermal expansion coefficients, denoted by *l* and *v*, respectively. Using Equations 12 and 13, the expansion coefficients can be expressed as:

$$(14) \qquad \alpha_L = \frac{1}{L}\frac{\Delta L}{\Delta T} = \frac{lB}{P}$$

$$(15) \qquad \alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{vB}{P}$$

These equations are derived under simplifying assumptions and may not be directly applicable in practical scenarios. However, they effectively illustrate the relationship between temperature and the expansion of the bond distances between particles (atoms or molecules), revealing the fundamental mechanism of thermal expansion in materials. The coefficients *l* and *v* are determined by the molecular structure of a substance, particularly the nature of its bonds. The equations indicate that expansion is inversely proportional to ambient pressure (*P*), consistent with physical intuition. Notably, they predict that substances with a greater number of molecular bonds (*B*) tend to exhibit higher thermal expansion coefficients. These theoretical predictions are supported by empirical measurements of both linear and volumetric expansion coefficients, as shown in Table 1.

Name	**Formula**	**Bonds**	**Linear coefficient at 20 °C (x10^{-6}K^{-1})**	**Volumetric coefficient at 20 °C (x10^{-6}K^{-1})**
Water	H_2O	2	69	207
Propylene	C_3H_6	9	150	450
Gasoline	C_8H_{18}	25	317	950

Table 1: Comparison of thermal expansion coefficient with different numbers of bonds in molecules. The coefficient is generally greater with more bonds in molecules, as predicted by Equations 10, 11, 14, and 15. The liquid thermal expansion coefficients in the table are measured at 1 atm and 20 °C (x10^{-6}K^{-1}).

Since thermal expansion is influenced by the molecular bond structure, it is understandable that it may not be uniform in all directions, particularly in crystalline materials. Depending on the arrangement of molecules, some substances may exhibit greater expansion along certain directions than others, leading to anisotropic thermal behavior.

The Cause of Thermal Contraction

Because the bond structure determines the spacing between particles, a substance typically exhibits uniform thermal expansion as long as its bond structure remains unchanged. However, in certain materials, changes in bond structure can lead to significant variations in thermal expansion, and in some cases, even thermal contraction. A well-known example is water near 4 °C, where thermal contraction occurs due to structural changes in hydrogen bonding, illustrating how bond configuration can directly influence thermal behavior.

A water molecule consists of one oxygen atom covalently bonded to two hydrogen atoms. Because the oxygen nucleus contains significantly more protons, and due to its high electronegativity, it attracts the shared electrons more strongly, resulting in an uneven distribution of charge. As a result, the oxygen atom carries a partial negative charge, while the hydrogen atoms carry partial positive charges. This polarity enables the oxygen atom of one water molecule to attract the hydrogen atoms of adjacent molecules, forming hydrogen bonds. These hydrogen bonds are intermolecular forces and are much weaker than the intramolecular covalent bonds within each water molecule.

In both water and ice, hydrogen bonds are responsible for the intermolecular attraction. At lower temperatures, these bonds become shorter and stronger. Around 4 °C, they are strong enough to act like scaffolding, fixing the relative positions of water molecules and forming less dense, hollow structures, such as those found in snowflakes. As the temperature continues to drop, this crystalline arrangement becomes more pronounced, resulting in volume expansion despite decreasing dynamic energy. Although conventional thermal expansion due to bond lengthening still occurs, its effect is outweighed by the structural changes caused by the reorganization of hydrogen bonding at lower temperatures.

At higher temperatures, the hydrogen bonds lengthen and weaken. Eventually, transimpacts disrupt these scaffolds, causing molecules to lose their fixed relative positions. Without this structural framework, water molecules pack more densely than in ice. As a result, above 4 °C, normal thermal expansion driven by changes in bond length becomes dominant, governing water’s typical expansion behavior.

Additionally, it is important to note that attractive forces between particles can manifest both as bond forces between atoms or molecules and as the attraction between an electron and its host nucleus. Therefore, substances composed of monatomic molecules also exhibit thermal expansion, which is typically uniform in all directions. In contrast, asymmetric thermal expansion and contraction are more likely to occur in crystals with complex bond structures.

Conclusions

Thermal expansion primarily arises from changes in the bond structures between particles within a substance. As bonds absorb energy, their lengths can increase to store additional potential energy. This bond spacing may appear as the distance between molecules in intermolecular bonds, the separation between atoms in intramolecular bonds, or the orbital radius of electrons. Dynamic energy is predominantly stored as potential energy within these bonds, closely correlating with temperature changes. Thermal contraction can also occur, particularly in materials with specific bond arrangements that favor the formation of less dense structures.

Revision History

- 11/18/2023: 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)
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- 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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