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Phase Transitions

States of Matter and Exotic Phases

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Contents

Introduction

Chapter 1: The Discovery of Phase Transitions

Chapter 2: Key Characteristics of Phase Transitions

Chapter 3: The Science Behind Phase Transitions

Chapter 4: Observation and Measurement of Phase Transitions

Chapter 5: Important Features of Phase Transitions

Chapter 6: Phase Transitions in Context

Chapter 7: Research and Exploration of Phase Transitions

Chapter 8: Significant Discoveries About Phase Transitions

Chapter 9: Challenges and Mysteries of Phase Transitions

Chapter 10: Future Directions in Phase Transitions Research

Chapter 11: Fun Facts and Trivia About Phase Transitions

Chapter 12: Conclusion: The Significance of Phase Transitions

Conclusion

This free sample contains the Introduction and Chapter 1. The complete book contains the full contents above.

Introduction

In physics, chemistry and biology, a phase transition (or phase change) is the physical process of transition between one state of a medium and another. Commonly the term is used to refer to changes among the basic states of matter: solid, liquid, and gas, and in rare cases, plasma. A phase of a thermodynamic system and the states of matter have uniform physical properties.

During a phase transition of a given medium, certain properties of the medium change as a result of the change of external conditions, such as temperature or pressure. This can be a discontinuous change; for example, a liquid may become gas upon heating to its boiling point, resulting in an abrupt change in volume. The identification of the external conditions at which a transformation occurs defines the phase transition point.

Phase transitions commonly refer to when a substance transforms between one of the four states of matter to another. At the phase transition point for a substance, for instance the boiling point, the two phases involved - liquid and vapor, have identical free energies and therefore are equally likely to exist. Below the boiling point, the liquid is the more stable state of the two, whereas above the boiling point the gaseous form is the more stable.

Common transitions between the solid, liquid, and gaseous phases of a single component, driven by temperature and pressure, form the everyday map of the subject. For a single component, the most stable phase at different temperatures and pressures can be shown on a phase diagram. Such a diagram usually depicts states in equilibrium.

A phase transition usually occurs when the pressure or temperature changes and the system crosses from one region to another, like water turning from liquid to solid as soon as the temperature drops below the freezing point. In exception to the usual case, it is sometimes possible to change the state of a system diabatically (as opposed to adiabatically) in such a way that it can be brought past a phase transition point without undergoing a phase transition.

The resulting state is metastable, i.e., less stable than the phase to which the transition would have occurred, but not unstable either. This occurs in superheating and supercooling, for example. Metastable states do not appear on usual phase diagrams. Phase transitions can also occur when a solid changes to a different structure without changing its chemical makeup. In elements, this is known as allotropy, whereas in compounds it is known as polymorphism.

The change from one crystal structure to another, from a crystalline solid to an amorphous solid, or from one amorphous structure to another (polyamorphs) are all examples of solid to solid phase transitions. The martensitic transformation occurs as one of the many phase transformations in carbon steel and stands as a model for displacive phase transformations. Order-disorder transitions such as in alpha-titanium aluminides. As with states of matter, there is also a metastable to equilibrium phase transformation for structural phase transitions.

A metastable polymorph which forms rapidly due to lower surface energy will transform to an equilibrium phase given sufficient thermal input to overcome an energetic barrier. Many dynamic, or soft, microporous materials exhibit structural phase transitions between closed and open forms. Metal-organic frameworks, in particular, have been extensively studied for this behavior.

Near the critical temperature, measurable quantities stop behaving smoothly: a heat capacity, for instance, will typically follow a power law rather than leveling off.

The heat capacity of amorphous materials has such a behaviour near the glass transition temperature where the universal critical exponent $\alpha = 0.59$ A similar behavior, but with the exponent ν instead of α, applies for the correlation length.

For

Chapter 1: The Discovery of Phase Transitions

Here the book's first practical lesson appears: transitions are reluctant. Water free of dust can sit far below its freezing point, supercooled and waiting for a nucleus to grow on; a superheated liquid, finally disturbed, flashes to vapor with startling violence. In solids the same reluctance preserves metastable polymorphs — crystal arrangements that persist for years even though another structure is the true energy minimum, because climbing over the barrier takes thermal input nobody supplies. White tin slowly going gray in a cold winter, or a diamond surviving indefinitely at room pressure, are the classic exhibits.

The phase landscape can be more complex, with intermediate phases discovered. Further examples show that guest molecules can stabilize specific phases, resulting in crystal configurations that depend on the composition of the surrounding atmosphere. Phase transitions can also describe the change between different kinds of magnetic ordering. The most well-known is the transition between the ferromagnetic and paramagnetic phases of magnetic materials, which occurs at what is called the Curie point.

Another example is the transition between differently ordered, commensurate or incommensurate, magnetic structures, such as in cerium antimonide. A simplified but highly useful model of magnetic phase transitions is provided by the Ising model. Phase transitions involving solutions and mixtures are more complicated than transitions involving a single compound.

While chemically pure compounds exhibit a single temperature melting point between solid and liquid phases, mixtures can either have a single melting point, known as congruent melting, or they have different liquidus and solidus temperatures resulting in a temperature span where solid and liquid coexist in equilibrium. This is often the case in solid solutions, where the two components are isostructural.

There are also a number of phase transitions involving three phases: a eutectic transformation, in which a two-component single-phase liquid is cooled and transforms into two solid phases. The same process, but beginning with a solid instead of a liquid is called a eutectoid transformation. A peritectic transformation instead starts from a solid: on heating, a two-component single-phase solid splits into a solid phase and a liquid phase. A peritectoid reaction resembles a peritectic one, except that only solid phases are involved.

A monotectic reaction consists of change from a liquid and to a combination of a solid and a second liquid, where the two liquids display a miscibility gap. Separation into multiple phases can occur via spinodal decomposition, in

which a single phase is cooled and separates into two different compositions. Non-equilibrium mixtures can occur, such as in supersaturation. Other phase changes include a stop halfway: some materials melt through a liquid-crystal mesophase, neither fully solid nor fully liquid, before arriving at the ordinary liquid.

The dependence of the adsorption geometry on coverage and temperature, such as for hydrogen on iron (110). The emergence of superconductivity in certain metals and ceramics when cooled below a critical temperature. The emergence of metamaterial properties in artificial photonic media as their parameters are varied. Quantum condensation of bosonic fluids (Bose-Einstein condensation). The superfluid transition in liquid helium is an example of this. The breaking of symmetries in the laws of physics during the early history of the universe as its temperature cooled.

Isotope fractionation occurs during a phase transition, the ratio of light to heavy isotopes in the involved molecules changes. When water vapor condenses (an equilibrium fractionation), the heavier water isotopes (18O and

2H) become enriched in the liquid phase while the lighter isotopes (16O and 1H) tend toward the vapor phase. Phase transitions occur when the thermodynamic free energy of a system is non-analytic for some choice of thermodynamic variables (cf.

This condition generally stems from the interactions of a large number of particles in a system, and does not appear in systems that are small. Phase transitions can occur for non-thermodynamic systems, where temperature is not a parameter. Examples include: quantum phase transitions, dynamic phase transitions, and topological (structural) phase transitions. In these types of systems other parameters take the place of temperature. For instance, connection probability replaces temperature for percolating networks.

Paul Ehrenfest classified phase transitions based on the behavior of the thermodynamic free energy as a function of other thermodynamic variables. The Ehrenfest classification allows for both phase transitions whose lowest derivative of the free energy is discontinuous at the transition, as well as for continuous phase transformations, where the bonding character of a material changes, but there is no discontinuity in any free energy derivative.

Under the Ehrenfest scheme, discontinuous phase transitions are labeled by the lowest derivative of the free energy that is discontinuous at the transition: e.g., first-order phase transitions exhibit a discontinuity in the first derivative of the free energy with respect to some thermodynamic variable. The various solid/liquid/gas transitions are classified as first-order transitions because they

involve a discontinuous change in density, which is what one gets by differentiating free energy against pressure, then inverting.

Transition to a mesophase between solid and liquid, such as one of the "liquid crystal" phases.

Second-order phase transitions are continuous in the first derivative (the order parameter, the gradient of free energy against the external field, stays continuous across the boundary) but exhibit discontinuity in a second derivative of the free energy.

These include the ferromagnetic phase transition in materials such as iron, where the magnetization, obtained as the free energy's slope against applied field strength, increases continuously from zero as the temperature is lowered below the Curie temperature; the magnetic susceptibility, the second derivative of the free energy with the field, changes discontinuously.

Under the Ehrenfest scheme, there could in principle be third, fourth, and higher-order phase transitions, but in practice, only first- and second-order phase transitions are generally observed. Examples of exceptions to this include the Gross-Witten-Wadia phase transition in 2-D lattice quantum chromodynamics, which is a third-order phase transition, and the Tracy- Widom distribution, which can be interpreted as a third-order transition. The Curie points of many ferromagnetics are also considered third-order transitions, as shown by their specific heat having a sudden change in slope.

The concept of the second-order phase transition, was for a while, controversial, as it seemed to require two "sheets" of the Gibbs free energy to osculate exactly, which was considered so unlikely as to likely never occur. Cornelis Gorter replied the criticism, pointing out that the Gibbs free energy surface might have two sheets on one side, but only one sheet on the other side, creating a forked appearance.

The first example of a phase transition discovered that did not fit into the Ehrenfest classification was the exact solution of the Ising model, discovered in 1944 by Lars Onsager. The exact specific heat differed from the earlier mean-field approximations, which had predicted that it has a simple discontinuity at critical temperature; instead, the exact specific heat diverged logarithmically at the critical temperature. In the following decades, the Ehrenfest classification was replaced by a simplified scheme that is able to incorporate such transitions.

In the modern classification scheme, phase transitions are divided into two broad categories, named similarly to the Ehrenfest classes: First-order phase transitions are those that involve a latent heat. During such a transition, a

system either absorbs or releases a fixed (and typically large) amount of energy per volume.

During this process, the temperature of the system will stay constant as heat is added: the system is in a "mixed-phase regime" in which some parts of the system have completed the transition and others have not. Familiar examples are the melting of ice or the boiling of water.

Second-order phase transitions, also called "continuous phase transitions", are characterized by a divergent susceptibility, an infinite correlation length, and a power law decay of correlations near criticality. Examples of second-order phase transitions are the ferromagnetic transition, the superconducting transition, and the superfluid transition. Lev Landau has presented a phenomenological theory of second-order phase transitions.

In contrast to viscosity, thermal expansion and heat capacity of amorphous materials show a relatively sudden change at the glass transition temperature, a change that enables accurate detection using differential scanning calorimetry measurements. Several transitions are known as infinite-order phase transitions. They are continuous but break no symmetries. The most famous example is the Kosterlitz-Thouless transition in the two-dimensional XY model. Many quantum phase transitions, e.g., in two-dimensional electron gases, belong to this class.

Apart from isolated, simple phase transitions, there exist transition lines as well as multicritical points, when varying external parameters like the magnetic field or composition. The liquid-glass transition is observed in many polymers and other liquids that can be supercooled far below the melting point of the crystalline phase. This is atypical in several respects. It is not a transition between thermodynamic ground states: it is widely believed that the true ground state is always crystalline.

Glass is a quenched disorder state, and its entropy, density, and so on, depend on the thermal history. Therefore, the glass transition is primarily a dynamic phenomenon: on cooling a liquid, internal degrees of freedom successively fall out of equilibrium. Some theoretical methods predict an underlying phase transition in the hypothetical limit of infinitely long relaxation times. No direct experimental evidence supports the existence of these transitions.

This continuous variation of the coexisting fractions with temperature raised interesting possibilities. On cooling, some liquids vitrify into a glass rather than transform to the equilibrium crystal phase.

This happens if the cooling rate is faster than a critical cooling rate, and is attributed to the molecular motions becoming so slow that the molecules

cannot rearrange into the crystal positions. This slowing down happens below a glass-formation temperature Tg, which may depend on the applied pressure. If the first-order freezing transition occurs over a range of temperatures, and Tg falls within this range, then there is an interesting possibility that the transition is arrested when it is partial and incomplete.

Extending these ideas to first-order magnetic transitions being arrested at low temperatures, resulted in the observation of incomplete magnetic transitions, with two magnetic phases coexisting, down to the lowest temperature. First reported in the case of a ferromagnetic to anti- ferromagnetic transition, such persistent phase coexistence has now been reported across a variety of first-order magnetic transitions. These include colossal-magnetoresistance manganite materials, magnetocaloric materials, magnetic shape memory materials, and other materials.

The interesting feature of these observations of Tg falling within the temperature range over which the transition occurs is that the first-order magnetic transition is influenced by magnetic field, just like the structural transition is influenced by pressure. The relative ease with which magnetic fields can be controlled, in contrast to pressure, raises the possibility that one can study the interplay between Tg and Tc in an exhaustive way.

Phase coexistence across first-order magnetic transitions will then enable the resolution of outstanding issues in understanding glasses. In any system containing liquid and gaseous phases, there exists a special combination of pressure and temperature, known as the critical point, at which the transition between liquid and gas becomes a second-order transition. Near the critical point, the fluid is sufficiently hot and compressed that the distinction between the liquid and gaseous phases is almost non-existent.

This is associated with the phenomenon of critical opalescence, a milky appearance of the liquid due to density fluctuations at all possible wavelengths (including those of visible light). Phase transitions often involve a symmetry breaking process. For instance, the cooling of a fluid into a crystalline solid breaks continuous translation symmetry: each point in the fluid has the same properties, but each point in a crystal does not have the same properties (unless the points are chosen from the lattice points of the crystal lattice).

Typically, the high-temperature phase contains more symmetries than the low-temperature phase due to spontaneous symmetry breaking, with the exception of certain accidental symmetries (e.g. An order parameter is a measure of the degree of order across the boundaries in a phase transition system; it normally takes on the value of zero in one phase (usually above the

critical point) and nonzero in the other.

At the critical point, the order parameter susceptibility — its response to a change in the controlling intensive variable — will usually diverge. An example of an order parameter is the net magnetization in a ferromagnetic system undergoing a phase transition. For liquid/gas transitions, the order parameter is the difference of the densities. From a theoretical perspective, order parameters arise from symmetry breaking. When this happens, one needs to introduce one or more extra variables to describe the state of the system.

For example, in the ferromagnetic phase, one must provide the net magnetization, whose direction was spontaneously chosen when the system cooled below the Curie point. However, note that order parameters can also be defined for non-symmetry-breaking transitions. Some phase transitions, such as superconducting and ferromagnetic, can have order parameters for more than one degree of freedom.

In such phases, the order parameter may take the form of a complex number, a vector, or even a tensor, the magnitude of which goes to zero at the phase transition. There also exist dual descriptions of phase transitions in terms of disorder parameters. These indicate the presence of line-like excitations such as vortex- or defect lines. Symmetry-breaking phase transitions play an important role in cosmology. As the universe expanded and cooled, the vacuum underwent a series of symmetry-breaking phase transitions.

For example, the electroweak transition broke the SU(2)×U(1) symmetry of the electroweak field into the U(1) symmetry of the present-day electromagnetic field. This transition is important to explain the asymmetry between the amount of matter and antimatter in the present- day universe, according to electroweak baryogenesis theory. Progressive phase transitions in an expanding universe are implicated in the development of order in the universe, as is illustrated by the work of Eric Chaisson and David Layzer. See also relational order theories and order and disorder.

Continuous phase transitions are easier to study than first-order transitions due to the absence of latent heat, and they have been discovered to have many interesting properties. The phenomena associated with continuous phase transitions are called critical phenomena, due to their association with critical points. Continuous phase transitions can be characterized by parameters known as critical exponents. The most important one is perhaps the exponent describing the divergence of the thermal correlation length by approaching the transition.

Over 2000 °C already performed, theoretical possible up to the highest crystal

material, such as tantalum hafnium carbide 4215 °C.)

Phase transitions play many important roles in biological systems.

In physics, a quantum phase transition (QPT) is a phase transition between different quantum phases (phases of matter at zero temperature).

A phase transition from water to ice, for example, involves latent heat (a discontinuity of the internal energy

The electroweak phase transition marks the moment the Higgs field first took a nonzero value, splitting the unified electroweak force and leaving electromagnetism standing on its own.

A GUT transition that breaks this hypothetical unified state into the Standard model's

Phase transition

Deposition is the phase transition in which gas transforms into solid without passing through the liquid phase. Deposition is a thermodynamic process.

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ABOUT THE AUTHOR

Aira Astralis is a science writer specializing in astronomy and space exploration. Her work spans the full breadth of humanity's relationship with the cosmos -- from the earliest naked-eye observations to the engineering marvels of modern space missions.

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She believes that the most important frontier is not out there but in the gap between what scientists discover and what the public understands. Her books exist to close that gap.