Thermodynamics and Phase Transitions in Elementary Matter

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Outline

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The fundamentals

Thermodynamics deals with isolated systems in equilibrium. These are isolated in the sense that the energy and material exchanged between the system and its surroundings can be totally controlled. They are in equilibrium in the sense that when they are left to evolve, they do not change.

Because equilibrium states are the only things of interest here, thermodynamics considers only transitions between one equilibrium state and another. So it is often stated in terms of reversible changes.

Reversibility and quasi-static changes

Mechanical energy can be stored in a fluid and completely recovered if changes are made slowly enough. Why slowly?

Variables of state and the problem of heat

How do we distinguish one equilibrium state from another? Thermodynamics deals with are extensive variables. Since these are used to specify the state of a system, they are also called variable of state.

An example

Since mechanical work (performed reversibly) can be stored in a system, the energy of a system must be a variable of state. Why is recoverable energy an extensive quantity?

When you raise the temperature of a body, you add heat to it. Heat seems to be additive. Is it a variable of state?

Joule's experiment and the first law

Joule's experiments showed that one unit mechanical work done on a body always produced exactly the same amount of heat always.

Natural units

Joule's results imply that heat is energy. So heat should be measured in the same units as energy. In that case Joule's constant is unity: $J = 1$.

The first law of thermodynamics is often stated as saying that the total amount of energy in a system is conserved. This means that the total energy in a system is a variable of state.

Systems without thermodynamics

Take a system of N electrons. The Coulomb energy is

$$E(N) = \frac{1}{2}\sum_{i\equiv j}\frac{e^2}{r_{ij}}, \qquad \text{where} \qquad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|\,.$$

Add one more electron, very far away from the rest, so that all $r_{i,N+1} \simeq r$, *i.e.*, these distances are nearly equal. Then

$$E(N+1) \approx E(N) + \frac{Ne^2}{r} = E(N) + NE',$$

instead of $E(N+1) = E(N) + E'$. So the energy is not extensive, and one cannot use thermodynamics for this system.

The same argument can be given for a system of particles attracting each other by gravity. There is no thermodynamics for systems with long-range interactions.

Globular clusters are not gases

M80 globular cluster contains $\mathcal{O}(10^5)$ stars. It is about 95 light years in diameter. The stars are about 12 Gyr old.

Conservation laws, state variables and symmetries

Every conserved quantity which is also extensive must be variables of state in thermodynamics. Noether's theorems relates conserved quantities to symmetries of Hamiltonians. So symmetries of a system dictate the variables of state.

Since electric charge is conserved and additive, it is a variable of state. The symmetry involved is the U(1) gauge symmetry of electrodynamics. The energy of the electromagnetic fields must be included in the first law of thermodynamics.

A puzzle

In the study of thermodynamics of a gas, the volume is taken as a variable of state. This is clearly additive. What is the conserved quantity which it is due to?

Summary

1. Thermodynamics deals with equilibrium states of isolated systems.
2. The Hamiltonian of a system has some symmetries. These give rise to conserved quantities.
3. All additive conserved quantities are needed to specify the state of a system.
4. Thermodynamics can be applied only to systems with time independent Hamiltonians. Then energy may be an additive conserved quantity.

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How to specify an equilibrium state

Variables of state have been derived from conservation laws. Even if a system evolves in time, these do not change. So conserved quantities are not enough to specify an equilibrium state. There has to be at least one more macroscopic extensive variable which tells us whether a system is in equilibrium.

There is exactly one such variable. This is the entropy. Entropy is dimensionless.

Gibbs space

Let us assume that there are D conserved quantities. Denote the variables of state by X_i, where $1 \leq i \leq D$. Let the entropy be S. Then the quantities $\{S, \mathbf{X}\}$ parametrize Gibbs space. The dimension of Gibbs space is $D+1$.

The second law of thermodynamics

The second law of thermodynamics states that an isolated system always changes so that $dS \geq 0$. As a result the equilibrium state is a state in which entropy is maximum. There must be a surface in Gibbs space on which all the equilibrium states lie: $S(\mathbf{X})$.

Define thermodynamic couplings to be the gradients

$$K_i = \frac{\partial S}{\partial X_i}.$$

One of these is $\beta = \partial S / \partial E = 1/T$. As a result, when heat is added to a sytem at fixed temperature, one has $dS = dQ/T$.

The second law of thermodynamics also implies that the couplings are continuous over the equilibrium surface (so the surface is also continuous), and that the equilibrium surface is convex (so thermal equilibrium is stable).

Photon gas: 1

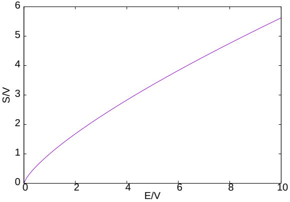
The only conserved quantity in a gas of photons is the energy, E. So Gibbs space is 2 dimensional. The equilibrium states are given by $S(E)$. As always, $\partial S/\partial E = 1/T$.

Natural units

Photons travel at the speed of light. It is natural to choose units so that $c = 1$. Then energy and mass are measured in the same units, and length and time are also measured in the same units.

Photons also obey quantum mechanics so it is natural to choose $\hbar = 1$. Then energy and inverse of length are measured in the same units.

Photon gas: 2



V is a trivial quantity (why?), so one can work in terms of the energy density, $\mathcal{E} = E/V$, and entropy density, $\mathcal{S} = S/V$. Dimensionally $[\mathcal{S}] = M^3$ and $[\mathcal{E}] = M^4$, so we must have $\mathcal{S} = c\mathcal{E}^{3/4}$. Is $S(E)$ continuous and convex?

By definition,

$$\frac{1}{T} = \frac{\partial \mathcal{S}}{\partial \mathcal{E}} = \frac{3c}{4\mathcal{E}^{1/4}}.$$

This implies that

$$\mathcal{E} = \left(\frac{3cT}{4}\right)^4, \qquad \mathcal{S} = c\left(\frac{3cT}{4}\right)^3.$$

We have derived the Stefan-Boltzmann Law.

Energy representation

Invert the function $S(E,\mathbf{X})$ to write $E(S,\mathbf{X})$. The geometry of the equilibrium surface does not change by changing this description.

Intensive variables are defined to be

$$T=\frac{\partial E}{\partial S},\qquad K_i=\frac{\partial E}{\partial X_i}$$

One also defines thermodynamic response functions

$$\chi_i=\frac{\partial X_i}{\partial K_i}=\left(\frac{\partial^2 E}{\partial X_i^2}\right)^{-1}.$$

Thermodynamic stability (convexity) requires that all $\chi_i>0$.

Example: For the photon gas, the specific heat

$$C=\frac{\partial\mathcal{E}}{\partial T}=\frac{3}{4}\mathcal{S}>0$$

Neutrino gas: 1

Neutrinos are uncharged elementary particles with a mass m which is very small. Their interactions are so small that they can be neglected. For $T \ll 1$ TeV, the number of neutrinos is conserved. If $T \gg m$ and the Fermionic nature of neutrinos is taken into account, then they are both relativistic and quantum.

The Gibbs space is 3-dimensional. The state variables are S, E, and the volume V of a certain fixed number of neutrinos. The equilibrium states of the gas is given by a function $S(E, V)$ or $E(S, V)$. Then we have

$$T = \frac{\partial E}{\partial S}, \quad P = -\frac{\partial E}{\partial V}, \qquad C_V = \frac{\partial E}{\partial T}, \quad \kappa_T = \frac{\partial E}{\partial P}$$

The equation of state is the function $E(T, P)$.

Neutrino gas: 2

Instructive to work with state variables S, E, and the number of neutrinos N. Then the equilibrium states are given by the function $S(E,N)$ or $E(S,N)$. In this case we have

$$T = \frac{\partial E}{\partial S}, \quad \mu = \frac{\partial E}{\partial N}, \qquad C = \frac{\partial E}{\partial T}, \quad \chi = \frac{\partial E}{\partial \mu}$$

The equation of state is the function $E(T,\mu)$.

By the usual dimensional argument, when $T \gg m$, then

$$\mathcal{E} = T^4 f\left(\frac{\mu}{T}\right), \qquad \mathcal{S} = T^3 g\left(\frac{\mu}{T}\right).$$

Since neutrinos are non-interacting, the EoS can be found using the statistical mechanics of an ideal Fermi gas. It would be much harder to compute the EoS if neutrinos were interacting.

Neutrino gas: 3

Since $E(S,N)$, one may write

$$\frac{\partial}{\partial N}\,\frac{\partial E}{\partial S}=\frac{\partial}{\partial S}\,\frac{\partial E}{\partial N},$$

since this is just taking the derivatives in two different orders. But the two first derivatives define intensive variables, so

$$\frac{\partial T}{\partial N}=\frac{\partial\mu}{\partial S}.$$

This is called a Maxwell relation. They always arise from an interchange of the order of taking derivatives.

For the neutrino gas, using the representation $E(S,V)$, one also has the Maxwell relation

$$\frac{\partial T}{\partial V}=-\frac{\partial P}{\partial S}.$$

There are no Maxwell's relations for the photon gas.

Summary

1. Thermodynamics needs a new extensive quantity called the entropy, S. This is maximum in equilibrium for fixed values of other state variables $\mathbf{X}$. Gibbs space is the space with coordinates $\{S, \mathbf{X}\}$.
2. The equilibrium states of a system are specified by functions $S(\mathbf{X})$ which are continuous and convex.
3. In the energy representation intensive variables and response functions were defined.
4. The thermodynamics of an ideal fluid of bosons and another of fermions was examined.

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Surfaces and tangents

Within the Gibbs space we have an equilibrium surface $E(\mathbf{X})$. The equation of the tangent to this surface at $\mathbf{X} = \mathbf{X}^0$ is

$$\mathcal{T}(\mathbf{X}) = E(\mathbf{X}^0) + \sum_i K_i (X_i - X_i^0), \qquad \text{where} \quad K_i = \left.\frac{\partial E}{\partial X_i}\right|_{X_i = X_i^0},$$

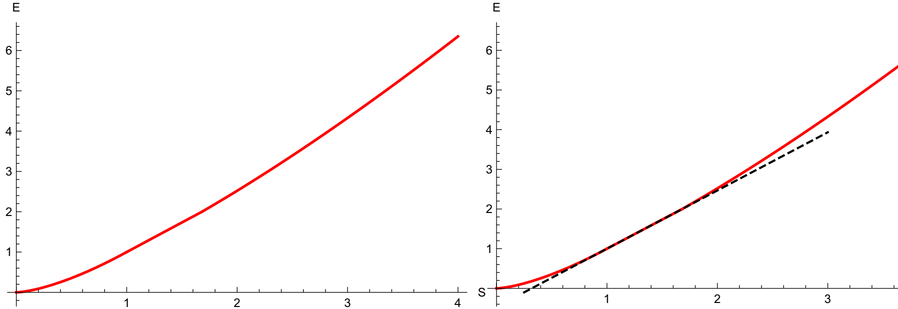
At any ordinary point, $E(\mathbf{X})$ has a Taylor expansion

$$E(\mathbf{X}) = E(\mathbf{X}^0) + \sum_i K_i (X_i - X_i^0) + \frac{1}{2} \sum_i \chi_i (X_i - X_i^0)^2 + \cdots$$

As a result, the difference between the surface and the tangent increases quadratically as one moves away from $\mathbf{X}^0$.

Wherever the difference $E(\mathbf{X}) - \mathcal{T}(\mathbf{X})$ increases slower than quadratically, the system is said to have a phase transition.

A simple example

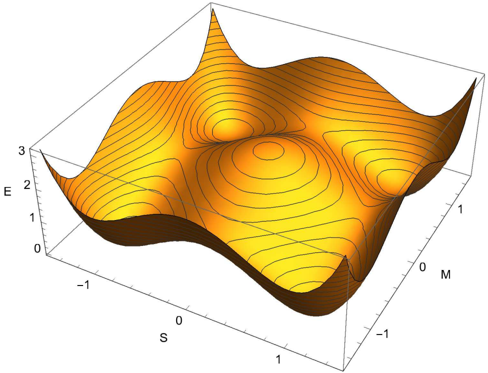


2-dimensional Gibbs space. $E(S)$ has a portion which is a straight line; T remains constant as E and S increase. This means a latent heat, therefore first order transition. This example is for a gluon gas.

In general if the difference between the equilibrium surface and the

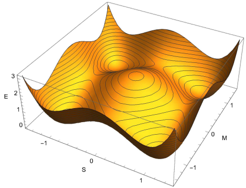
Ginzburg-Landau Model

$$E(S,M) = (S^2-1)^2 + (M^2-1)^2$$



This is not convex. Maxwell's construction is to draw a tangent plane which touches the minima. The resulting surface is convex.

What is a first order transition?



Each of the four minima corresponds to one state of matter in the system. The tangent plane joining the minima contain all equilibrium states which are mixtures of these four states in various combinations.

So a first order transition region is the region where more than one phase can coexist.

Since the region contains more than one phase, this part of the equilibrium surface does not describe homogeneous systems. Everywhere else the system is homogeneous.

A technical aside

A function $f(x)$ is not completely specified if we give $f'(x)$. This is because the integral of $f'(x)$ can be shifted by a constant to give any one of the family of functions $f(x) + c$.

One way to specify a function through its tangent is to give the value of tangent at $x = 0$. The equation of the tangent is $\mathcal{T}(x) = f(x^0) + f'(x^0)(x - x^0)$. In the intercept $\mathcal{T}(0)$ we use $p = f'(x^0)$ to eliminate x^0 and replace it by p. Then we can write

$$\mathcal{E}(p) = \mathcal{T}(0) = f(x^0(p)) - x^0(p)p$$

$\mathcal{E}(p)$ is called the Legendre transform.

Example: If $f(x) = x^3$, then $p = f'(x) = 3x^2$. So we have $x = \sqrt{p/3}$. As a result, we can write

$$\mathcal{E}(p) = f(x) - xp = \left(\frac{p}{3}\right)^{3/2} - 3\left(\frac{p}{3}\right)^{3/2} = -2\left(\frac{p}{3}\right)^{3/2}.$$

Helmholtz free energy

Helmholtz free energy is a Legendre transform of the energy, $E(S,\mathbf{X})$, given by $F(T,\mathbf{X})=E-TS$.

Photon gas

For the photon gas, since the Gibbs space is two dimensional, this is specially simple. Writing $\mathcal{E}=(\mathcal{S}/c)^{4/3}$, as before, we can find T in terms of $\mathcal{S}$. Inverting this gives the Stefan-Boltzmann Law, which we have written earlier

$$\mathcal{E}=\left(\frac{3cT}{4}\right)^4,\qquad T\mathcal{S}=\frac{4}{3}\left(\frac{3cT}{4}\right)^4.$$

Then one can write the free energy density as

$$\mathcal{F}=\mathcal{E}-T\mathcal{S}=-\frac{1}{3}\left(\frac{3cT}{4}\right)^4.$$

First order transition

Suppose that a system undergoes a first order phase transition. Then the temperature remains constant at T_c while the energy and entropy change continuously from (E_0, S_0) to (E_1, S_1). In the transition the energy changes as

$$E(S) = E_0 + \frac{E_1 - E_0}{S_1 - S_0}\,(S - S_0), \qquad T_c = \frac{E_1 - E_0}{S_1 - S_0}$$

The latent heat is $L = E_1 - E_0$. Clearly, from the above equation one finds $L = T_c(S_1 - S_0)$.

The Helmholtz free energy goes from $F_0 = E_0 - T_c S_0$ to $F_1 = E_1 - T_c S_1$. The change in free energy is

$$F_1 - F_0 = (E_1 - E_0) - T_c(S_1 - S_0) = 0.$$

There is no change in free energy for a first order transition.

Phase diagrams

If a system has a Gibbs space with dimension $1+D$, then the number of intensive variables is D. The phase diagram is a plot of all the first order transition points in this D dimensional space of $\mathbf{K}$.

If the free energy in one phase is given by a function $F_1(\mathbf{K})$ and in the other by $F_2(\mathbf{K})$. At first order phase transitions one has

$$F_1(\mathbf{K}_c) = F_2(\mathbf{K}_c).$$

So the first order phase transitions lie on a $(D-1)$-dimensional surface in the phase diagram. This is the Gibbs phase rule.

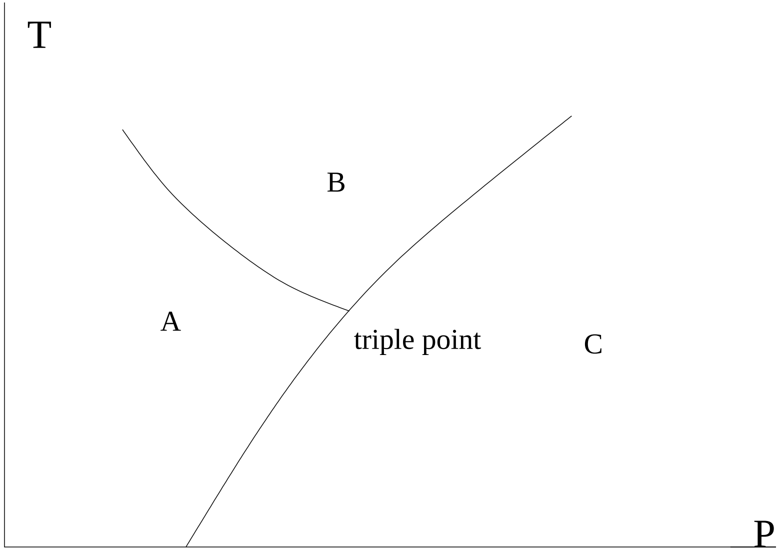
Example: For the gluon gas $D=1$. The phase diagram is labelled by T. There is a first order phase transition at one temperature, T_c.

Other phase diagrams

For a chemically pure substance there are two conserved quantities: the energy and the number of atoms (mass). So $D = 2$. The gas-liquid phase transition occurs along a line in the space labelled by (T, P). The solid-liquid phase transition also occurs along a different line. At a triple point the free energies of the liquid, gas and solid are equal. There may be different structural phases of the solids. Phase transitions between these can also occur along a line. There may be further triple points of these phases. Generally, more than three phases of a pure substance cannot coexist at a single point.

For a relativistic field theory of fermions there are two conserved quantities: the energy and the fermion number. So $D = 2$. Any first order phase transition occurs along a line in the space labelled by (T, μ). If there are more than two phases, then there may be triple points.

Two conserved quantities



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Critical point

If the difference between the energy surface and the tangent at any point $E(\mathbf{X}) - \mathcal{T}(\mathbf{X})$ is non-zero but changes slower than quadratically, then we have a critical point.

Divergent response functions

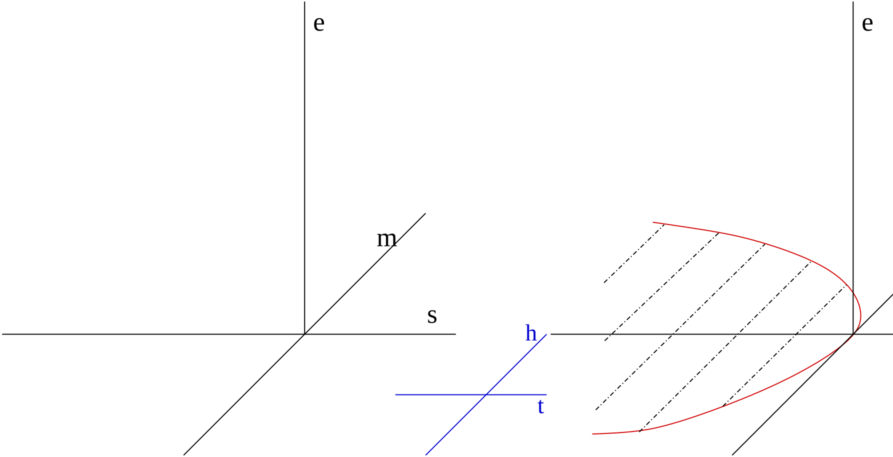
If several derivatives of $E(\mathbf{X})$ vanish at $\mathbf{X}^0$, then $F = E - \mathcal{T} \propto (X_i - X_i^0)^{1+n}$, where $n > 1$. As a result, $\mathbf{X}^0$ is a critical point.

Write $\mathbf{x} = \mathbf{X} - \mathbf{X}^0$ and $E(\mathbf{X}) - E(\mathbf{X}^0) = e(\mathbf{x})$. By the usual definitions, $x_i \propto k_i^{1/n}$. As a result we have

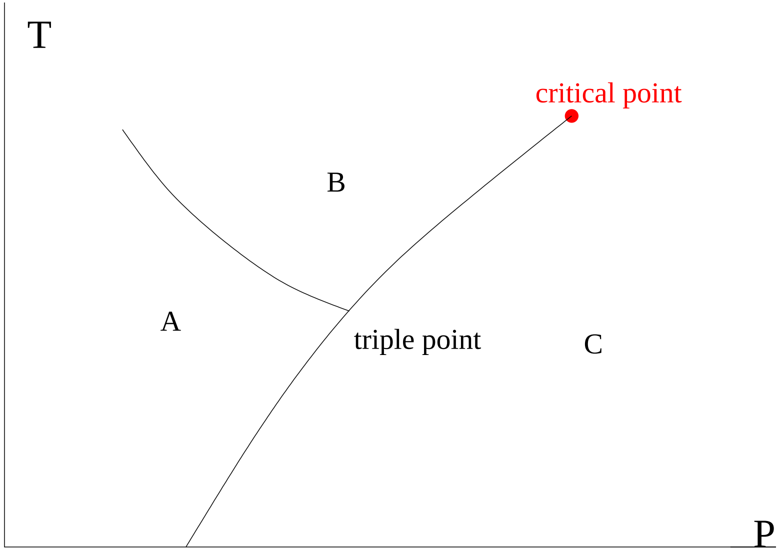
$$\chi_i = \frac{dx_i}{dk_i} \propto k_i^{1/n-1}.$$

This is divergent for $n > 1$. Free energy is singular.

Phase diagram



Two conserved quantities



Three conserved quantities: strong interactions

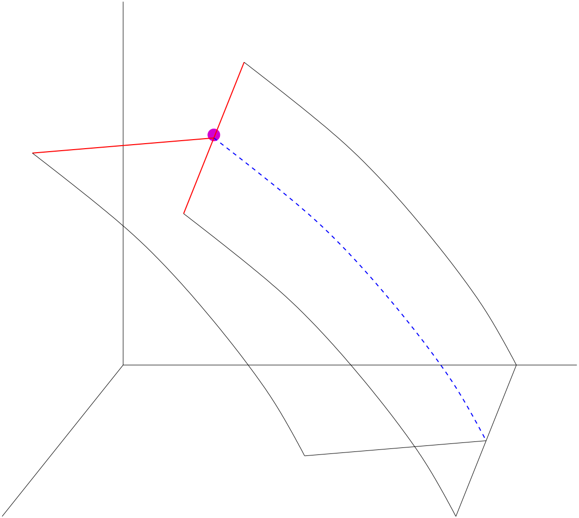
Strong interactions are the theory of the constituents of hadrons, *i.e.*, baryons (such as protons, neutrons, Ω^-) and mesons (such as pions, kaons, ρ). The theory contains fermions called quarks interacting by exchanging gluons. There is a non-abelian gauge symmetry in the theory. There are three conserved quantities: energy (E), baryon number (B) and isospin (Q). B and Q are two different finds of "conserved charge" of quarks.

Gibbs space is 4-dimensional. There are 3 intensive variables

$$T = \frac{\partial E}{\partial S}, \quad \mu_B = \frac{\partial E}{\partial B}, \quad \mu_Q = \frac{\partial E}{\partial Q}$$

So the phase diagram is 3-dimensional

Three conserved quantities: strong interactions



Summary

1. Phase transitions occur at points where the equilibrium surface departs from its tangent slower than quadratically. First order phase transitions occur when the tangent and the surface coincide. These are places where two phases coexist. Free energies of two phases are equal at first order phase transition.
2. If Gibbs space is $(D+1)$-dimensional, then the phase diagram is D-dimensional. This presents a picture of where the phase transitions take place. First order transitions occur along $(D-1)$-dimensional surfaces. Two first order surfaces meet along a triple point (or triple surface).
3. First order transitions can end only in critical points. Here the free energies are singular and response functions diverge. Critical surfaces are $(D-2)$-dimensional boundaries of first order surfaces.
4. Critical surfaces meet at $(D-2)$-dimensional tricritical surfaces. These are also boundaries of $(D-2$ dimensional) triple surfaces.

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