

Lecture I

Thermodynamics and Phase Transitions

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1 Thermodynamics

Thermodynamics deals with isolated systems of macroscopic dimensions. Typical **macroscopic** systems contain about 10^{23} particles. The systems are isolated from their surroundings in that the input of any form of energy to them is totally controlled. Thermodynamics is concerned with the behaviour and inter-relations of a set of **extensive variables**, such as the molar volume, V , of a fluid, the total internal energy, U , of a system, or the total magnetisation, M , of a metal. These variables are called extensive because they depend linearly on the amount of material being studied. All other factors remaining the same, if we double the number of molecules in the system, all these quantities double. The number of such extensive variables is very much smaller than the number of microscopic degrees of freedom. We shall carry over into thermodynamics the notion of an **equilibrium** state as one in which the energy is at its minimum, for fixed values of every other extensive variable. The thermodynamical state of any system is the specification of all the extensive quantities that characterise such an isolated macroscopic system in equilibrium.

The **first law of thermodynamics** codifies the result of Joule’s experiments on the interconvertibility of heat, Q , and forms of mechanical energy—

$$dU = \delta Q + \mathbf{F} \cdot d\mathbf{X}, \quad (1)$$

where each X_i stands for an extensive quantity and F_i for a “force”. If one of the X_i is V , then the corresponding $F_i = -P$ (where P is the pressure in equilibrium). The change in mechanical energy is just $\mathbf{F} \cdot d\mathbf{X}$. The internal energy differs from this mechanical energy by taking into account the heat. Note that U , P and V are all **functions of state**, i.e., they depend only

on the thermodynamical states of the system, and not, for example, on its previous history. However, Q is not a state function. The value of every state function, X_i , can be measured— either directly, or by the work done in changing the state. This gives unambiguous results, because the work put into the system to change X_i can be extracted out of it by letting x_i revert back to its old value in a controlled way. While the amount of heat added to a system, δQ can also be measured, the notion of a total heat content of a system turns out to be meaningless.

Why?

Reversible changes of a system are those in which the system always remains in equilibrium, and hence can be described by thermodynamics while it changes. Usually this means changing the system very slowly, *i.e.*, in a quasi-static manner. An adiabatic change in a system is one in which no heat is added or removed from the system; in other words, an adiabatic change happens to a thermally isolated system. Irreversible changes lie outside the scope of thermodynamics.

The **second law of thermodynamics** postulates the existence of a new extensive state variable— the entropy, S , which is an increasing function of U . The law states that in an adiabatic change in the state of a system, the entropy always increases—

$$dS(\text{adiabatic}) \geq 0. \quad (2)$$

Almost all thermodynamical identities follow from these two laws and the notions that surround them. In the remainder of this lecture, we shall restate these notions in a way that allows us to deal in a very straight-forward manner with phase transition.

A word about units. The first law tells us that heat is measured in units of energy. If we take the entropy to be dimensionless, then $\delta Q = TdS$ codifies the view that temperature is also to be measured in energy units. Boltzmann's constant, k , is then dimensionless and set equal to unity. If historical relics, such as the Kelvin scale, make an appearance then it is a simple matter to reinstate $k = 1.380\,658\,(12) \times 10^{-23}$ J/K.

2 Geometrical View

The space of all extensive variables, including the entropy, is called the **Gibbs space**. Thermodynamics is the study of relationships and movements of a system in Gibbs space. The equilibrium states of a system correspond to

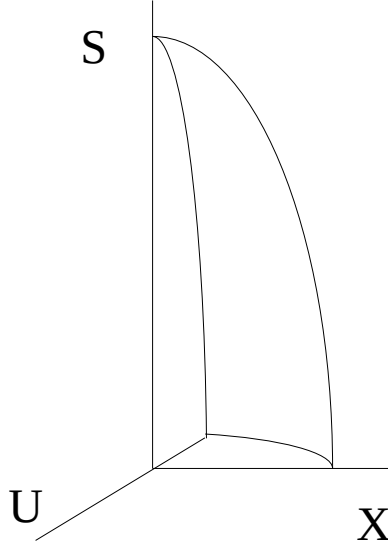


Figure 1: A three dimensional Gibbs space. The curved surface shown is a possible section of the entropy surface.

those of maximum entropy for given values of other extensive variables. Each equilibrium state thus corresponds to a point on the hypersurface $S(X)$ called the **entropy surface**. The **coupling** conjugate to X_i is defined to be

$$\mathbf{K}_i = \frac{\partial S}{\partial X_i}. \quad (3)$$

For example, the coupling $\beta \equiv 1/T = \mathbf{K}_U$.

An entropy surface must satisfy the properties

1. **Continuity**: The couplings, $\mathbf{K}_i$, are continuous over the surface.
2. **Stability**: The surface is **convex**, *i.e.*, lies entirely below the tangent plane drawn anywhere on the surface. This implies that $\partial^2 S / \partial X_i^2 \leq 0$ everywhere on the surface.

The whole entropy surface may not be physical. Extra conditions govern the physical region of Gibbs space: for example, the condition that $T \geq 0$

is necessary to impose the condition that S increases with U . This representation, $S(X)$, of the stable states of the system is called the **entropy representation**.

An alternative representation of the same geometry is called the **energy representation**. It is obtained by describing the surface of stable states by the functional dependence of the internal energy, U , on the rest of the extensive variables, including S . This is just a change of variables from $S(U, \mathbf{X})$ to $U(S, \mathbf{X})$; the entropy surface remains the same in the two representations.

The **intensive variables** are defined, analogous to the couplings, through

$$K_i = \frac{\partial U}{\partial X_i}. \quad (4)$$

It is also customary to define the **response functions**

$$\chi_i = \frac{\partial X_i}{\partial K_i} = \left(\frac{\partial^2 U}{\partial X_i^2} \right)^{-1}. \quad (5)$$

The stability condition now leads to the more familiar statement that the energy is at a minimum. This also implies that the surface is everywhere above any tangent plane, *i.e.*, $\partial^2 U / \partial X_i^2 > 0$, globally. This further leads to the usual form of the stability conditions, $\chi_i > 0$.

Example I.1 (A single component fluid) The Gibbs space is three dimensional, consisting of S , U and the molar volume, V . The two dimensional entropy surface is given by a relation $S(U, V)$. In the energy representation the same surface has the description $U(S, V)$. The familiar intensive variables, the temperature T and the pressure P are given by

$$\begin{aligned} T &= K_S = \frac{\partial U}{\partial S} \Big|_V = \frac{1}{\mathbf{K}_U} \\ P &= -K_V = -\frac{\partial U}{\partial V} \Big|_S = \frac{\partial S}{\partial V} \Big|_U \Big/ \frac{\partial S}{\partial U} \Big|_U = \frac{\mathbf{K}_V}{\mathbf{K}_U}, \end{aligned} \quad (6)$$

and are seen to have a simpler form in the energy representation. The stability condition on the specific heat at constant volume, C_V , is obtained as

$$C_V = \frac{\partial U}{\partial T} \Big|_V \geq 0 \quad \text{since} \quad 0 \geq \frac{\partial^2 S}{\partial U^2} \Big|_V = \frac{\partial(1/T)}{\partial U} \Big|_V = -\frac{1}{T^2} \frac{\partial T}{\partial U} \Big|_V \quad (7)$$

Given that $T \geq 0$, it is continuous over the entropy surface, and the surface is convex, the entropy of a fluid increases with T .

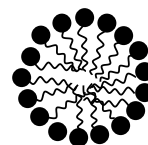
Do we have everything we need? By assuming $T \geq 0$ we have ensured that the entropy increases with U . Reversible changes move along the entropy surface. Equilibrium states are stable. What about the second law? By definition we have

$$dS = \mathbf{K}_i dX_i = \beta dU + \mathbf{K}_i dX_i = \beta \delta Q + (F_i + \mathbf{K}_i) dX_i. \quad (8)$$

Now, for adiabatic changes, $\delta Q = 0$ and $dS \geq 0$, which implies that $f_i \geq -\mathbf{K}_i$.

Problem set I.1

1. Check that the form $S(U, V) = \log UV$ gives an admissible entropy surface. Show that $PV = T = U$.
2. From all the definitions encountered till now, show that for reversible processes of a single component fluid, $dE = TdS - PdV$.
3. A rubber band is stretched by a weight hanging from it. The Gibbs space is three dimensional— $\{S, U, L\}$, where L is the length of the band. What are the intensive quantities? What are the stability conditions? What are their physical interpretations?
4. Amphipathic molecules, such as the active ingredients in soaps, have a polar head and a non-polar tail. When added to water, they form globules with all the polar heads sticking out and the tails tucked in together. These structures are called **micelles**. The Gibbs space is three dimensional— $\{S, U, N\}$, where N is the number of moles of the amphipathic molecule per unit mole of water. What are the intensive quantities? What are the stability conditions? What are their physical interpretations?
5. For some system, if U'' and U''' vanish for some X , then what are the stability conditions? (Primes denote derivatives with respect to X .)
6. For a ferromagnetic solid with bulk magnetisation M , what is the dimension of Gibbs space? What are intensive quantities, the stability conditions, and their physical significance?



7. In the three dimensional Gibbs space of a single component fluid, draw an admissible entropy surface. Show the paths corresponding to reversible and adiabatic changes. Also show the path corresponding to a Carnot cycle.

8. If

$$C_P = \left. \frac{\partial U}{\partial T} \right|_P,$$

then show that $C_P \geq C_V$. Apart from the proof, give a simple physical argument why this should be so.

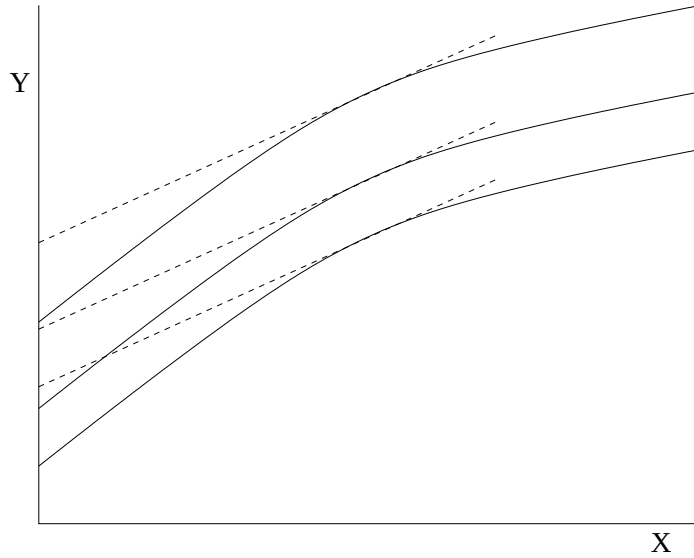


Figure 2: At each X , all three curves have the same derivative, Y' . They are distinguished by the intersection of the tangent with the Y axis. The Legendre transform is the function which specifies how this intersection point varies with the slope.

Since the surface $U(S, X)$ is globally convex, each tangent touches it at one point and cannot intersect it elsewhere. As a result, each point on the surface has a unique value of the intensive variables K_i . It would then seem possible to describe the entropy surface entirely in terms of the K_i . However

this is wrong. The entropy surface cannot be obtained by only specifying its derivatives, since such a specification will generate all rigid translations of the surface. Instead, the surface has to be specified by its derivatives at all points and the intersection of the tangent plane with the U axis. Such a description is called a **Legendre transform**. Consider the tangent plane to U at X^0 , i.e., $\mathcal{T}(X; X^0) = U(X^0) + \sum_i \mathbf{K}_i(X_i - X_i^0)$. Its intercept on the U axis is given by

$$\mathcal{T}(\mathbf{K}_i) = U(X^0) - \sum_i \mathbf{K}_i X_i^0. \quad (9)$$

After elimination of $U(X_0)$ and X_0 through the definition of the function and its derivatives, this defines the Legendre transform. We can also transform only a subset of the extensive variables. Convexity of $U(X)$ implies convexity of $\mathcal{T}(\mathbf{K})$.

Prove!

Legendre transforms of U with respect to subsets of K_i are called **free energies**. The familiar **Helmholtz free energy** is the transform $F = U - TS$. The **enthalpy** $H = U - PV$. The **Gibbs' free energy** is the full transform $G = U - TS - PV$. The convexity of U leads to the familiar condition that equilibrium states minimize free energy.

The **Maxwell's relations** give the equality of mixed derivatives for the energy surface or its Legendre transforms. For example, starting from $U(S, V)$, we obtain

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right) = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right) \quad \text{implying} \quad \left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial P}{\partial S} \right|_V. \quad (10)$$

Three other relations may be obtained for simple fluids. In Gibbs spaces of higher dimensions further relations are obtained.

Problem set I.2

1. Show that the following functions $f(x)$ have the Legendre transforms $g(y)$ shown, where, in each case, $y = f'(x)$.

- (a) $f(x) = x^{1+n}$, and $g(y) \propto |y|^{1+1/n}$, and hence, $g(y)$ has a cusp for $n > 1$.
- (b) $f(x) = \exp x$, and $g(y) = y(1 - \log y)$.
- (c) $f(x) = -1/(1+x)$, and $g(y) = y - 2\sqrt{y}$.

For an entropy surface $S(X)$, and the plane $S_T(X; X^0)$ tangent to it at X^0 , we have the relation

$$S(X^0 + x) = S_T(X^0 + x; X^0) + s(x), \quad (x \rightarrow 0) \quad (11)$$

where $s(x) \leq 0$ and both s and s' vanish at $x = 0$. At a generic point, since S has a Taylor expansion with a non-vanishing second derivative, $s(x)$ decreases quadratically. The special points where $s(x)$ is non-quadratic, thermodynamic stability is achieved in different ways. These points are called **phase transition points**. We shall deal with them next.

3 Phase Transitions: 2-d Gibbs Spaces.

An old thermodynamic definition of orders of phase transitions is known as **Ehrenfest's classification**. According to this, if some extensive variable X has a discontinuity as the conjugate intensive variable, K , is tuned, then a **first order phase transition** is said to occur. If X is continuous but the derivative $\partial X/\partial K$ is infinite, then a **second order phase transition** is deemed to have occurred. Sometimes this is extended to $(n + 1)$ -th order phase transitions when $(n - 1)$ partial derivatives of X (with respect to K) are continuous but the n -th has a discontinuity or is infinite. In order to develop ideas in simple concrete situations, we now deal with a two dimensional section of the Gibbs space, passing through the entropy axis. The perpendicular direction we call X .

It is possible for a function $\Sigma(X)$ to satisfy the condition on the continuity of the derivative $K = \Sigma'(X)$, while violating that on the stability. In this case an acceptable entropy function, $S(X)$, is generated by taking the outermost envelope of the tangent lines to $\Sigma(X)$. If we imagine constructing $S(X)$ by rolling a line over Σ , then this line bridges over re-entrant portions of the surface. Thus the entropy function has a portion which is precisely flat. This describes a region of two-phase mixtures, or **first order phase transitions**.

In this two-phase region every tangent line makes contact with the surface Σ at two points, P_- and P_+ . The line joining these two points is a **generator** of the surface. Along any such line, the system is a mixture of the two pure phases achieved at P_- and P_+ , and is specified by the fraction f of one of these states. The value of any extensive variable, X , along the generator is

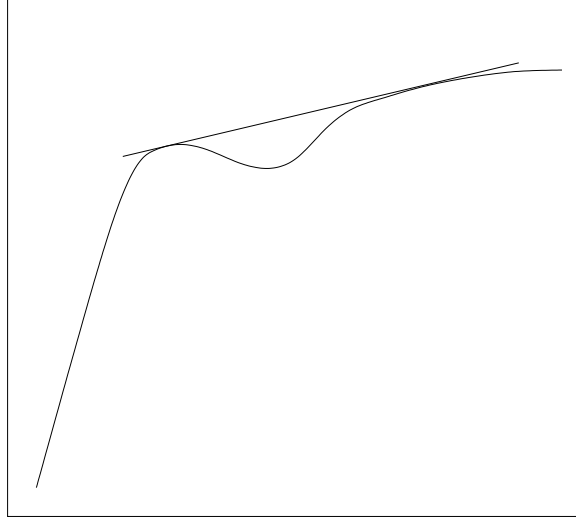


Figure 3: A globally convex function can be formed from the non-convex curve shown by rolling a straight line over it. This is the generic situation at a first order phase transition.

given by $X(f) = fX_- + (1 - f)X_+$. The distribution of X over subsystems is not peaked at $X(f)$ but at the two pure phase values X_- and X_+ . There is no restoring force for disturbances of the system along the generator. Such a disturbance merely changes f , *i.e.*, increases the amount of one phase as the expense of the other.

Example I.2 (Ginzburg-Landau form) Consider, the explicit form $\Sigma(X) = -(X^2 - 1)^2 - BX$. Then, the globally convex entropy is

$$S(X) = \begin{cases} -(X^2 - 1)^2 - BX & \text{for } |X| \geq 1, \\ -BX & \text{for } |X| < 1. \end{cases} \quad (12)$$

The coupling $\mathbf{K} = S'(X)$ is continuous, and equal to the constant $-B$ in the region $-1 < X < 1$. The second derivative $S''(X) \leq 0$ everywhere. For $-1 < X < 1$, S is flat. This region corresponds to a mixture of the pure phases obtained at $X = 1$ and $X = -1$, with $S_+ = B$ and $S_- = -B$. If a system has fraction f of the first phase, then $S(f) = fS_+ + (1 - f)S_-$.

Such a definition of a first order phase transition is equivalent to Ehrenfest's classification. The coupling, $\mathbf{K} = \mathbf{K}^*$, is constant over the two phase

region, and hence does not specify the thermodynamic state completely. S considered as a function of $\mathbf{K}$ has a jump at $\mathbf{K}^*$. The same consideration applies in the energy representation, and further leads to the condition that the Legendre transform, the free energy F , is equal for the two phases and everywhere in the two-phase region. Show!

Next consider a function, $S(X)$, which has slower than quadratic contact with the tangent line at a point X^0 . Then the system undergoes a **second order phase transition** at this point. Disturbances of the system lead to unbounded fluctuations, and hence the system is called **critical**. The deviation from the tangent line, $s(x) \sim x^{1+n}$. In general, n is not a number, since $s(x)$ may be non-analytic at $x = 0$. For such cases we may write $n = n(x)$. The deviation function for the Legendre transform is of the form $|k|^{1+1/n}$, where k is the distance from the point of tangency $\mathbf{K}^0$. Thus, the Legendre transform is regular if and only if $n = 1$. Also, the response function $\chi = dx/dk \propto k^{1/n-1}$, and hence, for $n > 1$, goes to infinity as k goes to zero, as a power of k . This power is called a **critical exponent**. Clearly, this situation corresponds to a second order phase transition in Ehrenfest's classification.

4 Homogeneous Functions, Critical Indices

If X is some extensive variable, and the corresponding density is x , with a thermodynamic expectation value $\bar{x}$, then we can define the correlation function between fluctuations as

$$C(r) = \langle (x(r) - \bar{x})(x(0) - \bar{x}) \rangle. \quad (13)$$

Here $x(r)$ is the value of x in a volume around the point r which is much larger than any microscopic length scale, but much smaller than the system size. In general, the asymptotic fall-off of $C(r)$ defines a correlation length, ξ , through the relation

$$\lim_{r \rightarrow \infty} C(r) = \exp(-r/\xi). \quad (14)$$

At a critical point ξ diverges and the correlations are unbounded. The critical point is reached by tuning all the intensive variables of the problem to their critical values. For example, in one-component fluids, a critical point is specified by the critical temperature, T_c , and the critical pressure, P_c .

In ferromagnetic systems, the temperature and the external magnetic field must be tuned to their critical values, T_c and H_c respectively. In this case, symmetry conditions imply $H_c = 0$.

At P_c (or H_c) the divergence of the correlation length

$$\xi = \begin{cases} \xi_+ |T - T_c|^\nu & (T > T_c) \\ \xi_- |T - T_c|^{\nu'} & (T < T_c) \end{cases} \quad (15)$$

defines two critical exponents ν and ν' . They need not be equal. Precisely at the critical point, the correlation function has the form

$$C(r) \sim |r|^{2-d-\eta}, \quad (16)$$

where η is yet another critical index. The indices ν and η are related to fluctuations in equilibrium.

Since the free energy has a singular part at the critical point, response functions diverge here. At P_c (or H_c) the singular part of the specific heat diverges as

$$C_V \sim \begin{cases} A_+ |T - T_c|^{-\alpha} & (T > T_c) \\ A_- |T - T_c|^{-\alpha'} & (T < T_c). \end{cases} \quad (17)$$

These define the exponents α and α' . Similarly the inverse bulk compressibility also diverges at P_c , and the magnetic susceptibility at H_c . These give two new exponents

$$\chi \sim \begin{cases} A_+ |T - T_c|^{-\gamma} & (T > T_c) \\ A_- |T - T_c|^{-\gamma'} & (T < T_c). \end{cases} \quad (18)$$

Again, the exponents on the two sides of the critical point need not be equal.

In both these examples two phases coexist for $T < T_c$. For the fluid, the difference of the molar volumes from the critical value, V_c , for each of the two pure phases (say, gas and liquid) as a function of T defines two more critical exponents

$$|V - V_c| \sim \begin{cases} (T_c - T)^\beta & (\text{liquid phase}) \\ (T_c - T)^{\beta'} & (\text{gas phase}). \end{cases} \quad (19)$$

The magnetic case is simplified by symmetry. The critical value of the spontaneous magnetisation, $M_c = 0$. Furthermore, the two phases have equal and opposite magnetisations. As a result, $\beta = \beta'$.

The coexistence curves are also described by other exponents. In the magnetic case this exponent describes the vanishing of M at T_c with the applied magnetic field H . Thus,

$$M \sim H^{1/\delta}. \quad (T = T_c) \quad (20)$$

In the fluid case, one may describe the variation of $|V - V_c|$, in the two phases, by two exponents δ and δ' , not necessarily equal.

These exponents are not all independent. With the hypothesis that the internal energy is a homogeneous function of the other extensive variables near a critical point, many relations between them can be obtained. We defer the derivation of such relations to the next section, and end this with some theorems on homogeneous functions.

Theorem I.1 (Power law behaviour of homogeneous functions)

If $F(x)$ is a homogeneous function of x of degree n , then $F(x) \propto x^n$.

Proof: By definition, $F(\lambda x) = \lambda^n F(x)$. Taking $y = \lambda x$ at fixed x , we have $dF(y)/dy = n\lambda^{n-1}F(x)/x$. Dividing both sides of this equality by $F(y)$, we get

$$\frac{d \log F(y)}{dy} = \frac{n}{y}. \quad (21)$$

This has the solution $F(y) \propto y^n$. ■

Theorem I.2 (Euler's theorem)

If F is a generalised homogeneous function of n variables such that

$$F(\lambda^{a_1}x_1, \lambda^{a_2}x_2, \dots) = \lambda^N F(x_1, x_2, \dots), \quad (22)$$

then

$$NF(x_1, x_2, \dots) = \sum_{i=1}^n a_i \frac{\partial F}{\partial x_i} x_i. \quad (23)$$

Proof: Writing $F_\lambda = F(\lambda^{a_1}x_1, \lambda^{a_2}x_2, \dots)$, and $F = F(x_1, x_2, \dots)$, we have

$$\frac{dF_\lambda}{d\lambda} = \sum_i \frac{d\lambda^{a_i}}{d\lambda} x_i \frac{\partial F_\lambda}{\partial x_i}. \quad (24)$$

Also $dF_\lambda/d\lambda = N\lambda^{N-1}F$. Hence, putting $\lambda = 1$, the theorem follows. ■

Theorem I.3 (Factorisation of homogeneous functions)

If F is a generalised homogeneous function of n variables such that

$$F(\lambda^{a_1}x_1, \lambda^{a_2}x_2, \dots) = \lambda^N F(x_1, x_2, \dots), \quad (25)$$

then F can be written in the factorised form

$$F(x_1, x_2, \dots) = x_1^{N/a_1} G(x_2/x_1^{a_2/a_1}, \dots). \quad (26)$$

Proof: Choose $\lambda = x_1^{-1/a_1}$. The theorem follows. ■

Euler's theorem has an application not connected with phase transitions. In the energy representation, $U(X)$, since both U and X are extensive, and scale linearly with the amount of material, we have $U(\lambda X) = \lambda U(X)$. Then Euler's theorem leads to the Gibbs-Duhem relation

$$U = K_i X_i. \quad \text{which gives} \quad U = TS - PV, \quad (27)$$

for a single component fluid.

5 Phase Transitions: The General Case.

We return to the geometric description of phase transitions, now working in Gibbs spaces of larger than two dimensions. Given a primitive entropy surface $\Sigma(X)$, which may obey the continuity condition but violate that on stability, we can proceed as before to construct a globally convex entropy function $S(X)$ by taking the outermost envelope of the tangent hypersurfaces to Σ . As before, re-entrant portions of Σ are bridged by planar sections, leading to a description of multi-phase coexistence. However, more complicated situations may arise in these higher dimensional cases. We classify the phenomena here.

The two-phase region of an entropy surface consists of a ruled surface. The **generators** of such a surface are straight lines joining two pure-phase points, also called **separation points**. The locus of the two ends of the generators trace out a pair of lines called the **coexistence curve**. There are three topologies available to these curves—

1. They terminate at the limit of some physical property, e.g., at $T = 0$.
2. The two curves intersect at a critical point. The direction of the limiting generator at this point defines the **order parameter**.

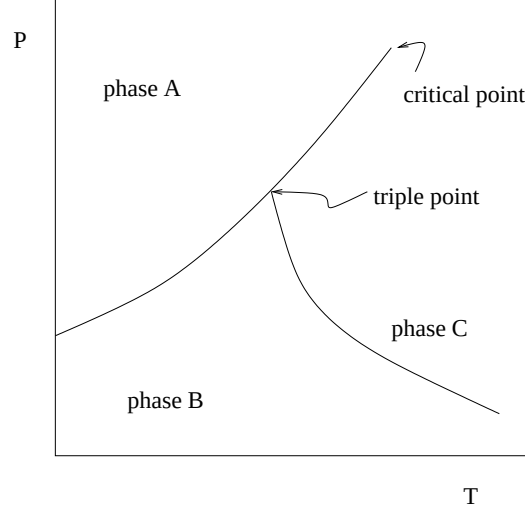


Figure 4: Possible phase diagram of a single component fluid illustrates various definitions.

3. More than two curves intersect at **multicritical points**. This phenomenon can only occur in Gibbs spaces of three or more dimensions.

The image of the entropy surface in the plane of two independent intensive variables is called a **phase diagram**. The image of a phase coexistence region on the phase diagram is a line called the **transition line**. Such a line ends at a critical point (see Figure 4).

Example I.3 (Ginzburg-Landau energy) Consider the entropy surface given in the energy representation by

$$U(x, y) = \begin{cases} Ax^2 + (x + y^2)^2 & (x > -y^2) \\ Ax^2 & (x \leq -y^2). \end{cases} \quad (28)$$

The primitive function $\mathcal{U}(x, y) = Ax^2 + (x + y^2)^2$ is re-entrant between the coexistence curves

$$y = \pm\sqrt{-x}, \quad (x < 0). \quad (29)$$

Hence, $U(x, y)$ contains a ruled surface in this region corresponding to two phase coexistence. The origin is a critical point. The generators are the lines of constant (negative) x , and the order parameter is the line $x = 0$, i.e.,

the y -axis. The phase diagram is the plane corresponding to the intensive couplings

$$p = \begin{cases} 2(1+A)x + 2y^2 \\ 2Ax \end{cases} \quad q = \begin{cases} 4y(x + y^2) \\ 0 \end{cases} \quad (30)$$

In this plane the transition line is given by $q = 0$, ending in the critical point $p = q = 0$.

Recall that each point in the space of intensive parameters corresponds to a tangent to the entropy surface. Hence the generators of the two-phase region correspond to the intersection of two almost parallel tangents. The directions of the generators are given in terms of first derivatives along the transition line. Such a relation is called the **Clausius-Clapeyron equation**.

Example I.4 (One component fluid) Since the Gibbs' free energy in the two pure phases are equal at the two ends of a generator, $G_+(T, P) = G_-(T, P)$. Hence, under infinitesimal changes of T and P , we obtain $dG_+ = dG_-$. This gives $-S_+dT + V_+dP = -S_-dT + V_-dP$, and therefore,

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}. \quad (31)$$

The derivative is the slope of the transition line in the phase diagram. ΔS and ΔV are the differences between the pure phase values of these quantities along a generator. The Clausius-Clapeyron equation above gives the direction of the generator in terms of these quantities.

We now examine the relations between the critical exponents α , β , γ and δ . It turns out to be useful to set up some shorthand notation. First we define the deviation between a function, F , and the surface F_T tangent to it at X^0

$$F(X^0 + x) = F_T(X^0 + x; X^0) + f(x). \quad (32)$$

The deviation function $f(x)$ and its derivatives are zero at $x = 0$. This corresponds to a shift in the origin. The same shift can be simultaneously applied to the Legendre transform.

In the following discussion we shall follow the conventions that

1. The Gibbs space has dimension 3, unless otherwise stated.

2. We shall work in the energy representation and use the deviation function $u(x, y)$. This is sufficient unless the energy itself is the order parameter. We name the intensive variable t and h . They are defined as $t = u_x$ and $h = u_y$.
3. The critical point is at the origin, *i.e.*, $x_c = y_c = 0$.
4. The Legendre transform of the internal energy, $g(t, h)$, is also shifted so that the critical point is at the origin of the phase diagram, $t_c = h_c = 0$. Thus, derivatives of u vanish at the critical point.
5. The y -axis is the direction of the order parameter.
6. The order parameter is a symmetry direction, so that $u(x, y) = u(x, -y)$ and $g(t, h) = g(t, -h)$.
7. The two phase region occurs for $x < 0$.
8. $u(x, y)$ is regular except at the origin and in the two-phase region.
9. $u_{yy} = 0$ at the origin. Thus, the energy surface is anomalously flat at the critical point in the direction of the order parameter. This includes the case of both a power-law behaviour $u \sim y^k$ and a logarithmic singularity $u \sim y^2 / \log |y|$.

Now we discuss in detail the case of a **scaling form** for the energy function $u(x, y)$. Assume that near the origin $u \sim x^{1+a}$ for constant y , and $u \sim y^{1+\delta}$ for constant x . By the requirement (8) at least one of a and δ is greater than unity. The requirement (9) specifies that $\delta > 1$. Using Euler's theorem we can write

$$u(x, y) = \begin{cases} y^{1+\delta} u_+(z) & (y > 0) \\ |y|^{1+\delta} u_-(z) & (y < 0) \end{cases} \quad \text{where } z = \frac{x}{|y|^h} \quad \text{and } h = \frac{1+\delta}{1+a}. \quad (33)$$

The functions $u_+(z)$ and $u_-(z)$ are regular and non-zero near $z = 0$. Then, with $u_+(0) = u_0$, we find that

$$y = (u_0 h)^{1/\delta}. \quad (34)$$

Hence, δ is precisely the critical exponent defined in eq. (20). A similiar argument can be given for δ' in terms of u_- .

The behaviour of u_+ and u_- are also constrained for $z \rightarrow \infty$. The analysis is made simpler by writing $b = 1/h$ and

$$u(x, y) = \begin{cases} x^{1+a}\phi_+(z) & (x > 0) \\ |x|^{1+a}\phi_-(z) & (x < 0, y_c \leq y \leq y_{c'}) \\ |x|^{1+a}\psi(z) & (x < 0, y_c > y) \\ |x|^{1+a}\psi'(z) & (x < 0, y_{c'} < y) \end{cases} \quad \text{where } z = \frac{y}{|x|^b}. \quad (35)$$

Here $y_c(x)$ and $y_{c'}(x)$ denote the coexistence curves, and enclose the two-phase region. Both ϕ_+ and ϕ_- are non-zero and regular near the origin. Hence, along the line $y = 0$, the definition $t = u_x$ yields the relation $x \propto t^{1/a}$.

Since $C_v \propto 1/u_{xx}$, we find

$$\alpha = 1 - \frac{1}{a}. \quad (36)$$

Similarly, using the definition $\chi \propto 1/u_{yy}$ and a Taylor series expansion of ϕ_+ and ϕ_- , we find

$$\gamma = \frac{(1+a)(\delta-1)}{a(1+\delta)}. \quad (37)$$

The coexistence curve $y_c(x)$ is given by the matching condition $\psi(z_c) = \phi_-(z_c)$. Given the solution z_c , we find that

$$y_c = z_c |x|^b \sim t^{b/a}. \quad (38)$$

This immediately gives the remaining exponent

$$\beta = \frac{1+a}{a(1+\delta)}. \quad (39)$$

A similar analysis with ψ' gives the other coexistence curve $y_{c'}(x)$, and hence $\beta' = \beta$. In most cases of interest, we have $a < \delta$, and hence $b, b' < 1$. In this case, the coexistence curves become tangential to the line $y = 0$ at the critical point. Also, $\beta < 1$ for all admissible values of a and δ , even in the case $a > \delta$.

The example of eq. (28) corresponds to $a = 1$ and $\delta = 3$. This gives $\alpha = 0$, $\beta = 1/2$ and $\gamma = 1$. These go under the name of **classical exponents**, or **mean field exponents**. The first theory to yield these exponents was the Van der Waals' theory for the gas-liquid transition. Subsequently, it was put

System	Material	α	β	γ
Ferromagnets	Fe	0.12 ± 0.01	0.34 ± 0.02	1.33 ± 0.01
	Ni	0.10 ± 0.03	0.33 ± 0.03	
	YFeO ₃		0.35 ± 0.02	
Gas-liquid	CO ₂		0.32	1.23–1.24
Binary mixtures	Na-ND ₃	0.014 ± 0.011	0.324 ± 0.005	1.228 ± 0.039
Micellization			0.34 ± 0.08	1.216 ± 0.013

Table 1: Critical exponents for several systems with three dimensional Gibbs space. The exponent δ is between 4.6 and 4.8 in those of the above systems where it has been measured.

into modern form by Landau, and found uses as diverse as the description of ferromagnetic ordering and superconductivity.

From the analysis above, it is clear that there are only two independent critical exponents when the Gibbs space is three-dimensional. Thus, there must be two relations between the four exponents. These can clearly be written in many forms. Conventionally, they are given as

$$\alpha + 2\beta + \gamma = 2 \quad (\text{Rushbrooke's law}), \quad (40)$$

$$\alpha + \beta(\delta + 1) = 2 \quad (\text{Griffith's law}). \quad (41)$$

It turns out that critical exponents for real systems, such as those tabulated in Table 1, satisfy these relations very well. However, these exponents differ significantly from mean field exponents.

Relations between ν and η and these indices can be obtained from a scaling hypothesis for the correlation function of eq. (13). Correlation functions are not extensive variables, nor are they intensive variables (in the sense of being derivatives of the internal energy with respect to another extensive variable). Hence they lie outside the purview of thermodynamics. However, a scaling hypothesis for this function yields two further relations between ν , η and these four exponents (see problem on correlations). Thus, the number of independent exponents remains two. This finds a justification in the **renormalisation group**.

Problem set I.3

1. Show that the scaling form for the energy density leads to scaling for

the equation of state in the form

$$q = y^\delta F\left(\frac{p}{y^{1/\beta}}\right). \quad (42)$$

This leads to the **law of corresponding states**, the equation of state is an universal relation between the ratios q/y^δ and $p/y^{1/\beta}$. (Note that p , q and y are the deviations of the corresponding quantities from their critical values.)

2. Show that the **Kadanoff scaling form**

$$C(r) = |r|^{2-D-\eta} \mathcal{C}\left(\frac{r^\nu}{p}\right), \quad (43)$$

where $C(r)$ is the correlation function in eq. 13 for a D -dimensional system, and $g(x)$ has finite range, gives the relation between exponents

$$\gamma = \nu(2 - \eta), \quad (\text{Fisher's law}), \quad (44)$$

$$\nu D = 2 - \alpha, \quad (\text{Josephson's law}). \quad (45)$$

Use the definition $\chi = \int d^D r C(r)$. Relations between exponents which explicitly involve the spatial dimension D are called **hyperscaling** relations.

3. Devise a statistical test that all the systems listed in Table 1 have the same critical exponents. Use the scaling laws to fill in the missing entries, and give estimates of their uncertainties (assume that the error estimates are of one-sigma Gaussian errors). What possible thermodynamic criteria can you devise for systems to belong to this universality class of critical behaviour?

The scaling form for the internal energy leads to the observation that h/y^δ and t/x^a are functions only of the ratio y/x^b . As a result, one can write **Widom's scaling form** for the Gibbs' free energy,

$$g(t, h) = \begin{cases} t^{2-\alpha} \mathcal{G}_+(h/t^{\beta\delta}) & (t > 0), \\ |t|^{2-\alpha} \mathcal{G}_-(h/|t|^{\beta\delta}) & (t < 0). \end{cases} \quad (46)$$

where both G_+ and G_- are regular at the origin. Such a form describes only the leading behaviour of the free energy close to the critical point; a regular

part, neglected here, also exists. We shall later return to a brief consideration of it.

We saw that the critical behaviour of a system, in the sense of values of the exponents eqs. (17–20), is specified completely by the scaling form of the internal or the free energy. As a result, it is possible that very different physical systems may show the same critical behaviour (see, for example, Table 1). This notion is called **universality**. The critical indices specify an **universality class**. Not just the critical exponents, but the full functions $\mathcal{G}_{\pm}$ could be universal. As a result, ratios of certain quantities taken just above and below the critical point also turn out to be universal. For example, $C_V(0^+)/C_V(0^-)$ is equal to $\mathcal{G}_+(0)/\mathcal{G}_-(0)$, and hence universal. The Rushbrooke and Griffiths’ relations can be obtained from eq. (46).

The description of a C -component fluid requires a Gibbs space of $C + 2$ dimensions, which are C molar fractions and U and S . By a Legendre transform, $C - 1$ extensive variables can be traded for the corresponding intensive quantities, and U for the corresponding free energy. When the intensive variables are held fixed, the system has an effective description equivalent to that of the one-component fluid. In the full Gibbs space, however, multicritical points may exist. At such points the number of independent exponents may be as large as $C + 1$. Even if only a normal critical point occurs, there may be more than 2 independent critical exponents, and several more dependent ones.

Homogeneity of a function of two variables is not preserved under linear transformations. Hence, in general, there are corrections to the scaling forms given above. nevertheless, it is possible for the scaling property to be valid for the dominant term of an asymptotic expansion. This gives, as an example, the **asymptotic scaling form**

$$u(x, y) = |x|^{1+a} \phi \left(|x|^{1-b}, \frac{y}{|x|^b} \right). \quad (47)$$

This gives corrections to the scaling formulæ in eqs. (17–20), in the form of subleading exponents.

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