

# Statistical mechanics handout 2

Give an expression for the differential  $df$  in terms of the differentials  $dx$  and  $dy$ .

Explain how the coefficients of the  $dx$  and  $dy$  terms in your equation can be obtained by making reference to power series and limits.

**Differentials** We write the differential of a function of  $x$  and  $y$  as  $df = C_x(x, y)dx + C_y(x, y)dy$ , where  $C_x$  and  $C_y$  are functions of  $x$  and  $y$ . In other words we can write the differential  $df$  as a linear combination of the differentials  $dx$  and  $dy$  with coefficients  $C_x(x, y)$  and  $C_y(x, y)$ . Linear combinations are intuitive - what is difficult is the interpretation of the symbols  $dx$  and  $dy$  as these are used to represent infinitesimally small changes in the  $x$  and  $y$  values respectively. It is thus perhaps simpler to start by considering a finite change in  $\delta x$ . When we make this change (holding  $y$  fixed) the corresponding change in  $f$  can be written as:

$$f(x + \delta x, y) - f(x, y) = \sum_{i=1}^{\infty} C_i(x, y)(\delta x)^i$$

where here the right hand side comes about because we can express any real number in terms of a power series. Dividing both sides of the above by  $\delta x$  and taking the limit as  $\delta x \rightarrow 0$  brings us to:

$$\lim_{\delta x \rightarrow 0} \frac{f(x + \delta x, y) - f(x, y)}{\delta x} = C_1(x, y) + \lim_{\delta x \rightarrow 0} \sum_{i=2}^{\infty} C_i(x, y)(\delta x)^{i-1} = C_1(x, y)$$

We thus arrive at a rather neat definition of our  $C_x(x, y)$  function. It is simply the coefficient of the leading order term in the above power series. By a similar logic  $C_y(x, y)$  is the coefficient of the leading order term in the power series expansion for  $f(x, y + \delta y) - f(x, y)$  that can be written in terms of  $\delta y$ . The limit on the right hand side of the above equation is the definition of the partial derivative so we may rewrite our expression for a differential using:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

In writing all this last formula have assumed that the function  $f(x, y)$  is exact (see below). If the differential is not exact the above formula is not strictly correct as it makes little or no sense to talk about  $\left(\frac{\partial f}{\partial x}\right)_y$  when the function  $f(x, y)$  does not exist.

What is the property of an exact differential

**Exact differentials** are differentials that have the all important property:

$$\left(\frac{\partial C_x}{\partial y}\right)_x = \left(\frac{\partial C_y}{\partial x}\right)_y \quad \text{or} \quad \left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right)$$

If the above expression does not hold for the coefficients in  $df = C_x(x, y)dx + C_y(x, y)dy$  then a function for  $f$  in terms of  $x$  and  $y$  cannot be written down because integrals around closed paths will be non-zero. This makes it nonsensical to ascribe a single value,  $f(x, y)$ , to the point  $(x, y)$  as one can always go around a closed loop and change it.

## Summary

The differential of a function is  $df = C_x(x, y)dx + C_y(x, y)dy$ . If the coefficients in this expression satisfy  $\left(\frac{\partial C_x}{\partial y}\right)_x = \left(\frac{\partial C_y}{\partial x}\right)_y$  the differential is said to be exact and the function  $f(x, y)$  exists. A differential that is not exact (i.e. one that does not have this property) does not have a corresponding  $f(x, y)$  as integrals around closed paths can be non-zero.

Give a formula for the fundamental theorem of calculus

Explain when the integral between  $a$  and  $b$  depends on the path taken

**Integration** The fundamental theorem of calculus states:

$$\frac{d}{db} \int_a^b f(x)dx = f(b)$$

In other words if we want to calculate how much the value of some quantity changes on moving **via a particular path** from point  $a$  to point  $b$  we can do so by calculating an integral. Notice that it is a differential  $f(x)dx$  that appears underneath the integral sign here and that as such the change in the value of the quantity on moving from  $a$  to  $b$  is only independent of the path taken if the differential is exact.

Explain the difference between heat and work

For which of the following quantities does the amount done during a transition from state  $a$  to state  $b$  depend on path taken: heat, work and change in internal energy.

**Heat and work** In the previous handout we learnt about the various types of systems (isolated, closed and open) we have in thermodynamics and the types of walls that can surround a system. This classification was based on what things are allowed to transfer from the rest of the universe into and out of the system. There is a very important distinction between heat transfer  $\delta q$  and work transfer  $\delta w$  in thermodynamics. When work is transferred from the system we can harness it in engines to lift weights, drive cars and so on. By contrast when heat is transferred from the system we cannot harness it in engines directly. **Notice that neither of these objects are exact differentials.** Consequently, during a change in state **the heat output and the work done will depend on the manner in which the change of state is performed.**

State the first law of thermodynamics

Internal energy is an exact differential give three consequences of this fact

**The first law of thermodynamics** states:

$$dE = \delta q + \delta w$$

In other words we measure the change in internal energy by adding together the work done on the system and the heat absorbed by the system. We assume that the internal energy is an exact differential. This has three important consequences:

- The change in internal energy on moving from equilibrium state  $A$  to state  $B$  does not depend on the path taken.
- The change in internal energy on moving around a closed path that starts and ends in equilibrium state  $A$  is zero.
- The internal energy of an isolated system is constant.

## Summary

Physical or chemical systems interact with their surroundings by exchanging heat and work. To understand the transfer of heat and work we introduce a conserved quantity known as the internal energy  $E$ . We define the change in internal energy as the sum of the work done on the system and the heat absorbed by the system. Because the internal energy is an exact differential the change in internal energy on moving from equilibrium state  $A$  to equilibrium state  $B$  is independent of the path taken. By contrast the individual amounts of heat absorbed and work done on the system will depend on the path taken because these quantities are not exact differentials.

State the second law of thermodynamics

When does the equality sign in the second law hold and when is it an inequality

Write an expression that combines the first and second laws of thermodynamics

How are the temperature, pressure and chemical potential related to derivatives of the internal energy

How are the Maxwell relations derived.

The second law of thermodynamics states:

$$\Delta_{A \rightarrow B} S \geq \int_A^B \frac{dq}{T}$$

The equality sign holds when the transition is reversible, the inequality holds when the transition is irreversible. In the lecture we proved the above formula by starting from the statement the passage of heat from a cold body to a hot body cannot be the sole result of any transformation. The entropy is once again an exact differential so:

- The change in entropy on moving from equilibrium state A to state B does not depend on the path taken.
- The change in entropy on moving around a closed path that starts and ends in equilibrium state A is zero.

Importantly, however, because of the inequality sign in the second law of thermodynamics, the heat absorbed during a transition will depend on the path taken and during moves around closed paths heat will be input/output from the system. The consequence of this is that it is impossible to build an engine that converts 100 % all of the heat it absorbs into work.

Combining the first and second laws gives:

$$dE = TdS - PdV + \mu dN$$

This expression is derived by considering the differentials that it is possible to derive for reversible transitions (see handout 1) and by remembering that the internal energy is an exact differential so the change internal energy does not depend on the path taken between equilibrium states. In other words the above expression holds for both reversible and irreversible transitions. The theory of exact differentials tells us that:

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{V,S} dN$$

Equating coefficients in these two expressions gives:

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{V,S}$$

Furthermore, using the equality of the second, crossed derivatives  $\left(\frac{\partial^2 E}{\partial V \partial S}\right) = \left(\frac{\partial^2 E}{\partial S \partial V}\right)$  (Maxwell relation) we arrive at:

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

## Summary

The second law of thermodynamics defines an exact differential known as the entropy and tells us that it is impossible to build an engine that is 100 % efficient. By combining the first and second laws of thermodynamics you can arrive at an expression for the differential of the internal energy that is given entirely in terms of the thermodynamic variables. You can then connect intensive variables to derivatives of the internal energy with respect to intensive variables and derive Maxwell relations.

Which thermodynamic variables must be minimised/maximised at equilibrium

**Minimum energy maximum entropy** When a system is at equilibrium the entropy must be maximised and the internal energy must be minimised. When this is not the case it is possible to extract energy as work thereby lowering the internal energy. The internal energy extracted can then be returned as heat thereby increasing the entropy. The same argument can be made the opposite way around.

Explain how two systems in contact reach an equilibrium

**Extensive and intensive quantities and equilibrium** If two systems are placed in contact then the extensive quantities for one of the systems will increase while the extensive quantities for the other system will decrease until equilibrium is attained. Equilibrium is achieved when the values of all the intensive variables are equal in the two systems.

Explain what is meant by the term reservoir when it is used in thermodynamics?

**Reservoirs** We often talk about systems placed in contact with a very large reservoirs. We do this because when we do so we can assume that the reservoir is so large that the exchange of extensive variables with the system does not affect the values of the reservoirs intensive quantities. In other words, when a system is placed in contact with a reservoir it will have equilibrated with the reservoir once all its intensive thermodynamic variables are equal to values of the intensive thermodynamic variables of the reservoir. We use the thermodynamic potentials discussed on the next pages to describe systems in contact with various reservoirs. In particular, enthalpy is used to describe systems surrounded by adiabatic walls that are in contact with a volume reservoir. Helmholtz free energy is used to describe closed systems surrounded by diabatic walls that in contact with an internal energy reservoir (or heat bath). Gibbs free energy is used to describe closed systems surrounded by walls that can exchange both heat and work with the reservoir but that cannot exchange material. The reservoir for the Gibbs free energy is both a volume reservoir and an energy reservoir (or heat bath).

Explain why new thermodynamic potentials are required

Give the definition of enthalpy

**Enthalpy** is defined as:

$$H = E + PV$$

Write an expression for the differential of the enthalpy

We can thus write the differential of the enthalpy as:

$$\begin{aligned}dH &= dE + PdV + VdP = TdS - PdV + \mu dN + PdV + VdP \\ &= TdS + \mu dN + VdP\end{aligned}$$

Explain which thermodynamic variables are related to the derivatives of the enthalpy

In the second step above we insert the result for  $dE$  that we obtained by combining the first and second laws.

Enthalpy is an exact differential so we can write:

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP + \left(\frac{\partial H}{\partial N}\right)_{P,S} dN$$

Give the Maxwell relation that can be derived based on the definition of the enthalpy

Equating coefficients in these two expressions gives:

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N} \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N} \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{P,S}$$

Equality of second, crossed derivatives gives:

$$\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}$$

Define the Helmholtz free energy,  $F$

Write the differential of the Helmholtz free energy

Which thermodynamic variables are related to the derivatives of the  $F$

Give the Maxwell relation that can be derived based on the definition of the  $F$

**Helmholtz free energy** is defined as:

$$F = E - TS$$

We can thus write the differential of the Helmholtz free energy as:

$$\begin{aligned}dF &= dE - TdS - SdT = TdS - PdV + \mu dN - TdS - SdT \\ &= -PdV + \mu dN - SdT\end{aligned}$$

In the second step above we insert the result for  $dE$  that we obtained by combining the first and second laws.

Helmholtz free energy is an exact differential so we can write:

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{V,T} dN$$

Equating coefficients in these two expressions gives:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

Equality of second, crossed derivatives gives:

$$\left(\frac{\partial P}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial V}\right)_{T,N}$$

Define the Gibbs free energy,  $G$

Write the differential of the Gibbs free energy

Which thermodynamic variables are related to the derivatives of the  $G$

Give the Maxwell relation that can be derived based on the definition  $G$

**Gibbs free energy** is defined as:

$$G = H - TS$$

We can thus write the differential of the Gibbs free energy as:

$$\begin{aligned}dG &= dH - TdS - SdT = TdS + VdP + \mu dN - TdS - SdT \\ &= VdP + \mu dN - SdT\end{aligned}$$

In the second step above we insert the result for  $dH$  that we obtained above. Gibbs free energy is an exact differential so we can write:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dV + \left(\frac{\partial G}{\partial N}\right)_{P,T} dN$$

Equating coefficients in these two expressions gives:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

Equality of second, crossed derivatives gives:

$$\left(\frac{\partial V}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial P}\right)_{T,N}$$

## Summary

We introduce reservoirs so that we can understand the behaviours of systems at constant pressure and constant temperature. New extensive thermodynamic variables that are known as thermodynamic potentials are required to understand systems in contact with reservoirs.

At what kind of stationary point must all thermodynamic potentials be at equilibrium

At equilibrium what constraints are placed on the values of second derivatives of the internal energy and why

What constraints does this requirement place on the values of the intensive thermodynamic quantities.

Define the heat capacity  $C_v$

Define the isotropy compressibility  $\kappa_S$

Explain why  $\left(\frac{\partial E}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$

**Stability conditions** Consider a system in contact with a reservoir with which it is able to exchange both work and heat. The appropriate thermodynamic potential to use to describe the system is the Gibbs free energy which is given by  $G = E + PV - TS$ . We know that the energy must be minimised at equilibrium and that the entropy must be maximised. Consequently, if we move away from equilibrium the Helmholtz free energy must increase (as  $E$  will increase and  $-S$  will increase). If the move away from equilibrium is small we can write:

$$\delta G = \delta E - T\delta S + P\delta V > 0$$

This equation holds because the system is in contact with a reservoir at temperature  $T$  and pressure  $P$  so the values of the two intensive variables do not change when the extensive variable is exchanged between the system and the reservoir.

We can rearrange the expression above to give the following and then we can expand the energy as a Taylor series:

$$\begin{aligned} T\delta S - P\delta V &< \delta E \\ T\delta S - P\delta V &< \left(\frac{\partial E}{\partial S}\right)_{N,V} \delta S + \left(\frac{\partial E}{\partial V}\right)_{N,S} \delta V + \frac{1}{2} \left(\frac{\partial^2 E}{\partial S^2}\right)_{N,V} (\delta S)^2 \\ &\quad + \frac{1}{2} \left(\frac{\partial^2 E}{\partial V^2}\right)_{N,S} (\delta V)^2 + \left(\frac{\partial^2 E}{\partial V \partial S}\right) \delta V \delta S + \dots \\ \rightarrow 0 &< \frac{1}{2} \left(\frac{\partial^2 E}{\partial S^2}\right)_{N,V} (\delta S)^2 + \frac{1}{2} \left(\frac{\partial^2 E}{\partial V^2}\right)_{N,S} (\delta V)^2 + \left(\frac{\partial^2 E}{\partial V \partial S}\right) \delta V \delta S + \dots \end{aligned}$$

The last line here comes once we remember that  $T = \left(\frac{\partial E}{\partial S}\right)_{V,N}$  and  $P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}$ . Clearly, to satisfy this expression we must have  $\left(\frac{\partial^2 E}{\partial S^2}\right)_{N,V} > 0$  and  $\left(\frac{\partial^2 E}{\partial V^2}\right)_{N,S} > 0$ , which in turn implies that:

$$\left(\frac{\partial T}{\partial S}\right)_V > 0 \quad \text{and} \quad -\left(\frac{\partial P}{\partial V}\right)_S > 0$$

**Response functions** The derivatives of the thermodynamic variables are known as response functions. Some of the most important are:

$$\text{Constant volume heat capacity: } C_v = \left(\frac{\partial E}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$\text{Isoentropic compressibility: } \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S$$

**All response functions must be positive** because of the requirements for stability discussed above. N.B. The fact that  $\left(\frac{\partial E}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$  holds because the derivative on the left hand side of this expression allows us to write  $dE = C_v dT$ . The second law of thermodynamics meanwhile tells us that the internal energy change associated with any **constant volume** transition is given by  $dE = T dS$ . Equating these two expressions and rearranging gives the equality required.

## Summary

The fact that enthalpy is minimised at equilibrium and entropy is maximised ensures that the second derivatives of the internal energy must be positive. This in turn places restraints on the values of the so called response functions.

Write out the Taylor series expansion of a function

What does it mean when we say that a function is analytic at all points

**Analytic functions** A function,  $f$ , is said to be analytic if the following holds at all points,  $x$ , along it:

$$f(x + \delta x) = f(x) + \frac{df(x)}{dx}\delta x + \frac{1}{2!}\frac{d^2f(x)}{dx^2}(\delta x)^2 + \frac{1}{3!}\frac{d^3f(x)}{dx^3}(\delta x)^3 + \dots$$

In other words, it can be expanded using the Taylor series at all points. In order for the above to hold all the derivatives of the function  $f(x, y)$  must be finite. If any derivative of the function is infinite then the above expansion will fail to converge.

What happens to the derivatives of the thermodynamic potentials when a system crosses a phase boundary?

What can one say about the formula for any thermodynamic potential at the points when a system crosses a phase boundary?

**Phase transitions** If we compress a gas it will eventually reach a point when it will convert into a liquid. When this happens the volume of the material will suddenly decrease dramatically. We know that this change in phase happens at a specific pressure (the coexistence point) so we therefore infer that there is a discontinuity in any function that tells us the volume given the pressure. In other words, at coexistence  $P_c$ , our function for the volume  $V(P)$  behaves as follows:

$$\lim_{\epsilon \rightarrow 0} V(P_c + \epsilon) \neq \lim_{\epsilon \rightarrow 0} V(P_c - \epsilon)$$

The volume is related to a derivative of the enthalpy via  $V = \left(\frac{\partial H}{\partial P}\right)_{N,S}$ . Consequently, the discontinuous change in  $V$  at  $P_c$  implies that at  $P_c$  the enthalpy can no longer be expanded around this point as a Taylor series and hence that our function for the enthalpy cannot be analytic.<sup>a</sup> Consequently, **phase transitions are points where the derivatives of thermodynamic potentials change discontinuously and where functions for thermodynamic potentials are non-analytic.**

<sup>a</sup>At coexistence the derivative of the volume (the second derivative of the enthalpy) will be infinite because of the discontinuity.

## Summary

At phase boundaries some thermodynamic variables change discontinuously. Because thermodynamic variables are related to derivatives of thermodynamic potentials this implies that the thermodynamic potentials change non-analytically as you cross phase boundaries.