

Potentials

Basics

▶ Mechanically, a potential $A(\underline{r})$ was the difference $A(\underline{r}_2) - A(\underline{r}_1)$ and equal to the work needed to go from \underline{r}_1 to \underline{r}_2 .

- The decisive point was that $A(\underline{r})$ did *not* depend on the particular way chosen to go from \underline{r}_1 to \underline{r}_2 as long as the acting forces $F(\underline{r})$ were given as the derivative of the potential $A(\underline{r})$ with respect to the coordinates. We have

$$F(\underline{r}) = -\text{grad}[A(\underline{r})] = -\nabla[A(\underline{r})] = -\left(\frac{\partial A}{\partial x}, \frac{\partial A}{\partial y}, \frac{\partial A}{\partial z}\right)$$

▶ These are the well known relations for mechanic (and electrostatic) potentials. If one knows the potential and the momentum of a massive (and charged) particle, one knows everything one can know and needs to know.

- The history, i.e. how the particle came to its present position \underline{r} with the potential $A(\underline{r})$ and momentum, is totally irrelevant.
- Potential *and* momentum together then define the **state** of the particle.

▶ We may first generalize the idea of a potential by allowing **generalized coordinates**, i.e. any variables (and not just space coordinates) that describe the state of a system.

- This allows to treat thermodynamic systems consisting of *many particles*, where individual coordinates loose significance and average values describing the system take precedence.

▶ Lets consider the free energy as a first example. It is a thermodynamic potential *and* at the same time a **state function**, i.e. it describes *completely* the state of systems with the generalized coordinates temperature T , volume V and particle numbers N_i . The mechanical potential by itself, in contrast, is *not* a state function (we would need the momentum, too, to describe the state of a mechanical system).

- A change of state thus necessarily demands a change in at least one of the three generalized coordinates from the above example.
- In formulas we write

$$F = \text{thermodynamic potential} = F(V, T, N_1, \dots, N_i)$$

- The N_i denote the number of particles of kind i .

▶ *Is it that easy? Can we elevate all kinds of functions to the state of thermodynamic potentials and state functions?*

▶ The answer, of course, is *No!* The statement that the function $P(\mathbf{x}_i)$ is a potential with respect to the generalized coordinates \mathbf{x}_i is *only* true if a number of conditions are met. *For the case of equilibrium* (which requires that nothing changes and therefore that all $\partial P / \partial \mathbf{x}_i = 0$) those requirements are:

- The values of the generalized coordinates describe the state of the system *completely* (this means you have the right number *and* the right kinds of coordinates).
- The value of $P(\mathbf{x}_i)$ for a set of values of the generalized coordinates is *independent from the path chosen* to arrive at the particular state and thus from the history of the system. In formulas:

$$\Delta P = \text{change in } P \text{ between a state 1 and a state 2} = \int_1^2 dP = \int_1^2 \frac{\partial P}{\partial x_1} \cdot dx_1 + \int_1^2 \frac{\partial P}{\partial x_2} \cdot dx_2 + \dots := P_2 - P_1$$

- i.e. the difference depends *only* on the starting and end state.

▶ This can only be true if dP is a **total differential** of P , i.e.

$$dP = \frac{\partial P}{\partial x_1} \cdot dx_1 + \frac{\partial P}{\partial x_2} \cdot dx_2 + \dots$$

- i.e. the changes in the generalized coordinates describe unambiguously the total change in P .

▶ The numerical values of the partial derivatives of the thermodynamic potentials describe the "effort" it takes to change the potential by fiddling with the particular coordinate considered. This can be understood as a **generalized force**. If the derivative happens to be taken with respect to a *space coordinate* of the system, the *generalized* force is a *real* mechanical force - it describes the change of energy with space as it should.

- If the derivative happens to be taken with respect to a *particle number*, however, the resulting quantity is not called, e.g., "*particle number changing force*" (which would have been a perfectly good name), but **chemical potential**, which might be a bit confusing at times.

▶ How do we know if a given function is a thermodynamic potential and a state function? For a given function (in differential form), it is not necessarily obvious if it is a total differential. You have to resort to *physical* or *mathematical* reasoning to find out. Lets first look at an example of physical reasoning:

▶ The **first law of thermodynamics** was defined as follows:

$$dU = dQ - dW$$

▶ Are these three differential quantities total differentials and thus state function and thermodynamic potentials, or are they not?

- *Physical* reasoning tells us that **dU** *must* be a total differential because **U** must be a thermodynamic state function - otherwise we can construct a **perpetuum mobile**! Lets see why:
- If we start from some value **U₁**, characterized by as many variables **x₁** (= coordinates) as you like (e.g. pressure **p₁**, volume **V₁**, temperature **T₁**) and than move to a second value **U₂** by adding, for example, a heat quantity **Q**; we have described a path **1** to move from **U₁** to **U₂**.
- If we return to the same values of the generalized coordinates by a different path; e.g. by now extracting some mechanical work, but have a value **U₁'** that is not identical to **U₁**, we are now in a position to construct a cycle between the states **1** and **2** as characterized by the generalized coordinates that allows us to extract work in every cycle - we have a *perpetuum mobile*.
- So **dU** must be a total differential - and this requires that **dQ** and **dW** are *not* total differentials! Because it is entirely possible to go from one state of **U** to another one by adding different amounts of **Q** and **W** - the path described by these circumstances must not matter!
- $\Delta Q = Q_2 - Q_1$ or $\Delta W = W_2 - W_1$ thus are not independent of the path, therefore they are *not* state functions and their differentials cannot be total differentials. This is essentially tied to the fact that the system entropy may change in these cases.

▶ Now lets turn to *mathematical* reasoning. Obviously, if a function **P(x_i)** of several variables **x_i** is given, it is always possible to calculate the total differential **dP(x_i)**. *But the reverse is not necessarily true:*

- If **P** is given in differential form, it always can be written as

$$dP(x,y) = g(x,y) \cdot dx + f(x,y) \cdot dy$$

- We used only two variables **x** and **y** for simplicities sake. The functions **g(x,y)** and **f(x,y)** are arbitrary functions - what ever you like is allowed.

▶ *If dP* is a total differential, we have *necessarily*

$$g(x,y) = \frac{\partial P}{\partial x}$$

$$f(x,y) = \frac{\partial P}{\partial y}$$

- On the other hand for *all* functions **P(x,y)** the following equalities must obtain

$$\frac{\partial}{\partial y} \left(\frac{\partial P}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{\partial P}{\partial y} \right)$$

- This requires that

$$\frac{\partial g(x,y)}{\partial y} = \frac{\partial f(x,y)}{\partial x}$$

Only if the above relation is fulfilled, is $dP(x,y) = g(x,y)dx + f(x,y)dy$ a total differential. So we have a simple checking procedure for a given differential function (a mathematical rule) to find out if it is indeed a total differential.