Thm. 4. Statistical Physics.

Lecture 3.

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Last time: Concept of equilibrium
0th law of thermodynamics

Today: 1st law of thermodynamics
Extensive + intensive variables / differentials + conjugates

Last time, we presented the 0th law of thermodynamics, which postulated that equilibrium is a transitive property.

We now present the 1st law of thermodynamics:

The amount of work required to change the state of an otherwise adiabatically isolated system depends only on the initial and final states. It does not depend on the means of the work performed nor any intermediate stage.

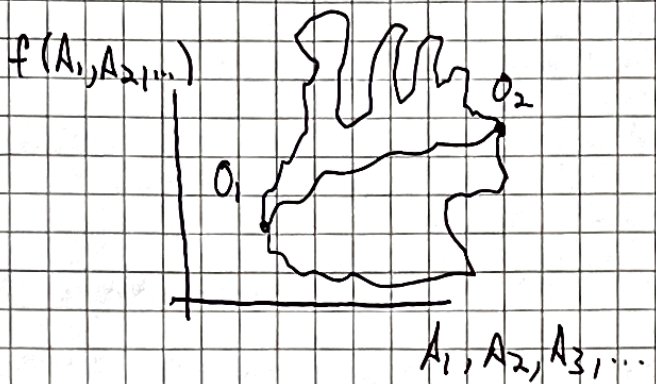
Recall that equilibrium was a dynamic concept, since two systems in equilibrium would be an example or instantiation of one equilibrium condition but changing the thermodynamic coordinates of one system would be matched by a corresponding change of the second system, such that a new equilibrium is realized.

(This is why the equilibrium equation of state traces out a manifold in the thermodynamic coordinates.)

Now, we can study trajectories in the state function. To be concrete, we will focus on scenarios where the state function expresses the total energy available to the system. We remark, however, that there are still some details to fix before ~~the~~ the precise nature of the type of energy is clarified, since different systems can have (express) the total energy in kinetic energy and potential energy differently. (In other words, the ways that potential energy is stored in the degrees of freedom of a system depends on the type of system under consideration. For example, a gas vs a liquid vs. a ~~spr~~ set of springs.)

Given that the state function measures the total energy, then the 1st law can be reexpressed as a statement that energy is conserved, and heat and work are both forms of energy. When a system arrives at a new value of the state function via some processes involving work and/or heat, then reconstructing the process is impossible knowing only the start & end points. Also, clearly, the net energy gained/lost by the system is the total of all the work and heat added or removed.

Obviously, conservation of energy is a familiar concept, but the path independence is also important and its consequences are helpful for understanding the concept of engines.



Sketch of three paths in the thermodynamic coordinate space $A_1, A_2, A_3 \ldots$ that changes $f = O_1$ at the start to $f = O_2$ at the end.
All paths require the same net change in energy.

This path independence is violated if the process that adds/subtracts energy is not <u>adiabatic</u>.
An <u>adiabatic process</u> is defined as a process that involves no transfer of heat and is also reversible.

(for a cool demonstration of a reversible process, look up laminar flow videos.)

Clearly, friction or dissipative processes violate adiabacity, since they are not reversible and typically result in heat loss to the environment.
This is why two different paths through the mountains expend different amounts of energy even if the starting point + ending point are the same.

Other scenarios with path independence reflecting energy conservation are in HW 2.

In performing work on a system, recall that $W = \int \vec{F} \cdot d\vec{l}$ is the standard formula from classical mechanics. In differential form, we can write $dW = \vec{F} \cdot d\vec{l}$, and in general, the total internal energy of the system we can denote by U and the heat added to the system is Q. For U, Q and W considered only as fcns. of the state variables (thermodynamic coordinates), then we can at best write $dU = đQ + đW$, where "$đ$" indicates an "inexact" differential.

See Blundell + Blundell, App. C.7.

Aside: "exact" differentials are characterized by integrals depending only on the endpoints, and so closed loops of exact differentials are zero.

"Inexact" differentials require knowledge of the path taken in order to evaluate the integral, & closed loop integrals of inexact differentials are generally nonzero. Functions of state will generally always have exact differentials.

For adiabatic processes, $đQ = 0$ & so $dU = đW$, and so the movement in thermodynamic coordinates reflected in $\int dU$ is entirely determined by the total work on the system $\int đW$. Since $\int dU$ only depends on the initial & final state of the system, we do not need to know the path of $đW$ because $đQ$ is zero.

It will be useful to remark now that work on a system takes many forms, and this leads to the notion of variables & conjugate variables as well as intensive & extensive quantities.

Revisiting $dW = F\,dl$, appling a force along some infinitesimal displacement dl generates dW work. We can turn this around and consider for some applied energy dW, what is the system variable that controls the response in a displacement "dl"?

In fact, there are several examples:

Table 1.1 of Kardar

System	Force	Displacement
Wire	tension F	length L
Film	surface tension S	area A
Fluid	pressure $-P$	volume V
Magnet	magnetic field H	magnetization M
Dielectric	electric field E	polarization P
Chemical reaction	chemical potential μ	particle number N
	⇓ typically intensive, does not scale wl system.	⇓ typically extensive, depends on system size

In other words, if intensive quantities match for two wildly differently sized systems, then they ~~are still in equilibrium~~ do no work on each other.

We can also make a brief preview of the study of conjugate variables. In the context at hand, where we are focused on the state function of internal energy, the generalized force & its corresponding displacement are the conjugate variable & the variable, respectively. This should be familiar from classical mechanics and Hamiltonians, since the equation of motion for a given variable in a Hamiltonian required constructing the canonical conjugate variable, i.e. some quantity that carried the right dimensions such that the product was in units of energy. We will return to this when we study Legendre transformations. From QM, conjugate variables have uncertainty relationships.

Having considered the consequence of the 1st law of thermodynamics & path independence in thermodynamic coordinate space related to net work on an adiabatically isolated system, we can now consider cycles or engines, which are closed loops in the space of thermodynamic coordinates. This will lead us to the second law of thermodynamics and further expand on the notion of (ir)reversibility in thermodynamics and introduce entropy as the conjugate variable to temperature