Lecture 4: Thermodynamics II

1 Mechanical change

In the previous lecture we considered briefly the volume of a thermodynamical system. We turn to this now in more detail. In general the external boundary of a thermodynamical system is of physical significance since it confines molecules. In a certain sense this boundary may be regarded as a confining external potential. By its nature this "wall" is not statistical but is simply prescribed. A system may interact with its surroundings by changing the wall location. If the system interacts with the environment only through movements in the wall and not through molecules inside and outside exchanging energy then the system is refered to as thermally isolated. Since the wall in such a system is not statistical it has effectively zero entropy. Further since there is no direct molecular interaction with the outside, the principle of increasing entropy with time holds for thermally isolated systems as well as closed systems.

Suppose we can specify the confinement using one parameter λ (an example is volume) and suppose the system is in thermal equilibrium if this parameter is not changing. Now the rate of change of entropy with time $\frac{dS}{dt}$ is a function of the time rate of change of the external parameter $\frac{d\lambda}{dt}$. If we assume that this latter change is small then we can perform a Taylor expansion of the former in terms of the latter. The constant term is zero since $\frac{d\lambda}{dt} = 0$ implies a system in equilibrium i.e. one with unchanging entropy. The next linear term must also be zero since changes in λ can occur in the opposite direction meaning this linear term reverses sign however $\frac{dS}{dt} \geqslant 0$ for changes either way. Thus to leading order we must have

$$\frac{dS}{dt} \approx A \left(\frac{d\lambda}{dt} \right)^2$$

which may be rearranged to

$$\frac{dS}{d\lambda} \approx A \frac{d\lambda}{dt}$$

Thus as the change in the wall occurs at a slower and slower rate with time, the rate of change of entropy with the external parameter also approaches zero i.e. the entropy does not change with the wall variation. Such a very slow change in a thermally isolated system is known as an adiabatic change and is also termed reversible since entropy is not changing as the system configuration is changing. Conversely changes in which the entropy increases are termed irreversible because the second law means they clearly cannot occur in reverse. An adiabatic change is one in which the change in the mechanical parameter λ is much slower than the thermal equilibration time i.e. as the mechanical change proceeds then the system at any time may be regarded as very close to thermal equilibrium. In practise this is not really a severe condition/restriction and many processes of practical interest are very close to adiabatic. For example if a piston is moving outward and so the volume of the gas within it is increasing then it may be shown that providing the velocity of the piston lid is much less than the speed of sound then the change is very close to adiabatic.

The rate of change of thermodynamical energy E[1] for an adiabatic process will be of interest to us later. Now this thermodynamical energy is the mean of the actual energy of many different systems in the same state of thermal equilibrium i.e.

$$E = \overline{E(\boldsymbol{p}, \boldsymbol{q}; \lambda)}$$

where $E(\boldsymbol{p}, \boldsymbol{q}; \lambda)$ is the energy of an arbitrary system with external parameter λ and we are assuming it is in a thermal state of equilibrium and hence has a Gibbs distribution. Remember that the form of this distribution will depend on λ since this parameter restricts the possible values for the position of molecules. Now in any system governed by Hamiltonian dynamics we have

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A, H\}$$

where the curly bracket is the Poisson bracket and H is the system Hamiltonian. In general the energy and the Hamiltonian have a zero Poisson bracket which means that

$$\frac{dE(\boldsymbol{p}, \boldsymbol{q}; \lambda)}{dt} = \frac{\partial E(\boldsymbol{p}, \boldsymbol{q}; \lambda)}{\partial t} = \frac{\partial E(\boldsymbol{p}, \boldsymbol{q}; \lambda)}{\partial \lambda} \frac{d\lambda}{dt}$$

with the last equality because the only explicit time dependency comes though $\lambda(t)$. Taking an ensemble average with respect to the appropriate Gibbs distribution we obtain

$$\frac{dE}{dt} = \overline{\frac{dE(\boldsymbol{p}, \boldsymbol{q}; \lambda)}{dt}} = \overline{\frac{\partial E(\boldsymbol{p}, \boldsymbol{q}; \lambda)}{\partial \lambda}} \frac{d\lambda}{dt} \tag{1}$$

Consider now an adiabatic change for a system which means that entropy is conserved. The time rate of change of thermodynamical energy as λ changes is given by

$$\frac{dE}{dt} = \left(\frac{\partial E}{\partial \lambda}\right)_S \frac{d\lambda}{dt} \tag{2}$$

Note that if the entropy were to change in a non-adiabatic process then an additional term would appear in this equation involving the time rate of change of entropy. Thus we obtain comparing (1) with (2)

$$\left(\frac{\partial E}{\partial \lambda}\right)_S = \overline{\frac{\partial E(\boldsymbol{p}, \boldsymbol{q}, \lambda)}{\partial \lambda}} \tag{3}$$

which enables a thermodynamical calculation of an important (equilibrium) ensemble mean i.e. the right hand side.

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[1] In what follows E will stand for the thermodynamical energy while $E(\boldsymbol{p}, \boldsymbol{q}; \lambda)$ will denote the total energy for a particular microstate of the system with external parameter λ.

2 Pressure

For a given body of arbitrary shape in thermal equilibrium we have seen that both the thermodynamical energy E and the entropy S are additive quantities in the sense that if we divide up the system into a series of subsystems all in thermal equilibrium (with the same temperature) then the total energy and entropy is the sum of these quantities for each subsystem. From this we deduce that these important quantities depend only on the total volume of the system and not on its particular shape since the system could be rearranged[2] so that the total energy and entropy are unaffected. The thermodynamical system may thus be specified by E, S and V and since in general there is a relation between these three variables (as we shall see in the next lecture in more detail) any two of them suffice to specify the thermodynamical state.

Consider now for the sake of pedagogical clarity[3] a piston in which the external parameter λ is the position of the moving end and that changes are made adiabatically i.e. the entropy is conserved. Changes in the volume of the gas in this system are clearly given by

$$\Delta V = A \Delta \lambda$$

where A is the piston cross-sectional area. Now if the piston end changes position it does so under a force due to the pressure of the gas. If the end moves counter to the pressure P then energy is added to the gas in the piston whereas if it moves in the same direction i.e. it expands, then the gas does work on the piston end and energy is lost. These energy amounts. by elementary physics, are simply the force exerted by the pressure multiplied by the distance travelled by the piston end. It follows then easily that for an infinitesimal change in λ that we must have

$$PA = F = -\frac{\partial E(\boldsymbol{p}, \boldsymbol{q}; \lambda)}{\partial \lambda}$$

Averaging over the appropriate Gibbs ensemble which is appropriate since we are considering an adiabatic change only we obtain using (3) that

$$\overline{F} = -\overline{\frac{\partial E(\boldsymbol{p}, \boldsymbol{q}; \lambda)}{\partial \lambda}} = -\left(\frac{\partial E}{\partial \lambda} \right)_S$$

and hence that the mean pressure $\overline{P}$ on the surface of the piston end is

$$\overline{P} = -\left(\frac{\partial E}{\partial V} \right)_S \tag{4}$$

Now when we defined temperature in the previous lecture we did so tacitly assuming the volume of the body V was constant as the thermodynamical

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[2] Note that this applies to gases and liquids where the rearrangement can be done without work but not for a solid which is rigid.

[3] The argument given generalises easily and this can be found in Landau and Lifshitz

equilibrium was achieved. In otherwords

$$T = \left(\frac{\partial E}{\partial S}\right)_V \tag{5}$$

It follows immediately[4] from the property of differentials and these two last equations that

$$dE = TdS - PdV \tag{6}$$

which is a fundamental relation of thermodynamics. How is this pressure P to be related to the quantity we defined in the last lecture using the maximum entropy principle for equilibrium states? As we saw we had for equilibrium that

$$\frac{\partial S}{\partial V} = constant$$

between the bodies concerned. Rewriting (6) in terms of entropy we have

$$dS = \frac{1}{T}dE + \frac{P}{T}dV$$

i.e.

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

and so the constant quantity between two bodies in equilibrium is just the quotient of their pressure and temperature as we anticipated earlier. We have now given a physical meaning to the P previously identified as the pressure of the two bodies on each other. This illustrates the power of the maximum entropy principle in identifying relevant thermodynamical variables. As we noted earlier as a practical matter when two bodies equilibrate their pressures will equalize generally much more rapidly than will their temperatures. Thus mechanical equilibrium is generally much more rapid than thermal equilibrium.

3 Mechanical work and heat

As noted above as the walls of a system change, mechanical work is done either by a system on its environment or by the environment on the system. By convention work is positive if done on the system. The work W is done by the pressure acting on an area of the walls of the piston. We have therefore

$$dW = -\overline{F}d\lambda = -PdV$$

If the body is thermally isolated then by conservation of energy this work changes the total energy E of the system by the same amount. If the system is not thermally isolated then the two things may not coincide since the internal

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[4] We drop the overbar on the pressure and regard P as a thermodynamical quantity henceforth.

energy of the system may change as a result of molecular interaction with the environment. We can therefore write the change in energy as

$$dE = dW + dQ = dQ - PdV \tag{7}$$

where the additional energy dQ is called the heat energy. Now if this interacting system is internally in thermal equilibrium (it may not be with its environment) then we can use (6) and this last equation to deduce that

$$dQ = TdS \tag{8}$$

We see therefore that equation (6) is really a statement of the conservation of energy of the total system (environment plus thermally interacting subsystem).

It should be noted that we have defined only infinitesimal differences of work and heat and in fact if one considers two different trajectories of a system within thermodyamical space[5] for which both trajectories have the same endpoints and starting points, then the amount of work ΔW (and heat ΔQ) added will be path dependent. Of course the total energy added ΔE will only depend on the starting and ending points since it is specified by the state. Given the path dependence of these quantities it makes no sense to refer to the heat energy or mechanical energy of a system. Only differences make sense.

Note also that in all considerations above the bodies concerned are assumed to be in thermal equilibrium. If this is not the case during a thermodynamical process then equation (8) must be modified to

$$dQ < TdS$$

since entropy may increase independently of the addition of external molecular energy i.e. heat energy.

4 Thermodynamical Potentials

As mentioned in the previous section, it is possible to specify the thermodynamical state using V, S and E and further there exists in general a functional relationship between these three variables which means two will suffice. Now this functional relationship may be written as

$$E = E(S, V) \tag{9}$$

and from this we can deduce P by differentiating partially with respect to V and T by differentiating partially with respect to S. Thus this functional relationship will determine all thermodynamical variables of interest[6]. This situation leads to the terminology that E is a thermodynamical potential when expressed via (9) since the gradient vector gives the other variables. It is possible to construct other thermodynamical potentials in other ways.

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[5] Specified by two of E, S and V

[6] We are ignoring the chemical potential for the present.

4.1 Enthalpy

If the pressure P is held constant during a thermodynamical process then we have

$$\begin{aligned} dQ &= d(E+PV) \equiv dH \\ H &\equiv E+PV \end{aligned}$$

The variable H is referred to as the enthalpy and represents the heat energy added to a system held at constant pressure. For a more general process we have

$$dH = dE + PdV + VdP$$

Combining this with (7) and (8) we obtain

$$dH = TdS + VdP$$

and hence that

$$\begin{aligned} T &= \left(\frac{\partial H}{\partial S}\right)_P \\ V &= \left(\frac{\partial H}{\partial P}\right)_S \end{aligned}$$

Thus $H(P,S)$ is also a thermodynamical potential from which T and V can be determined by partial differentiation.

4.2 Helmholtz Free Energy

Suppose now we hold the temperature fixed (isothermal change) as we alter the thermodynamical state. We have then that the work done is given by

$$\begin{aligned} dW &= dE - dQ = dE - TdS = d\,(E-TS) \equiv dF \\ F &\equiv E - TS \end{aligned}$$

which is the Helmholtz free energy representing the mechanical work done during isothermal change. In a similar fashion to the previous potential we have

$$dF = dE - TdS - SdT$$

and combining with (7) and (8) we obtain

$$dF = -SdT - PdV$$

and hence that

$$\begin{aligned} S &= - \left(\frac{\partial F}{\partial T}\right)_V \\ P &= - \left(\frac{\partial F}{\partial V}\right)_T \end{aligned}$$

Thus we identify a third thermodynamical potential $F(T,V)$.

4.3 Gibbs Free Energy

A potential called the Gibbs Free Energy can also be defined using the variables P and T (the variables that arise from the Lagrange multipliers of the previously mentioned maximum entropy principles). Thus we write

$$\Phi \equiv E - TS + PV = F + PV = H - TS$$

and we can easily derive in a fashion similar to the last two potentials that

$$d\Phi = -SdT + VdP$$

and hence that

$$\begin{aligned} S &= -\left(\frac{\partial \Phi}{\partial T}\right)_P \\ V &= \left(\frac{\partial \Phi}{\partial P}\right)_T \end{aligned}$$

Hence $\Phi(P, T)$ is a fourth thermodyamical potential.