

Lecture 8: Work and heat

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Introduction

- We've now done about as much as we can do with the kinetic theory, and extracted a lot of knowledge of how P , V , T and U fit together. We're now going to shift focus and start looking at the first law of thermodynamics, and start exploring on the relationships between work W , heat Q , internal energy U and temperature T .
- In this lecture, we will go through and make sure we have our definitions of work and heat straight. Next week we will get to the first law.
- We have already defined temperature T as that quantity which is equal between two bodies when they are at thermal equilibrium with each other, or for gases as the mean kinetic energy of the particles $\langle \frac{1}{2}mv^2 \rangle$ divided by $3/2k_B$ (or $\frac{1}{2}k_B$ for each of the three directions of kinetic motion).
- Let's now define our other three parameters, and then look at them more closely.



Internal energy, work and heat

- Let's now define our other three parameters, and then look at them more closely.

Internal Energy U : Internal energy is *all* of the energy of a system that is associated with its microscopic components – atoms and molecules – when viewed from a reference frame at rest with respect to the center of mass of the system.

Heat Q : Heat is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings.

Work W : Work is basically defined as any other transfer of energy into or out of the system.

Temperature T : A quantity that is equal in two bodies that are at thermal equilibrium and unequal in two bodies that aren't.

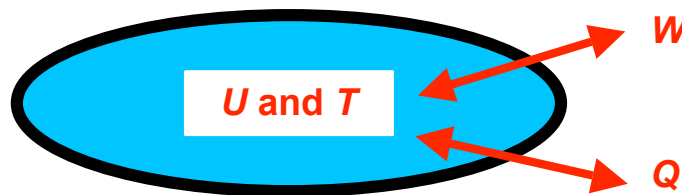
- The internal energy is not necessarily the temperature as we've already seen. In fact, temperature is the odd one out here, it's not an energy – it has no units of joules – despite the fact that for gases it is directly related to the average kinetic energy. Any change in the internal energy will be due to heat and work – it could be one or the other or some combination of the two.



Two important points

- There are two really important points to note here:
 1. Internal energy and temperature are properties of a system (**state variables**) they are finite and constant until some 'process' is done on the system in which case they may change. The third law says that they cannot be zero.

In contrast, work and heat are not properties of a system, they are properties of a process done on a system involving some transfer of energy to or from it (hence they are often called **transfer variables**). Work and heat can often be zero and only will be non-zero when the system changes in some way.



2. Heat is a spontaneous transfer of energy that occurs across a boundary between two systems with unequal temperature (i.e., that are out of thermal equilibrium). There is no external force mediating this process, and in a sense it is analogous to the diffusion process that we discussed last lecture.

In contrast, work involves either some external net force acting on the system to change its size or configuration, or the system producing some net force on its external environment by changing its size or configuration.



Work

- We will address some other forms of work later in the lecture, but for now I really want to get deep into one form of work called compressive/expansive work. Why is this important? Because it's the main form of work found in gases and it's vitally important to many useful thermodynamic applications such as engines, refrigerators, free expansion, liquefaction, etc.

You'll remember from the 2nd year mechanics course that if an applied force F causes an infinitesimal displacement ds then the work done dW is given by:

$$dW = \mathbf{F} \cdot d\mathbf{s} \quad (8.1)$$

and as that force keeps acting, those infinitesimal work contributions add up such that:

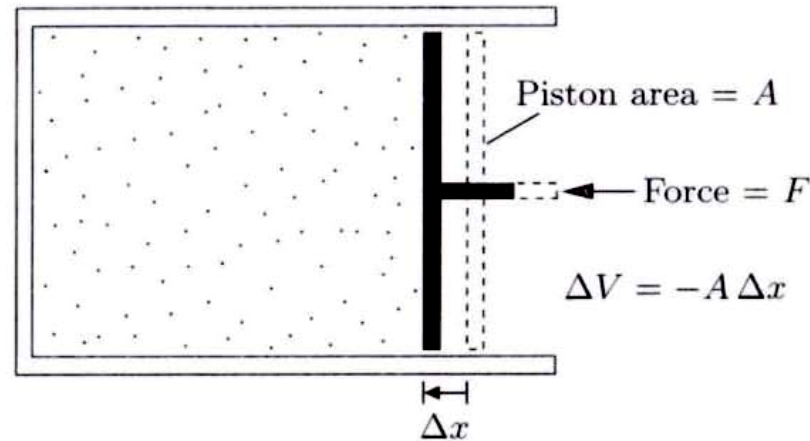
$$W = \sum dW = \int \mathbf{F} \cdot d\mathbf{s} \quad (8.2)$$

But for a gas, it's actually more convenient to go back to our piston and cylinder model again, as shown next slide.



Work

Figure 1.8. When the piston moves inward, the volume of the gas changes by ΔV (a negative amount) and the work done on the gas (assuming quasistatic compression) is $-P\Delta V$.



- Here we can apply a force F to the piston and cause it to be displaced by some amount dx . But as we did in lecture 2, it's better to talk about the pressure $P = F/A$ rather than the force because the pressure is size-independent. Making this shift gives a key result:

$$W = \int PA \cdot -dx = -\int PdV \quad (8.3)$$

Note that if the piston moves in, then dV is negative, so W is positive which means work is done on the system and its internal energy is increased. If the piston moves out, then dV is positive, so W is negative and the system does work on its environment and its internal energy is reduced.



Work and PV curves

- Note also that Eqn. 8-3 is a general expression for a gas, it isn't piston and cylinder specific. For example, in a balloon you use the same equation, but dV is just calculated slightly differently (for a spherical balloon say, it would be $4\pi r^2 dr$).

The relationship between work, pressure and volume means that the PV -diagrams that we saw in lecture 4 are very important. Because the change dV is important, for any process we are interested in what the initial volume V_i and the final volume V_f for any process are since $dV = V_f - V_i$. As shown below, the work done is just the area underneath the process on a PV -curve, with the sign being negative if $V_f > V_i$ and positive if $V_f < V_i$.

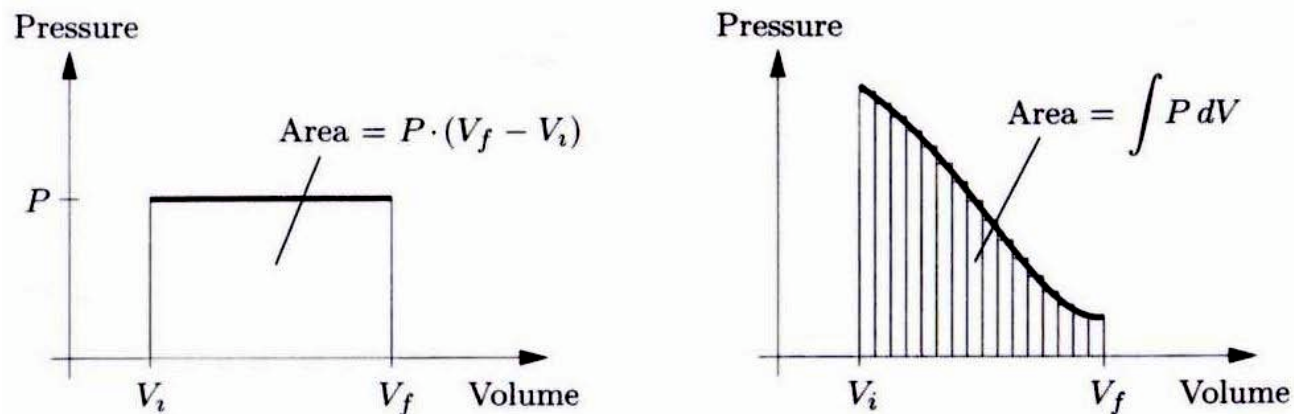
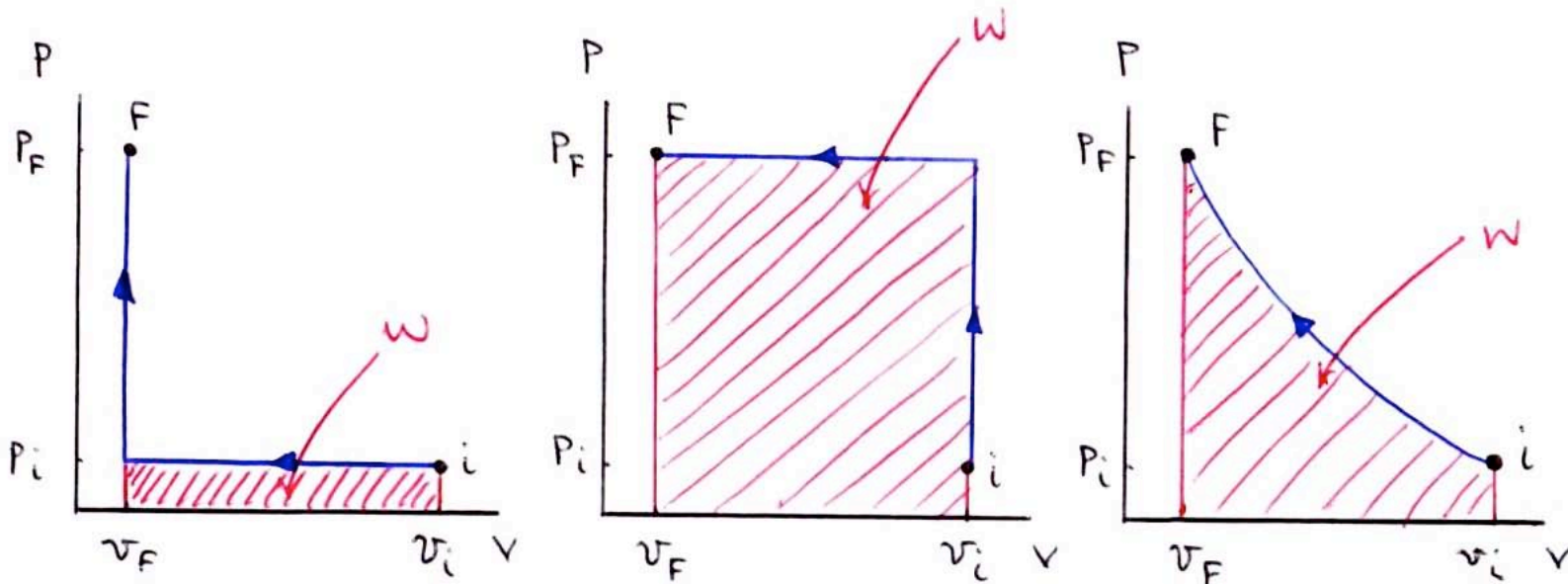


Figure 1.9. When the volume of a gas changes and its pressure is constant, the work done on the gas is minus the area under the graph of pressure vs. volume. The same is true even when the pressure is not constant.



Work and PV curves

- An important thing to realise is that this has significant ramifications on how much work is done by a particular process between a given (P_i, V_i) and (P_f, V_f) . If you look at the figure below, you'll see just three of many possible PV -processes between (P_i, V_i) and (P_f, V_f) , the areas under these curves are different, which means that each has a different W .



This is something known as a **path dependent** process. In contrast, a path independent process depends only on the start and end point and not how you get between them – an example is gravitational potential energy it only depends on the change in height, not the path you take in changing that height.



Some common examples

Constant Volume: This is an easy one. In a constant volume process $dV = 0$, and so the work W must be 0 also. There is no work in a gas unless it changes its volume.

Constant Pressure: Here P is a constant, so we can take it out the front of the integral. Hence:

$$W = -P \int_{V_i}^{V_f} dV = -P[V]_{V_i}^{V_f} = -P(V_f - V_i) \quad (8.4)$$

Isothermal Expansion: A good (and very common) example is an isothermal expansion. Starting from Eqn. 10-3, we can use the ideal gas law as $P = nRT/V$, given n , R , and T are constant, to obtain:

$$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT [\ln V]_{V_i}^{V_f} = -nRT (\ln V_f - \ln V_i) \quad (8.5)$$

Adiabatic Expansion: This is a bit trickier, it goes something like (you'd need to measure C or have some way to eliminate it):

$$W = -C \int_{V_i}^{V_f} \frac{dV}{V^\gamma} = -C \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_{V_i}^{V_f} = -\frac{C}{1-\gamma} (V_f^{1-\gamma} - V_i^{1-\gamma}) \quad (8.6)$$



Heat

- Heat can be loosely divided into two forms:

Specific heat (or heat capacity): is heat energy that enters or leaves a system to produce a change in temperature but no change in phase.

Latent heat (or heat of transformation): is heat energy that enters or leaves a system to produce a change in phase but no change in temperature.

- Now you'll remember that we earlier defined heat as 'as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings' that 'aims' to bring two bodies with different T to thermal equilibrium.

Latent heat, since T doesn't change, may seem not to fit with this, but it does. Suppose we bring some solid H_2O (ice) at -5°C in contact with a very large chunk of metal at 150°C . Heat will be transferred between the block and the H_2O in 5 stages because H_2O cannot exist as a solid at 150°C :

1. Specific heat to bring the ice to 0°C
2. Latent heat to transform it to liquid H_2O at 0°C
3. Specific heat to bring the water to 100°C
4. Latent heat to transform it to a gas (steam) at 100°C
5. Specific heat to bring the steam to 150°C



Heat capacity and Specific heat

- The **heat capacity** C of a system or a particular sample of a substance is defined as the amount of energy needed to raise the temperature by 1 Kelvin (or 1°C). Hence the amount of heat Q we need to add or remove from the system to achieve a temperature change ΔT (with no phase change) is:

$$Q = C\Delta T \quad (8.7)$$

Equation 10-7 doesn't account for the size of the system or sample though, so more commonly we use something called the **specific heat** C which is the heat capacity C per unit mass (or per mole). This ends up changing Eqn. 8-7 slightly to:

$$Q = mC\Delta T \quad (\text{for } C \text{ per unit mass}) \quad \text{or} \quad Q = nC\Delta T \quad (\text{for } C \text{ per mole}) \quad (8.8)$$

It is important to realise that the definition of C we've given above (i.e., that $C = Q/\Delta T$) is somewhat ambiguous, because the first law gives $\Delta U = Q + W$, so:

$$C = \left(\frac{\Delta U - W}{\Delta T} \right) \quad (8.9)$$

and because the work W could be anything, then C could be anything too. To solve this problem, we need to be a little more specific about our specific heat.



Heat capacity at constant volume/pressure

- In thermodynamics, there are two circumstances (or choices of W) that are most likely to occur: constant volume ($W = 0$) and constant pressure ($W = -PdV$).

Heat Capacity at Constant Volume C_V : At constant volume $dV = 0$ and so the compressive work $-PdV$ is also zero, and so we can define C_V as:

$$C_V = \left(\frac{\Delta U}{\Delta T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \quad (8.10)$$

Remember that U is a function of a number of parameters (e.g., P , V , T , N , etc.) so we need to use partial derivatives, the derivative in Eqn. 8-10 is the derivative of U with respect to T at constant V .

Heat Capacity at Constant Pressure C_P : Usually substances expand and contract as they heat and cool, respectively, so W is usually negative on heating and we'd expect C_P to be larger than C_V in most cases. Using $W = -PdV$ in Eqn. 8-9 gives:

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (8.11)$$



Heat capacity at constant volume/pressure

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (8.11)$$

The second term on the right is the additional heat needed to compensate for the energy lost as work. Notice that the more V increases with T , the larger this term is.

For solids and liquids, $(\partial V/\partial T)_P$ is usually so small that it can easily be neglected. For gases though, the second term is quite significant, and needs to be considered.

Note also that the first term $(\partial U/\partial T)_P$ is not quite the same as C_V , since it is P and not V that is held fixed in the partial derivative. For example, suppose U is a function of only P, V and T . Then $(\partial U/\partial T)_P$ and $(\partial U/\partial T)_V$ would be derivatives in directions perpendicular to each other (you should spend some time thinking about this – it's a four dimensional space of U, P, V and T).

Later on we will see that $C_P - C_V = nR$ and $\gamma = C_P/C_V$ – but these require some time to derive properly, so we'll devote a whole lecture to these later on in the course.



Heat capacity at constant volume/pressure

For example, suppose U is a function of only P, V and T . Then $(\partial U/\partial T)_P$ and $(\partial U/\partial T)_V$ would be derivatives in directions perpendicular to each other (you should spend some time thinking about this – it's a four dimensional space of U, P, V and T).

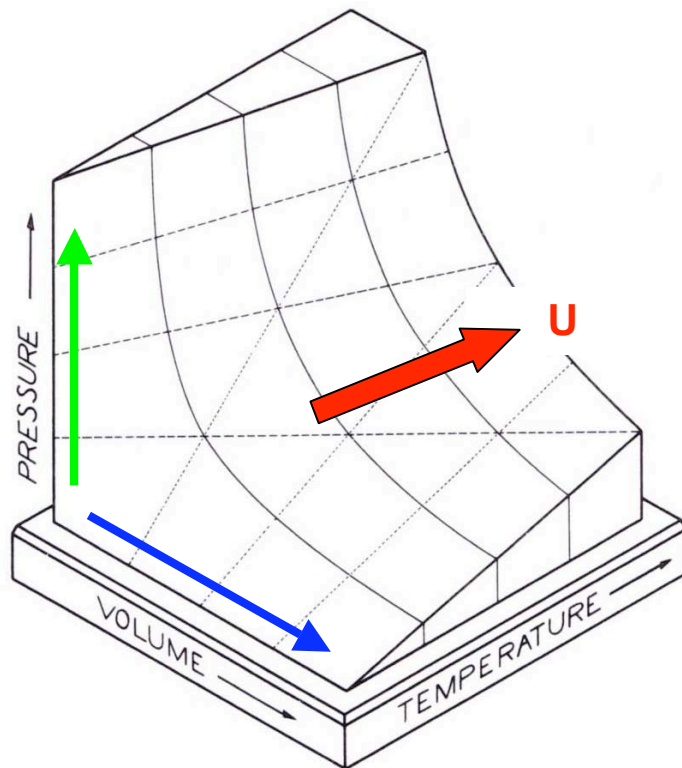


Fig. 2-2 P - v - T surface for an ideal gas.

How to fry your brain...

Imagine a fourth dimension to this graph, then $(\partial U/\partial T)_P$ is a derivative along the **green** direction and $(\partial U/\partial T)_V$ is a derivative along the **blue** direction. Note they are perpendicular.



Latent heat

- The **latent heat** L is defined as the heat Q added to or removed from a system or a particular sample of a substance, per unit mass, to produce a complete phase transition at a constant temperature. In contrast to the heat capacity, usually the latent heat is *automatically* defined per unit mass (i.e., just like the specific heat), so:

$$Q = mL \quad (8.12)$$

This is one of the historical quirks of physics, you could easily define a specific latent heat and a non-specific (or non per unit mass) latent heat if you like, just like the heat capacity, but we don't – Silly, but that's just the way it is I'm afraid.

Big hint: Probably the number 1 place where people get latent heat and specific heat questions wrong is that they aren't careful enough about the signs. People are in such a hurry to get into the algebra that they forget that the main part of the question is making sure you have the starting point right (this can be applied to ALL questions). Make sure you know where the heat is being added and removed and make sure you do your sums properly for where the heat is going. Once you get this bit right, the algebra is just algebra, but its *really* common that it's all wrong before you even start on the algebra to solve for the final answer.



The mechanical equivalent of heat

- In the 1800s Joule spent a lot of time pondering the quantitative relationship between different forms of energy, looking to see how much is lost in converting from one form to another. As you'll already know, when friction is present in some mechanical system we always end up losing some of the mechanical energy, and in 1843 Joule did a famous experiment showing that this lost mechanical energy is converted to heat.

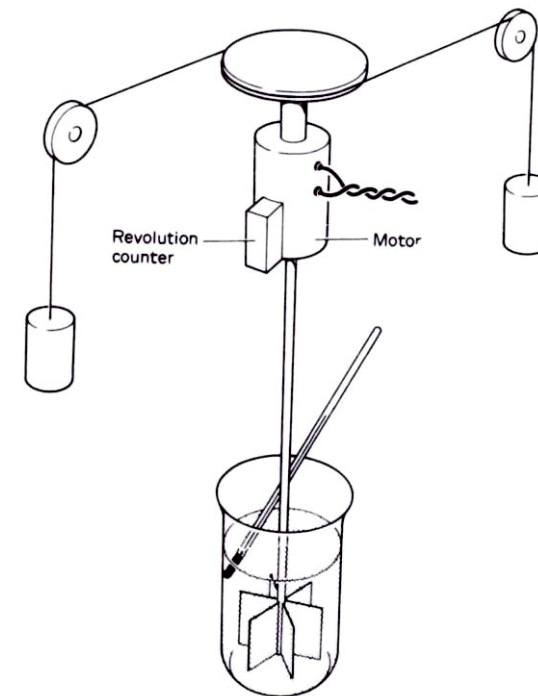


Figure 2.17 An arrangement for the direct mechanical determination of a heat capacity

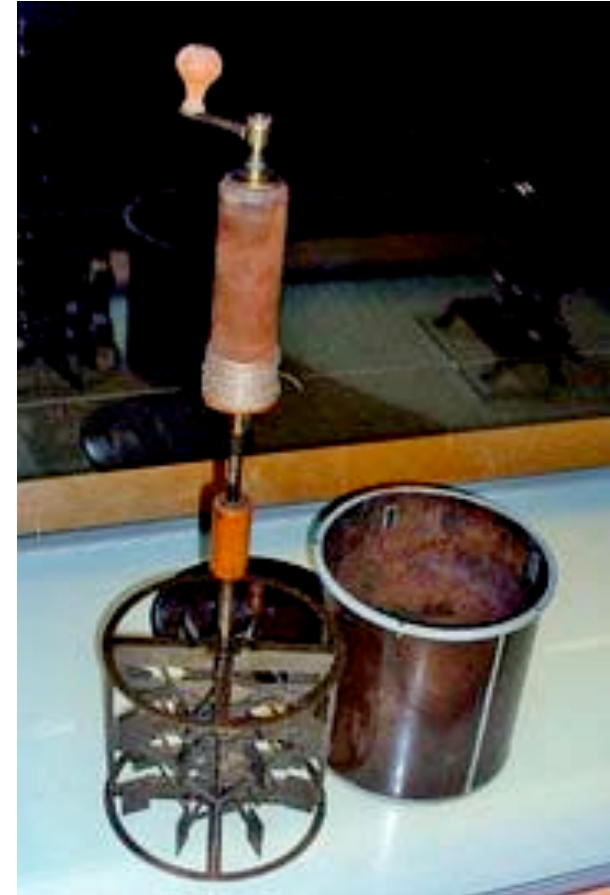


The mechanical equivalent of heat

- Joule's apparatus consists of water in a thermally insulated vessel. Heavy blocks falling at a constant speed (mechanical energy) are connected to a paddle immersed in the liquid. Some of the mechanical energy is lost to the water as friction between the water and the paddles. This results in an increase in the temperature of the water, as measured by a thermometer immersed in the water. If we ignore the energy lost in the bearings and through the walls (which if we're careful, we can make these really small), then the loss in gravitational potential energy associated with the blocks equals the work done by the paddles on the water.

By varying the conditions of the experiment, he noticed that the loss in mechanical energy $2mgh$ was proportional to the increase in water temperature ΔT , with a proportionality constant $4.18\text{J}/^\circ\text{C}$.

This was one of the key experiments leading up to the discovery of the 1st law of thermodynamics.



Some other forms of work

There are a number of other forms of work, simply because there are a lot of external forces that can produce a displacement (and because $dW = F \cdot dx$, this means work!). Let me quickly highlight a few key examples, you will meet more in the tutorials and you can probably even think of more beyond those!

1. **Electrical work:** Moving a charge through an electric field (i.e., with a voltage) gives a force $F = Eq$ and a displacement dx as it moves. Power $P = VI = dW/dt$, so $dW/dt = Vdq/dt$ and so $dW = Vdq$ or $W = Vq$.
2. **Surface tension:** You'll see this one in tutorial 2, but you have to do work to create a surface, and if the surface is closed and has a gas inside, you also have to have an excess pressure to stop the surface from collapsing.
3. **Gravity:** Pushing things uphill are hard work as you'll all know – you have to make some displacement dx against a gravitational force either $F = mg$ or $F = -GmM/R^2$.
4. **Magnetism:** This is more complex, but work is done to change the magnetization of a substance by an applied magnetic field. The details are beyond this course, but it illustrates the pervasiveness of thermodynamics across physics. For example, in low temperature physics, a process known as adiabatic demagnetisation is used to achieve temperatures below 1 millikelvin because the spins in a paramagnetic salt absorb heat to break their alignment as an external field is quickly turned off.



Summary

- Internal energy is *all* of the energy of a system that is associated with its microscopic components – atoms and molecules – when viewed from a reference frame at rest with respect to the center of mass of the system.
- Heat is defined as the spontaneous transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings. There is no external force mediating this process.
- Work is basically defined as any other transfer of energy into or out of the system. The most important form of work in thermodynamics is compressive work, which is due to a change in volume against or due to an external force (or pressure) on a gas.
- Heat can be loosely divided into specific heat and latent heat. Specific heat is heat that enters or leaves a system to produce a change in temperature but no phase change. Latent heat is heat that enters or leaves a system to produce a phase change at constant T .
- Joule showed that mechanical energy lost to friction becomes heat.

In the next lecture we will look at the three mechanisms by which heat is transferred: conduction, convection and radiation.

