

©2015 Yoni Kahn and Adam Anderson. All Rights Reserved.

www.physicsgreprep.com

Second edition, printing 1.1 (updated February 2015)

No part of this book may be reproduced without written permission from the authors.

ISBN-13 978-1479274635

Chapter 4

Thermodynamics and Statistical Mechanics

Statistical mechanics and thermodynamics form a small but important section of the exam. On the one hand, only 10% of the exam covers these topics. On the other, the questions tend to be at an easy level and students tend to perform poorly because statistical mechanics and thermodynamics are often poorly covered in undergraduate courses. A relatively small amount of knowledge translates into a large gain in performance on these questions.

In this section we will give a sketch of the basic structures of statistical mechanics and thermodynamics, and then we will consider their application to some model systems. Most problems will involve just a few of these model systems, so it is worth understanding them well.

4.1 Basic statistical mechanics

4.1.1 Ensembles and the partition function

State variables such as temperature and pressure characterize the *macrostate* of a system, and completely specify the macroscopic behavior of the system. On the other hand, many microscopic configurations or *microstates* correspond to the same macrostate. We can imagine preparing several copies of a system with slightly different initial conditions; if at the time of measurement, the copies have the same state variables, the systems will be macroscopically identical. Statistical mechanics is the business of calculating properties of macrostates without knowing the exact microstate of a system.

To carry out the calculation, we need to identify what *ensemble* applies to our system. An ensemble is the collection of all possible microscopic configurations of the system subject to some constraints, and formalizes the idea of different microstates corresponding to a single macrostate. The most common ensemble, by far, that appears on the GRE is the *canonical ensemble*. The canonical ensemble consists of all possible states of a system with

- fixed particle number (N)

- fixed volume (V)
- fixed temperature (T): the system is allowed to exchange energy with a large heat bath whose heat capacity is assumed to be so large that its temperature stays fixed.

So a system described by the canonical ensemble can have energy fluctuations, but the state variables N , V , and T must remain fixed. A somewhat less common ensemble is the *microcanonical ensemble*, which has fixed energy E rather than fixed temperature T , and whose temperature can fluctuate accordingly. There are other ensembles associated with other state variables, but these do not seem to ever be tested by the GRE. Unless otherwise specified, we will work with the canonical ensemble in the remainder of this chapter.

With this picture, how do we actually calculate anything? Consider a system with discrete energy states $\{E_i\}$. From a few very basic assumptions one can show that the probability of the system being in a state i is given by

$$p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}, \quad (4.1)$$

where

$$\beta = \frac{1}{k_B T}. \quad (4.2)$$

Here k_B is Boltzmann's constant; we will often use β and T interchangeably depending on which one is more convenient.¹ Equation (4.1) allows us to calculate extensive quantities, like average energy E or its variance σ_E^2 , by using the p_i as a probability distribution. For example, suppose the system is a magnet, and the energy states E_i have magnetizations M_i . The average magnetization is given by

$$\langle M \rangle = \sum_i p_i M_i.$$

In fact, whenever you encounter any system that has a discrete set of states in any parameter \mathcal{O} (energy, spin, magnetization, etc.), and you need to compute the average value of this parameter, just use the weighted sum of the different states

$$\langle \mathcal{O} \rangle = \sum_i p_i \mathcal{O}_i, \quad (4.3)$$

which should be familiar from basic probability.

It is equally instructive to rewrite equation (4.1) as

$$p_i = \frac{e^{-\beta E_i}}{Z}, \quad (4.4)$$

¹The GRE writes k instead of k_B in the Table of Information at the beginning of the exam, but to avoid any confusion with the many other uses of the letter k , we will stick to k_B in this chapter.

where Z is known as the *partition function*,

$$Z = \sum_i e^{-\beta E_i}. \quad (4.5)$$

The advantage of the partition function formalism is that the same quantities we computed above using probabilities can be computed from directly from Z . This is important enough to repeat: *if you know the partition function, you can compute all the state variables*. The expectation value of energy, for example, is

$$\langle E \rangle = \sum_i p_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{Z} = -\frac{\partial}{\partial \beta} \ln Z. \quad (4.6)$$

This last equality is an extremely useful trick because it allows us to compute the average energy directly from the partition function without even thinking about the probabilities or doing complicated sums: just find Z and differentiate its logarithm!

This n -state system arises very frequently on the GRE. In general, you might be given a system with n discrete states and corresponding energies E_i ; the quantum harmonic oscillator is a favorite example, but sometimes the GRE just gives you a list of states and their associated energies. Problems may ask you to compute the probability of the system being in certain states, ratios of probabilities of states, expectation values of energy, expectation values of other quantities, and the heat capacity, to be discussed in Section 4.2.5 below. The formulas in this section should be enough to get you through any of these kinds of problems.

4.1.2 Entropy

Another quantity of fundamental importance that constrains the behavior of systems in thermodynamics and statistical mechanics is the entropy. Entropy can be conceptually tricky, but for the purposes of the GRE, you will only be expected to know its mathematical definitions, and how to apply it in well-defined thermodynamic scenarios. Here we give two definitions and a useful formula, but more discussion will follow in Section 4.2.3.

- The most transparent and elegant definition is the one given by Boltzmann

$$S = k_B \ln \Omega, \quad (4.7)$$

where Ω is the number of microstates corresponding to the system's macrostate. For example, if a two-electron system is in a magnetic field with Hamiltonian $H \propto \mathbf{S} \cdot \mathbf{B}$, the states of the system are the spin singlet with $\mathbf{S} = 0$ and the spin triplet with $\mathbf{S} = 1$. The zero-energy state is the one with $S_z = 0$, for which there are two corresponding microstates: the spin singlet, and the $S_z = 0$ component of the spin triplet.² Thus the zero-energy state has entropy $k_B \ln 2$. The formula (4.7) is useful if you ever need to calculate the entropy of a system which either has a small number of states or a simple analytic expression for the number of states.

²If this discussion is unfamiliar to you, see Section 5.5.3.

- Another closely related expression for entropy is

$$S = -k_B \sum_i p_i \ln p_i = \frac{\partial}{\partial T} (k_B T \ln Z), \quad (4.8)$$

where p_i is the probability of the system being found in the i th microstate. (Exercise: derive the last equality from the definitions (4.4) and (4.5).) This definition has the advantage of being directly connected to the partition function, so it is useful if you happen to know the exact form of the partition function.

It turns out to be equivalent to (4.7) if we assume something called the “fundamental assumption of statistical thermodynamics” or sometimes the “postulate of equal *a priori* probability”. The justification for this is very deep and subtle, but for the purposes of the exam you can assume that these forms of the entropy are equivalent.

- For a *monoatomic ideal gas*, the expression for entropy is

$$S = Nk_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{5}{2} + \frac{3}{2} \ln \frac{2\pi m k_B}{h^2} \right), \quad (4.9)$$

where V is the volume, N is the number of particles, T is the temperature, m is the mass of the gas particles, and h is Planck’s constant. The important point here is not the constant numerical factors, but the scaling of S with state variables. It is most useful to remember

$$S = Nk_B \ln \frac{VT^{3/2}}{N} + \text{constants}. \quad (4.10)$$

We’ll discuss ideal gases more in Section 4.2, but we mention them here just to show what an explicit formula for entropy looks like.

The interpretation of entropy from these definitions is as a measure of the number of possible states that a system could have in a particular macroscopic state. Gibbs is rumored to have called it, more-or-less accurately, the amount of “mixed-up-ness” of a system. If a system could be in many possible states, then it has high entropy. Alternatively, we can think of entropy as a measure of our uncertainty about the underlying state of the system. If a system has low entropy, then it can only be in a small number of possible states, and we can be relatively certain what underlying state it is actually in.

4.1.3 Classical limit

The partition function formalism is very simple to apply to systems with a small number of states. But classical systems do not generally have a discrete set of states. Because position and momentum are continuous variables, there are formally an infinite number of microstates for a box of gas, for example. Nevertheless, we can extend the formalism above

to the continuum limit. The sum in the partition function becomes an integral and we obtain the partition function for N (identical) classical particles

$$Z_N = \frac{1}{N!h^{3N}} \int e^{-\beta H(\mathbf{p}_1, \dots, \mathbf{p}_n; \mathbf{x}_1, \dots, \mathbf{x}_n)} d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_n d^3\mathbf{x}_1 \cdots d^3\mathbf{x}_n, \quad (4.11)$$

where \mathbf{x}_i and \mathbf{p}_i are three-dimensional vectors, H is the classical Hamiltonian, h is Planck's constant, and the normalization factor $N!$ accounts for identical particles. The effects of identical particles can be rather tricky and irritating, but it is not too difficult to understand. When particles are identical, states formed by interchanging particles are not counted twice, and dividing by $N!$ accounts for this. That said, since N is a fixed quantity in the canonical ensemble, so the factors multiplying the integral in Z almost always disappear when you take the log and differentiate to find the state variables.

4.1.4 Equipartition theorem

The equipartition theorem is a simple application of equation (4.11), which gives a quick rule for determining the internal energy of a system. This is extremely useful for computing heat capacities, as discussed further in Section 4.2.5. The theorem states that

Each quadratic term (degree of freedom) in the Hamiltonian for a particle contributes $(1/2)k_B T$ to the internal energy of the particle.

For example, a particle in an ideal gas has a Hamiltonian $H = \mathbf{p}^2/2m = p_x^2/2m + p_y^2/2m + p_z^2/2m$, so the internal energy of such a particle is $U = (3/2)k_B T$. The proof of this is an exercise in manipulating Gaussian integrals, noting that we can integrate each quadratic term in the exponential of equation (4.11) one by one, but the details are not relevant for the GRE.

Often we can compute the internal energy from the equipartition theorem without ever writing down an explicit Hamiltonian, just by counting quadratic degrees of freedom. As an example, consider a diatomic gas at high temperatures. There are three translational degrees of freedom corresponding to the kinetic energy of the center of mass in the three spatial dimensions. There are two rotational degrees of freedom, corresponding to rotations around the axes perpendicular to the axis connecting the two atoms (since the atoms are assumed to be point-like, there is no energy associated with rotation along the axis connecting the atoms). And there are two vibrational degrees of freedom corresponding to the kinetic and potential energy of the vibrating molecules. Without writing anything, we see that there are 7 quadratic degrees of freedom and the internal energy is $(7/2)k_B T$. The explicit Hamiltonian for a diatomic gas composed of two atoms of mass m is

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{p_s^2}{m} + \frac{1}{2}ks^2,$$

where s is the separation between the atoms, k is the vibrational spring constant, $I_{1,2}$ are the two moments of inertia about the two rotational axes, and $L_{1,2}$ and p_s are the appropriate

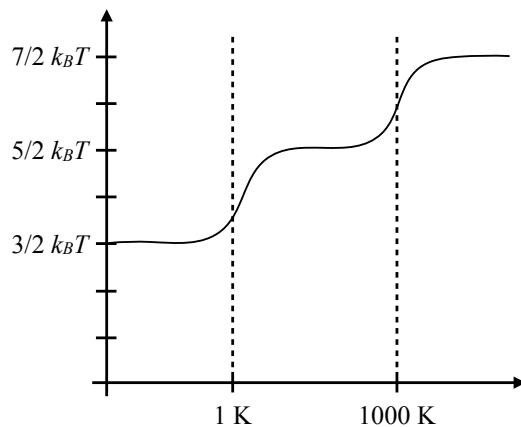
conjugate momenta (note that there is no factor of $1/2$ in the second-to-last term because vibrations are about the center of mass, and the reduced mass is $m/2$). But clearly, we didn't need to write down the Hamiltonian to get the answer. Other examples include the extreme relativistic gas and two-dimensional gases, whose internal energies you will calculate in the end-of-chapter problems.

Remember that the equipartition theorem is a *classical* statement, and it breaks down when the spacing between energy levels becomes large compared with $k_B T$. In this regime, the classical assumption that the energy levels form a continuum is no longer valid, and the equipartition theorem will tend to overestimate the internal energy of a system. This usually happens at low temperatures, when degrees of freedom are "frozen out." In the case of a diatomic ideal gas, for example, we saw that the internal energy at high temperatures was $(7/2)k_B T$. We know from quantum mechanics that the low-energy states of the harmonic oscillator are discrete, and it is straightforward to show that the low-energy states of the rigid rotor in 3 dimensions are also discrete. Using typical values for the harmonic oscillator angular frequency ω and the moment of inertia I , we can estimate the temperature at which quantum mechanics becomes important:

$$k_B T \sim \hbar\omega \implies T \sim 1000 \text{ K} \quad (\text{vibrational})$$

$$k_B T \sim \frac{\hbar^2}{2I} \implies T \sim 1 \text{ K} \quad (\text{rotational})$$

So vibrational degrees of freedom freeze out first; at room temperature, the equipartition theorem still applies to translational and rotational degrees of freedom, and the internal energy is $(5/2)k_B T$. At very low temperatures, if the substance still exists as a gas once rotational degrees of freedom have frozen out, all that is left are the energy states associated with the translational part of the Hamiltonian, or the free particle states. From quantum mechanics we know that such states form a continuum down to low energies. So at low temperatures, the equipartition theorem will continue to apply to the three translational degrees of freedom and the diatomic gas will have an internal energy approximately equal to $(3/2)k_B T$, the same as for a monoatomic ideal gas. This situation is conveniently summarized in the figure below, where the temperature axis is logarithmic.



4.1.5 Some mathematical facts

A few basic combinatorial facts occasionally come in handy. The first is the *binomial coefficient*. Suppose that we N distinguishable marbles and we want to know the number of ways of choosing a group of M of these marbles from a hat. The result is denoted

$$\binom{N}{M} = \frac{N!}{(N-M)!M!}, \quad (4.12)$$

which is read “ N choose M .”

Another useful identity known as *Stirling’s formula* is

$$\ln(n!) \approx n \ln n - n \quad (4.13)$$

for large values of n .

4.2 Thermodynamics

Statistical mechanics reproduces macroscopic physics by analyzing microscopic physics. Thermodynamics ignores the microscopic foundations and sets down rules for how macroscopic systems should behave. Even without the microscopic foundations, thermodynamics gives a complete description of thermal systems. Though thermodynamics is usually taught first, it can be derived from statistical mechanics, so hopefully the laws and formulas will seem straightforward in light of the more formal tone of the previous section.

4.2.1 Three laws

Thermodynamics can be summarized succinctly in three laws (plus a zeroth law) that completely determine the behavior of a system. The laws of thermodynamics are

1. *Energy cannot be created or destroyed.* This is just the conservation of energy from the statistical mechanical point of view, and it can be stated mathematically as

$$\Delta U = Q - W, \quad (4.14)$$

where ΔU is the change in the internal energy of a system, Q is the heat added *to* the system, and W is the work done *by* the system. Take care that the signs of your terms agree with your definitions of the quantities.

2. *There is no process in which the sole effect is to transfer heat from a body at a lower temperature to a body at a higher temperature.* There are several equivalent formulations of the second law of thermodynamics: the previous sentence is the so-called “refrigerator” statement, while the “engine” version is *no system can undergo a cyclic process where heat absorbed from a reservoir at a single temperature is completely converted into mechanical work.* The refrigerator statement says that refrigeration cannot

happen spontaneously, and the engine statement says that heat engines must always waste some heat. All equivalent statements of the Second Law imply the mathematical relationship

$$\Delta S \geq \int \frac{\delta Q}{T}, \quad (4.15)$$

which describes the well-known result that the entropy of a thermally isolated system (where $\delta Q = 0$) cannot decrease. Past GRE's have had questions involving conceptual applications of the Second Law, so it's useful to know both the words and the mathematical relationship.

3. *Entropy is zero at absolute zero temperature.* This statement follows from the definition of entropy (4.7). At absolute zero, there is only one microstate for a system and so the entropy is zero.

There is an additional law, called the *zeroth law* which states that if two systems are in equilibrium with a third, then they are in equilibrium with each other, easily remembered by the succinct statement “thermometers exist.” This is necessary in order for the notion of thermodynamic equilibrium to be well-defined.

4.2.2 Gases and equations of state

Thermodynamic systems are specified by an equation of state that constrains the values that the state variables may assume. The most famous example of this is the equation of state for an ideal gas,

$$PV = Nk_B T, \quad (4.16)$$

where P is the pressure, V is the volume, N is the number of particles, and T is the temperature. You probably know this as the *ideal gas law*, describing how the state variables P , V , and T are related. The only other equation of state you may see on the exam is the equation of state for the Van der Waals gas. The Van der Waals gas has particles with nonzero size and a pairwise attractive potential, and the equation of state is

$$\left(P + \frac{N^2 a}{V^2} \right) (V - Nb) = Nk_B T,$$

where a measures the attraction between particles, and b measures the size of the particles. Clearly $a = b = 0$ reduces to the ideal gas law. You should definitely not memorize this equation, as it will be given to you if needed, but you should be familiar with its interpretation.

4.2.3 Types of processes

Thermodynamic processes can be classified into several types that have important properties, mostly relating to holding certain variables constant. The words used to describe many of these processes are often used interchangeably, but this is sloppy: there are very precise

meanings, and it is crucial to keep definitions straight to know which formulas apply. Here is a list of the most important processes you will encounter on the GRE.

- **Reversible process** - A process that proceeds in infinitesimal steps such that the system is in equilibrium at each step, *and* each infinitesimal step can be reversed by somehow changing the state of the system. A common example is slowly heating a gas in a container of flexible size. As an infinitesimal amount of heat is added, the gas expands, and comes to equilibrium after enough time has elapsed; this can be reversed simply by cooling the system by removing an equal amount of heat.

Reversible processes imply several important conditions. If the process involves a gas, the work done in each infinitesimal step is given by

$$\delta W = P dV \quad (\text{reversible}). \quad (4.17)$$

Note that this is *not* true if the process is irreversible: see “free expansion” below. In addition, the *total* entropy change of the system and its surroundings must be zero. The entropy of the system *by itself* can change, however, and is given by

$$\delta Q = T dS \quad (\text{reversible}), \quad (4.18)$$

where T is the temperature and δQ is the heat input. The integral form of this equation is

$$\Delta S = \int \frac{\delta Q}{T}, \quad (4.19)$$

which is just the lower bound of the Second Law expression (4.15): a reversible process has the minimum possible entropy increase for a given δQ . Notice that if $\delta Q < 0$, ΔS is negative! There is no contradiction here: cooling a system reduces its entropy, but increases the entropy of its surroundings by an equal amount because of the heat deposited, so the total entropy change is zero. Finally, notice that if the initial and final states of the system are the same, the limits of integration degenerate onto each other, and $\Delta S = 0$: *the entropy change of a system undergoing a reversible cycle is zero.*

- **Quasistatic process** - A process that happens infinitely slowly, so that at each instant the system is in thermodynamic equilibrium. Reversible processes are always quasistatic, but a quasistatic process need not be reversible in general.
- **Adiabatic process** - A process for which $\delta Q = 0$: no heat is exchanged between a system and its surroundings.
- **Isentropic process/Reversible adiabatic process** - A process that is both adiabatic and reversible. One can prove that a process is reversible and adiabatic if and only if it has zero entropy change (an isentropic process). Here we mean that the entropy change of the system itself is zero, and consequently, the entropy change of the surroundings is zero as well. Compressing a gas in a cylinder by pressing down a piston

is the prototypical example. By applying a very small force, the piston is displaced a small amount; each compression step can be reversed by releasing the force, which causes the gas to expand again and the system to return to its initial state. Since no heat is exchanged during this process, adiabatic compression is isentropic.

One major reason that this type of process arises in problems is that for an ideal gas undergoing an isentropic process,

$$PV^\gamma = \text{constant}, \quad (4.20)$$

where $\gamma = C_P/C_V$ is the ratio of the heat capacity at constant pressure P to heat capacity at constant volume V . There is a particularly nice formula for γ for ideal gases, which we discuss further in Section 4.2.5.

Warning! Past GRE's have been known to use "adiabatic" to mean "reversible adiabatic." Keep the more restrictive definitions in mind, but be prepared to be flexible based on context because the GRE often does not define its terms in the test questions.

- **Iso-something process** - A process for which some state variable is held constant. "Isothermal" means constant temperature, "isobaric" means constant pressure, and "isochoric" means constant volume, though memorizing these terms is completely unnecessary. The key to figuring out the work done by a gas in such a process is to use the definition of work (4.17), supplanted by the ideal gas law equation of state (4.16), to solve for P in terms of the constant variables. For example, if P is constant, it can be pulled outside the integral and $W = P\Delta V$. If T is constant, then solve for P in terms of T :

$$P = \frac{Nk_B T}{V} \implies W = Nk_B T \int \frac{dV}{V}.$$

If V is constant, then no work is done since $dV = 0$. The isothermal process is perhaps the most common, so get familiar with the form of the integral and the appearance of $\ln V$ from integrating dV/V .

- **Free expansion** - This process occurs when a gas suddenly expands from a smaller region to a larger region: think of a balloon popping, where the gas initially inside the balloon rushes out to fill the whole volume of the room. The temperature of an ideal gas does not change during free expansion, so we have

$$pV = p'V' \quad (\text{free expansion})$$

Note that free expansion is adiabatic, but *not* reversible: one cannot force all the gas molecules back into the smaller volume once they have expanded, simply by changing the state variables of the system. Free expansion is the prototypical irreversible process, just as irreversible as an egg breaking. The fact that this process is irreversible means that there *is* an entropy change, despite the fact that $\delta Q = 0$; equation (4.19) simply does not apply to irreversible processes. We will see in the following Section 4.2.4 how to calculate the entropy change. Similarly, note that despite the fact that the volume

changes, *the gas does no work*. This is consistent with the First Law: $\Delta U = 0$ at constant temperature, $Q = 0$ since the process is adiabatic, and $W = 0$, so we trivially get $0 = 0 - 0$.

4.2.4 Relations between thermodynamic variables

Equations of state tell us what states are accessible to a particular system in terms of the system's state variables. What if we are interested in other variables that are not the state variables of a system? How would we calculate the entropy of an ideal gas, for example? There are a large number of thermodynamic identities that relate, under varying circumstances, all of the variables that we have been discussing.

The first identity is so useful that it is often called the *fundamental thermodynamic identity*. It relates the differentials of state variables U , S , and V :

$$dU = TdS - PdV. \quad (4.21)$$

This equation is simply the infinitesimal version of the First Law (4.14), $dU = \delta Q - \delta W$, supplanted by the definitions (4.18) and (4.17) for δQ and δW respectively. Notice that we write δQ and δW , not dQ and dW . This is because Q and W are not state variables, but refer to small quantities of heat and work added to or done by the system, respectively. In contrast, U is a state function, a mathematical representation of the internal energy of a system, which can thus be sensibly differentiated. Finally, note that (4.21) applies to *all* infinitesimal changes of state, not just reversible ones: this needs a tricky bit of reasoning, so this fact is best simply memorized.

Let's use this formula to calculate the entropy change for an ideal gas in a particular process, the adiabatic free expansion of a gas from volume V_1 to volume V_2 . The internal energy is $\frac{3}{2}Nk_B T$, which depends only on T , but since temperature is constant in free expansion, $dU = 0$. Thus $TdS = PdV$, and

$$\Delta S = \int_{V_1}^{V_2} P \frac{dV}{T} = \int_{V_1}^{V_2} \frac{Nk_B T}{V} \frac{dV}{T} = Nk_B \ln\left(\frac{V_2}{V_1}\right).$$

Of course, this matches the result you would obtain from using the full formula for the entropy (4.9). It's much more important to remember the steps that go into this derivation than memorize the equation for entropy change itself, since this same kind of reasoning is used often in thermodynamics problems.

The fundamental thermodynamic identity also implies a definition of temperature and pressure

$$T = \left(\frac{\partial U}{\partial S} \right) \Big|_V \quad (4.22)$$

$$P = - \left(\frac{\partial U}{\partial V} \right) \Big|_S. \quad (4.23)$$

The vertical bars refer to holding the subscript variable constant, so (4.22) holds at constant V , and (4.23) holds at constant S .

Another important class of thermodynamic relations are the Maxwell relations which related partial derivatives of thermodynamic variables. From the expressions for T and P above, we can equate mixed partial derivatives and determine

$$\left(\frac{\partial P}{\partial S}\right)_V = - \left(\frac{\partial T}{\partial V}\right)_S. \quad (4.24)$$

There are three other thermodynamic potentials, which we give here for completeness, though you almost certainly won't need them for the GRE:

$$dH = TdS + VdP \quad (4.25)$$

$$dA = -SdT - PdV \quad (4.26)$$

$$dG = -SdT + VdP. \quad (4.27)$$

The associated Maxwell relations are

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (4.28)$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (4.29)$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P. \quad (4.30)$$

4.2.5 Heat capacity

The heat capacity of an object is the amount of heat it takes to change the temperature of that object. More precisely, we can define the heat capacity at constant volume and pressure as

$$\left(\frac{\partial Q}{\partial T}\right)_V = C_V \quad (4.31)$$

$$\left(\frac{\partial Q}{\partial T}\right)_P = C_P, \quad (4.32)$$

respectively.³ The more common one is C_V , because referring back to the fundamental equation (4.21), constant volume is equivalent to $dV = 0$, so we can differentiate both sides with respect to T and get

$$\left(\frac{\partial Q}{\partial T}\right)_V = \frac{\partial U}{\partial T}. \quad (4.33)$$

Hence differentiating the energy you obtain from the equipartition theorem gives you C_V .

³Given our admonition to be careful about writing δQ rather than dQ , the abuse of notation ∂Q may seem strange, but it is a common one. Just make sure ∂Q only shows up when taking a derivative with respect to something, and not as a total differential as in (4.21).

In fact, for an ideal gas there is a very simple (but *very* tricky to derive) relation between C_P and C_V :

$$C_P - C_V = Nk_B. \quad (4.34)$$

where N is the number of particles. Note that this is true for *any* ideal gas: monoatomic, diatomic, or something more complicated. This in turn immediately gives you the ratio γ you need for an adiabatic process if you know the internal structure of the gas. For example, a monoatomic gas has internal energy $\frac{3}{2}k_B T$ per particle from the equipartition theorem, so we have

$$C_V = \frac{3}{2}Nk_B \implies C_P = \frac{5}{2}Nk_B \implies \gamma = \frac{C_P}{C_V} = \frac{5}{3}.$$

As defined, C_P and C_V are *extensive* variables, because they depend on the quantity of the substance being heated. If we normalize to the mass of the material, we get an *intensive* quantity c called the *specific heat* (or *specific heat capacity*), typically in units of $\text{JK}^{-1}\text{g}^{-1}$. From dimensional analysis, we can remember the formula for the amount of energy Q required to heat a mass m of specific heat c by ΔT degrees as

$$Q = mc\Delta T. \quad (4.35)$$

The specific heat capacity of water is famously equal to $4.18 \text{ JK}^{-1}\text{g}^{-1}$ at standard temperature and pressure. Because of this, specific heats are sometimes quoted in units of *calories* rather than Joules. One calorie is set to be 4.18 J , so that the specific heat capacity of water is conveniently $1 \text{ cal K}^{-1}\text{g}^{-1}$. We should note that the terms “heat capacity” and “specific heat” are often used interchangeably, and if a distinction is necessary, the units and context should tell you which one is meant.

4.2.6 Model systems

Two thermodynamic systems are almost guaranteed to appear on the GRE: heat engines and ideal gases. Gases also provide a nice system for studying the propagation of sound waves.

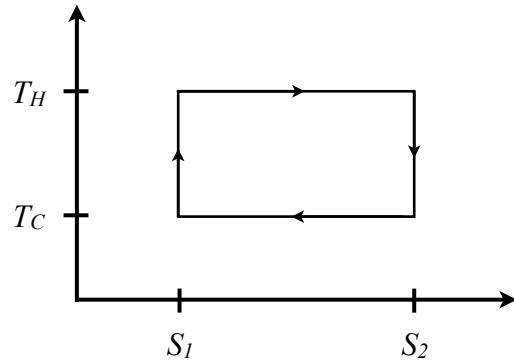
- **Heat engines, P - V , and T - S diagrams.** A heat engine is a process that converts heat into work. Schematically, the heat engine absorbs some heat Q_H from a hot reservoir at T_H , expels Q_C to a cold reservoir at T_C , and converts the remainder in work $W = Q_H - Q_C$. Since energy Q_C is not converted into work, the efficiency of the heat engine is

$$e = 1 - \left| \frac{Q_C}{Q_H} \right|. \quad (4.36)$$

(Note that there are various sign conventions for Q_C and Q_H , but the absolute value signs make sure $e < 1$ always.) The *maximum* theoretical efficiency for a heat engine is

$$e = 1 - \frac{T_C}{T_H}, \quad (4.37)$$

which is in fact the efficiency of the idealized Carnot cycle. The Carnot cycle consists of four steps. First, the gas undergoes reversible isothermal expansion at the hot temperature T_H . Entropy increases from S_1 to S_2 during this process. Next, the gas expands adiabatically at constant entropy until it has temperature T_C . The gas then is compressed at constant temperature T_C , and entropy decreases from S_2 back to S_1 . Finally, the gas is compressed adiabatically, increasing the temperature from T_C to T_H . The entire process is thus a rectangle in the TS -plane, illustrated below.

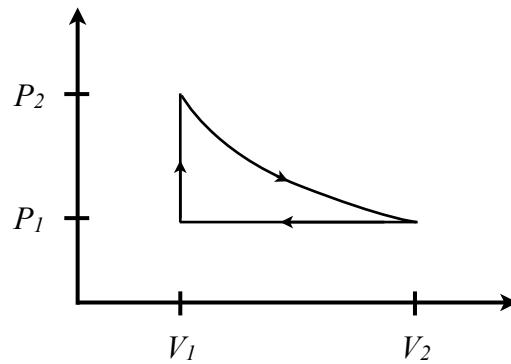


Since the system returns to its initial state, its change in internal energy over the cycle is zero: $\Delta U = 0$. The First Law then tells us that $Q = W$. The heat input in reversible processes is $Q = \int T dS$, so we can compute the work by

$$W = Q = \int T dS = (T_H - T_C)(S_2 - S_1).$$

In other words, the work is the area in the TS -plane bounded by the Carnot cycle. Problems on the GRE often involve analyzing cycles of systems in pressure-volume or entropy-temperature diagrams. The Carnot cycle is just one example of a problem that can be analyzed with ones of these diagrams.

A similar example with a P - V diagram is shown in the figure below.



This diagram could represent an ideal gas that undergoes compression at constant pressure, an increase in pressure at constant volume via heating, and then isothermal expansion. To find the work done during the process, just find the *area* in the PV -plane, since that's what the integral $\int PdV$ instructs you to do.

It is important to note that the areas are *signed* quantities: if you reverse the direction of the closed path bounding the area in question, you flip the sign of the area, and hence the sign of the work. This is often a crucial distinction, since it tells you whether the system is doing work on its surroundings, or vice versa. You can determine this sign with a right-hand type rule, but it's just as easy to use physical reasoning: the gas does positive work as it expands, and for a given volume change ΔV , it does more work at higher pressure. So imagining a rectangle in the PV -plane, the gas does positive net work when the upper horizontal edge is traversed left-to-right, and the bottom edge is traversed right-to-left. A similar analysis holds for $T - S$ diagrams, so to summarize,

Clockwise paths in the PV - and TS -planes do positive work.

Just remember which axis goes where!

- **Monatomic ideal gases.** Since ideal gases are so common, at a minimum you should know the internal energy, the entropy, and the rms velocity. Sometimes it's handy to know the partition function, because it allows you to calculate so many observables, but it is not essential knowledge.

The Hamiltonian for a particle in an ideal gas is just the Hamiltonian for a free particle in three dimensions. So using equation (4.11) with $H = \mathbf{p}^2/2m$, we have the partition function for a single particle

$$Z_1 = \frac{1}{h^3} \int e^{-\beta \mathbf{p}^2/2m} d^3 p d^3 x = \frac{V}{h^3} (2\pi m k_B T)^{3/2}.$$

For a gas of N identical particles, the partition function is just the product of all single-particle partition functions times the normalization factor $1/N!$ for identical particles

$$Z_N = \frac{V^N}{N! h^{3N}} (2\pi m k_B T)^{3N/2}.$$

From this, we can immediately derive the internal energy of a classical ideal gas using (4.6),

$$U = \frac{3}{2} N k_B T, \tag{4.38}$$

which implies $C_V = (3/2)Nk_B$ from the discussion in Section 4.2.5. You can turn this around and use the equipartition theorem to remind yourself about the factor of $3/2$ in the exponent of the partition function: there are three quadratic degrees of freedom in the Hamiltonian (one for each spatial dimension), giving the factor of $3/2$ in the internal energy.

Related to the average internal energy of a gas is the root-mean-square (rms) velocity of a gas molecule. This is given by

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}. \quad (4.39)$$

The rotational and vibrational motion of a gas molecule does not contribute to its velocity: a molecule can rotate however it wants, but if it has no translational energy, its rms velocity will be zero. The result of this is that even though monatomic and diatomic gases have different internal energies, the expressions for their rms velocities are equivalent. This makes the formula very easy to remember: the factor of 3 comes from 3 dimensions, and the rest of the factors come from dimensional analysis.

We can also calculate the entropy of an ideal gas just by differentiating the partition function, using (4.8), and derive equation (4.9) which we saw earlier, repeated here for convenience:

$$S = Nk_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{5}{2} + \frac{3}{2} \ln \frac{2\pi mk_B}{h^2} \right).$$

This expression is useful for demonstrating the *entropy of mixing*. Consider a box that is divided into two equal halves of volume V by an impermeable partition, with the same number N of gas particles in each half. If the gases are identical, then removing the partition does not change the entropy of the system. On the other hand, if the gases are different, then removing the partition produces a change in entropy

$$\Delta S_{\text{mix}} = 2Nk_B \left(\ln \frac{2V}{N} - \ln \frac{V}{N} \right) = 2Nk_B \ln 2. \quad (4.40)$$

This example demonstrates the importance of whether particles in a system are identical or distinguishable for determining the entropy. Once again, remembering the constant terms is probably not worth your time, since they tend to cancel when calculating entropy differences anyway, as they did in this example.

- **Sound waves in gases.** Sound waves need a medium in which to propagate, and in most everyday situations, this medium is a gas. As discussed in Chapter 3, the speed of sound in a material is given by

$$c = \sqrt{\frac{K}{\rho}},$$

where K is a measure of stiffness called the *bulk modulus* and ρ is the density. The “stiffness” of an ideal gas is tricky to define, but the general result is that

$$K = \gamma P,$$

where $\gamma = C_P/C_V$ and P is the pressure as usual. From this, we have the general result that the speed of sound in an ideal gas is just

$$c = \sqrt{\gamma \frac{P}{\rho}}. \quad (4.41)$$

This formula is also simple to memorize: higher pressure means faster speed of sound, higher density means lower speed of sound, and the square root comes from dimensional analysis. Notice, though, that this formula contains an implicit dependence on the temperature: since $\rho = m/V$, the ideal gas law gives

$$\frac{P}{\rho} = \frac{P}{m/V} = \frac{PV}{m} = \frac{Nk_B T}{m},$$

so the speed of sound can be written

$$c = \sqrt{\gamma \frac{Nk_B T}{m}}. \quad (4.42)$$

4.3 Quantum statistical mechanics

Though we discussed the role of identical particles when calculating the entropy, we have not considered the effect of distinguishability in a more general quantum context. Identical particles behave very differently in quantum mechanics than might be expected from classical mechanics; the best-known example is the Pauli exclusion principle (to be discussed in much more detail in the following chapter) which states that two identical fermions can't occupy the same quantum state. When we wish to calculate the energy of some large ensemble of particles, knowing how many particles are allowed to occupy each state with energy ϵ is obviously essential. More precisely, it affects the average occupation number of a particular energy state.

Deriving the *average occupation number* for bosons and fermions is straightforward, though a little lengthy, so we will not repeat it here and simply state the results. By average occupation number, we mean the average number of particles occupying a single-particle state at some energy ϵ_i . For *identical* fermions (particles with half-integer spin), the occupation number as a function of energy level ϵ_i is described by the *Fermi-Dirac distribution*

$$F_{FD}(\epsilon_i) = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}. \quad (4.43)$$

Notice that F_{FD} can never exceed 1: this is the Pauli exclusion principle at work, since there can be no more than one fermion per energy level. For identical bosons (integer spin), we have instead

$$F_{BE}(\epsilon_i) = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} - 1}. \quad (4.44)$$

Now, the change of sign in the denominator means that depending on the temperature, arbitrarily many bosons can occupy the same state. At zero temperature, this leads to

the familiar concept of *Bose condensation*: all the particles want to sit in the state with lowest energy. Both of these distributions limit to the usual exponential Boltzmann factor (4.4) when the system can be treated “classically” (large inter-particle distance and high temperature), which forces the exponential factor in the denominator to be much greater than 1.

To actually calculate anything with these distributions, we need a few extra ingredients. The new quantity appearing in all the above formulas is μ , the *chemical potential*, which roughly speaking is the energy associated with adding or removing a particle from the system. In the *grand canonical ensemble*, a generalization of the canonical ensemble, the number of particles is allowed to vary but the chemical potential is held fixed. So just like in the canonical ensemble, where we can fix T and ask about average E , in the grand canonical ensemble we can fix μ in the above formulas and ask about average particle number N . But first, we must take into account the fact that each energy level ϵ_i may have a *degeneracy* $g(\epsilon_i)$: for example, a free spin-1/2 fermion has two possible spin states with the same energy (see Section 5.5), so in that case $g(\epsilon_i) = 2$, independent of the energy. To get the average particle number, we just sum the distribution functions over all energy states weighted by the degeneracy,

$$\langle N \rangle = \sum_i g(\epsilon_i) F(\epsilon_i), \quad (4.45)$$

where F is either F_{FD} or F_{BE} as appropriate for fermions or bosons respectively. If the energy levels are spaced closely together enough, we can approximate the sum by an integral, and instead of a degeneracy factor we use the *density of states* $\rho(\epsilon)$, which counts the number of available states between energies ϵ and $\epsilon + d\epsilon$. We then have

$$\langle N \rangle = \int \rho(\epsilon) F(\epsilon) d\epsilon, \quad (4.46)$$

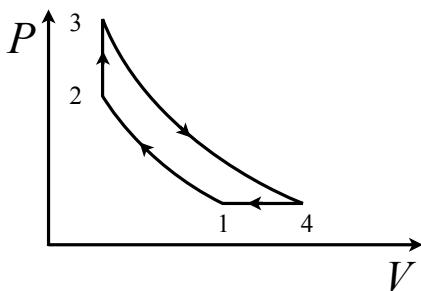
It is unlikely that you would ever have to evaluate integrals like this on the GRE, but knowing the physical meaning of the distribution functions and density of states comes in handy.

4.4 Review problems

1. What is the partition function of a 1-dimensional harmonic oscillator?
 - (A) $\exp\left(\frac{-\hbar\omega}{k_B T}\right)$
 - (B) $1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)$
 - (C) $\left(1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)\right)^{-1}$
 - (D) $\left(2 \cosh \frac{\hbar\omega}{2k_B T}\right)^{-1}$
 - (E) $\left(2 \sinh \frac{\hbar\omega}{2k_B T}\right)^{-1}$

2. A system has two states of energies $-\epsilon$ and 2ϵ . What is the probability of observing it in the higher energy state at temperature T ?
- (A) 0
 - (B) $\left(1 + \exp\left(\frac{3\epsilon}{k_B T}\right)\right)^{-1}$
 - (C) $\left(1 - \exp\left(\frac{3\epsilon}{k_B T}\right)\right)^{-1}$
 - (D) $\left(\exp\left(\frac{\epsilon}{k_B T}\right) + \exp\left(\frac{-2\epsilon}{k_B T}\right)\right)^{-1}$
 - (E) 1
3. A diatomic ideal gas of N particles is trapped on a layer of material, such that the gas molecules are free to move only in two dimensions. What is the heat capacity at constant volume of this gas at room temperature? You may assume that $k_B T \ll \hbar\sqrt{k/m}$, where m is the mass of the molecule and k is the Hooke's law constant associated with vibrational motion.
- (A) $(1/2)Nk_B$
 - (B) Nk_B
 - (C) $(3/2)Nk_B$
 - (D) $2Nk_B$
 - (E) $(5/2)Nk_B$
4. The heat capacity per particle at constant volume of a *relativistic* ideal gas is:
- (A) $k_B/2$
 - (B) k_B
 - (C) $3k_B/2$
 - (D) $2k_B$
 - (E) $3k_B$
5. The three-dimensional harmonic oscillator transitions from the $n = 1$ state to the $n = 2$ state. What is the change in entropy?
- (A) 0
 - (B) $\hbar\omega$
 - (C) k_B
 - (D) $k_B \ln 2$
 - (E) $k_B \ln 3$

6. Six cups numbered 1 through 6 each can hold one marble. There are three red marbles and 1 blue marble. How many different ways are there to fill the cups with all 4 marbles?
- (A) 6
 (B) 12
 (C) 24
 (D) 30
 (E) 60
7. Which of the following MUST be true of a closed system undergoing an adiabatic process?
- (A) no heat is exchanged with the environment
 (B) entropy is constant
 (C) the system does no work on its environment
 (D) entropy increases
 (E) the system is at constant pressure
8. A box is partitioned into equal volumes, each containing a different ideal monatomic gas. When the partition is removed, which of the following statements must be true?
- (A) the entropy decreases
 (B) the entropy increases
 (C) the entropy does not change
 (D) the change in entropy depends on the mass of particles
 (E) the change in entropy depends on the temperature of the gas



9. The P - V diagram above illustrates the Sargent cycle for an ideal gas. Paths 12 and 34 are reversible adiabatic, path 23 is at constant volume, and path 41 is at constant pressure. If T_i denotes the temperature at point i , which temperature is hottest?

- (A) T_1
 - (B) T_2
 - (C) T_3
 - (D) T_4
 - (E) it is impossible to tell from the information given
10. A Carnot engine absorbs 10 J of heat from a hot bath in one cycle and is 90% efficient. How much heat is dissipated to a cold bath?
- (A) 10 J
 - (B) 9 J
 - (C) 2 J
 - (D) 1 J
 - (E) 0.9 J
11. The effects of intermolecular attractions in a Van der Waals gas can be modeled by adding a constant term $-a$ to the single-particle Hamiltonian. Which of the following thermodynamic quantities depend(s) on the parameter a ?
- I. the partition function
 - II. the internal energy
 - III. the specific heat
- (A) I only
 - (B) II only
 - (C) I and II
 - (D) I and III
 - (E) I, II, and III
12. At zero energy, the Bose-Einstein distribution approaches infinity as the chemical potential approaches zero from below. What is the correct interpretation of this phenomenon?
- (A) The average occupation number of the ground state is infinite.
 - (B) There is no ground state for the ideal Bose-Einstein gas.
 - (C) The Fermi-Dirac distribution is the appropriate distribution function for the ground state.
 - (D) A macroscopic number of particles can occupy the ground state and must be treated separately from the occupation numbers of higher states.

- (E) None of the above.
13. A grand canonical ensemble of fermions at chemical potential μ has a density of states given by $\rho(\epsilon) = Ae^{-\kappa\epsilon}$. At zero temperature, what is the average number of particles in the system?
- (A) 1
 (B) $\frac{A}{\kappa}e^{-\kappa\mu}$
 (C) $\frac{A}{\kappa}(1 - e^{-\kappa\mu})$
 (D) $\frac{A}{\kappa} - e^{-\kappa\mu}$
 (E) 0

4.5 Solutions

1. E - The energies of the harmonic oscillator are just $E_n = \hbar\omega(n + 1/2)$, so the partition function is $Z = \sum_{n=0}^{\infty} e^{-\hbar\omega(n+1/2)/(k_B T)}$. Pulling out a factor of $e^{-\hbar\omega/(2k_B T)}$ gives us a geometric series, which we can sum as

$$\sum_{n=0}^{\infty} e^{-\hbar\omega n/(k_B T)} = \frac{1}{1 - e^{-\hbar\omega/(k_B T)}}.$$

Putting back in the factor we pulled out and doing a little manipulation with hyperbolic trig functions gives

$$e^{-\hbar\omega/(2k_B T)} \frac{1}{1 - e^{-\hbar\omega/(k_B T)}} = \left(2 \sinh \frac{\hbar\omega}{2k_B T}\right)^{-1}.$$

2. B - We can always shift the energies such that one of them is 0. This trick usually avoids unnecessary confusion with the notation. So we solve the problem for a system of energies 0 and 3ϵ . Using the expression for the probability of finding the system in a particular state, we have

$$p_i = \frac{e^{-E_i/(k_B T)}}{Z} = \frac{e^{-3\epsilon/(k_B T)}}{1 + e^{-3\epsilon/(k_B T)}} = \frac{1}{1 + e^{3\epsilon/(k_B T)}}.$$

3. C - The last sentence of the problem statement tells us we may assume that vibrational motion is frozen out. In this case, a diatomic gas in two dimensions has only three quadratic degrees of freedom: two translational for the center of mass, and one rotational (the only possible axis of rotation is perpendicular to the plane on which the gas is trapped). By the equipartition theorem, each contributes $(1/2)k_B T$ to the internal energy U , and $C_V = \partial U / \partial T$, so choice C is correct.

4. E - Unlike the previous problem, we can't just apply the equipartition theorem since the energy-momentum relation for a relativistic particle is *linear* rather than quadratic.⁴ On the other hand, the heat capacity of a relativistic gas shows up so often that it may be useful simply to memorize the result. The derivation is rather straightforward, though. In the canonical ensemble, we calculate the partition function in a box of volume V . There is no potential energy, so the energy of a single particle is pure kinetic, $E = |\mathbf{p}|c$. Thus the partition function is

$$Z = \frac{V}{h^3} \int d^3p e^{-\beta|\mathbf{p}|c},$$

where $\beta = 1/kT$ as usual. Going to spherical coordinates in momentum space and using the fact that the integrand is spherically symmetric,

$$Z = \frac{4\pi V}{h^3} \int_0^\infty p^2 e^{-\beta pc} dp = \frac{8\pi V}{(h\beta c)^3}.$$

(The integral can be done simply by repeated application of integration by parts.) Since we are calculating the heat capacity, we only care about the part of $\ln Z$ which depends on β :

$$\ln Z = -3 \ln \beta + \text{const.}$$

Continuing, $E = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{\beta} = 3k_B T$, so $C_V = \frac{dE}{dT} = 3k_B$, choice E.

5. D - The energy of the 3-dimensional harmonic oscillator is $E_n = \hbar\omega(n_x + n_y + n_z + 3/2)$, where $n = n_x + n_y + n_z$. There are three degenerate states corresponding to the $n = 1$ level. There are six degenerate states corresponding to the $n = 2$ level. From the Boltzmann expression for entropy, the initial entropy is $S_1 = k_B \ln 3$. The final entropy is $S_2 = k_B \ln 6$. The change in entropy is therefore $\Delta S = k_B \ln 2$.
6. E - There are 6 ways to place the blue marble. For each placement of the blue marble, there are $\binom{5}{3}$ distinct ways to place the remaining three red marbles. So there are

$$6 \times \frac{5!}{3! \times 2!} = 60$$

distinct ways of placing the marbles into the cups. Equivalently, we can choose the 4 cups out of the 6 to place the marbles in, then choose the one cup out of the 4 to place the blue marble in, giving

$$\binom{6}{4} \times 4 = 60,$$

the same answer.

⁴See Chapter 6 for a review of relativity.

7. A - By definition, an adiabatic process is a process for which there is no heat transfer to the environment. Entropy may be constant if the process is reversible, but can increase if the process is irreversible, as in adiabatic free expansion (incidentally, the pressure also changes in this situation, eliminating choice E). The system can do work on its environment, as it does in the expansion phases of the Carnot cycle.
8. B - The entropy of mixing causes the total entropy to increase. This can be seen immediately from equation (4.40).
9. C - An ideal gas undergoing a reversible adiabatic process has a constant value of PV^γ . This means that $TV^{\gamma-1}$ is constant. For any ideal gas, $C_P > C_V$, so $\gamma - 1 > 0$ and a decrease in volume leads to an increase in temperature. This implies that $T_3 > T_4$ and $T_2 > T_1$. From the ideal gas equation of state, we know that $PV = Nk_B T$, so $T_3 > T_2$ and $T_4 > T_1$. Collecting inequalities, we have $T_1 < T_2 < T_3$ and $T_1 < T_4 < T_3$, so T_3 is hottest.
10. D - From the expression for the efficiency of a Carnot engine, we have $Q_C = Q_H(1-e)$. Plugging in numbers we find that 1 J of heat is dissipated to the cold bath.
11. C - The effect of the constant term is to change the Hamiltonian to $H = \mathbf{p}^2/2m - a$. This shows up explicitly in the single-particle partition function $Z_1 \propto \int e^{-\beta H}$, but since it is constant, it can be pulled outside the integral:

$$Z_1 = e^{\beta a} Z_{1, \text{ ideal gas}}$$

$$Z_N = e^{N\beta a} Z_{N, \text{ ideal gas}}.$$

This just adds a constant term to the log of the partition function: $\ln Z_N = N\beta a + \dots$. The internal energy still depends on a : $U = -\partial \ln Z_N / \partial \beta = -Na + \dots$. However, the a -dependent term no longer depends on T , so taking the derivative to get $C_V = \partial U / \partial T$, this term disappears. Thus C_V is independent of a , so only I and II depend on a .

12. D - This is the statement of Bose condensation. Since the occupation number cannot be infinite for any finite sample of the gas, one must treat the two components of the gas separately: the macroscopic condensate occupying the ground state, and the rest of the particles occupying the excited states.
13. C - As temperature goes to zero, the Fermi-Dirac distribution limits to a step function: 1 for energies less than the chemical potential $\epsilon < \mu$ and 0 for energies above the chemical potential $\epsilon > \mu$. This is a useful fact to remember. Unlike the bosons of the previous problem, the chemical potential of fermions is not bounded by the lowest energy. In this case, we can just integrate the density of states from 0 to μ , and the number of particles is just

$$\langle N \rangle = \int_0^\mu A e^{-\kappa \epsilon} d\epsilon = \frac{A}{\kappa} (1 - e^{-\kappa \mu}).$$