

Physics GRE: THERMODYNAMICS & STATISTICAL MECHANICS

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1 Ensembles

All possible states for a system comprise an ensemble, with each microstate may be assumed to be equally likely. The probability of a macrostate will then be the proportion of microstates in those accessible which have the given property. For example, if the system has three equivalent degrees of freedom amongst which three quanta of energy are distributed, the following arrangements comprise the ensemble:

$$(3, 0, 0) \quad (0, 3, 0) \quad (0, 0, 3) \quad (2, 1, 0) \quad (2, 0, 1) \quad (1) \quad (1)$$

$$(1, 2, 0) \quad (1, 0, 2) \quad (0, 2, 1) \quad (0, 1, 2) \quad (1, 1, 1) \quad (2) \quad (2)$$

The probability of the system having one degree of freedom with all three quanta is thus $\frac{3}{10} = 0.3$ since exactly three microstates satisfy this condition out of the total ten.

It is convenient to introduce entropy, defined to be

$$S = k \log \Omega \quad (3)$$

One can show that when two systems, A and A' , interact and reach thermal equilibrium, then

$$S + S' = \text{maximal} \quad T = T' \quad (4)$$

where $\beta^{-1} = kT$ and β is defined by

$$\beta = \frac{\partial \log \Omega}{\partial E} = \frac{1}{k} \frac{\partial S}{\partial E} \quad (5)$$

If the two systems are not initially at the same temperature then they are in a highly unlikely configuration that will evolve to a state of higher total entropy; this is captured by the second law of thermodynamics.

2 Laws of Thermodynamics

The four laws of thermodynamics are

0. If two systems are each in thermal equilibrium with a third system then they are in thermal equilibrium with each other: i.e. thermal equilibrium is transitive.
1. Conservation of energy: $dQ = dE + dW$
2. $\Delta S \geq 0$ for any thermodynamic process when considering a large enough system.
3. The entropy of a system approaches a constant value as the temperature approaches absolute zero: $T \rightarrow 0 \implies S \rightarrow S_0$.

The zeroth law legitimizes the use of well-defined temperature scales, i.e. thermometers. The second law implies that cooler objects *never* heat warmer objects.

3 Thermodynamic Processes

A process is said to be quasistatic if it occurs slowly enough to ensure that the system remains in equilibrium throughout. A process is said to be reversible if two states may be reached from each other. A necessary condition for a process to be reversible is $dS = 0$ throughout.

3.1 Equations of State Any quantity that depends only on the current state of a system is called an equation of state. Examples include: energy; entropy; enthalpy; temperature; pressure; volume. Any quantity which depends on that “path” taken, such as work and heat, is not an equation of state.

$$dS = \frac{dQ}{T} \quad dE = dQ - dW = T dS - dW \quad (6)$$

3.2 Adiabatic Processes When no heat is transferred a process is called adiabatic. In this case the conservation of energy becomes

$$dE + dW = 0 \quad \implies \quad \Delta E = -\Delta W \quad (7)$$

From the relation $dS = \frac{dQ}{T}$, we see that the entropy is constant, and so adiabatic processes are reversible. In the case of an ideal gas one may show that the pressure, volume and temperature are related by

$$PV^\gamma = \text{const.} \quad TV^{\gamma-1} = \text{const.} \quad P^{1-\gamma}T^\gamma = \text{const.} \quad (8)$$

where $\gamma = \frac{C_P}{C_V}$ is $\frac{5}{3}$ for a monatomic ideal gas and $\frac{7}{5}$ for a diatomic ideal gas. Thus the change in energy between two states is

$$\Delta E = -\Delta W = -\int_1^2 P dV = -\int_1^2 \frac{P_1 V_1^\gamma}{V^\gamma} dV = \frac{P_1 V_1}{\gamma - 1} \left[\left(\frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right] \quad (9)$$

3.3 Isothermal Processes Here the temperature of the system is held fixed. For an ideal gas this means that the combination PV is constant. The work done in moving between two configurations is

$$W = \int_1^2 P dV = \int_1^2 \frac{P_1 V_1}{V} dV = nRT \log \left(\frac{V_2}{V_1} \right) \quad (10)$$

3.4 Isobaric Processes Here the pressure is constant, and for ideal gases this means that the temperature and volume are directly proportional. The work done through expansion is

$$W = P\Delta V \quad (11)$$

4 Ideal Gases

An idealized gas experiences no inter-molecular forces. Many real-world gases are approximately ideal at high temperatures and low pressures. The thermodynamic quantities associated with an ideal gas are related by the ideal gas law:

$$PV = nRT = NkT \quad (12)$$

n is the number of moles, while N is the number of molecules. The ideal gas constant, R , and the Boltzmann constant, k , are related through Avagadro’s number by

$$R = N_A k \quad (13)$$

Because the interactions between gas molecules are negligible, the energy of an ideal gas system only depends on the temperature:

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT \quad (14)$$

A generalization of the idea gas law is Van der Waals equation:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT = NkT \quad (15)$$

The constants a and b are determined empirically for any system and account for the intermolecular forces and nonzero volumes of the particles. The ideal gas law is the simplification $a = b = 0$.

5 Equipartition Theorem

Let A be a system described by the coordinates q_1, q_2, \dots, q_n . Assume that the energy of the system may be written

$$E(q_1, q_2, \dots, q_n) = E_1(q_1) + E'(q_2, \dots, q_n) = E_1 + E' \quad (16)$$

that is, the energy is separable in the coordinate q_1 . In addition assume that the system is in thermal equilibrium with its surroundings at a temperature T . We would like to find the average energy associated with q_1 , $\langle E_1 \rangle$.

$$\langle E_1 \rangle = \int E_1 P(E_1) dE_1 = \frac{\int E_1 e^{-\beta E} dq_1 dq_2 \dots dq_n}{\int e^{-\beta E} dq_1 dq_2 \dots dq_n} \quad (17)$$

$$= \frac{\int E_1 e^{-\beta E_1} e^{-\beta E'} dq_1 dq_2 \dots dq_n}{\int e^{-\beta E_1} e^{-\beta E'} dq_1 dq_2 \dots dq_n} = \frac{\int E_1 e^{-\beta E_1} dq_1}{\int e^{-\beta E_1} dq_1} \cdot \frac{\int e^{-\beta E'} dq_2 \dots dq_n}{\int e^{-\beta E'} dq_2 \dots dq_n} \quad (18)$$

$$= -\frac{\frac{\partial}{\partial \beta} \int e^{-\beta E_1} dq_1}{\int e^{-\beta E_1} dq_1} = -\frac{\partial}{\partial \beta} \log \left(\int e^{-\beta E_1} dq_1 \right) \quad (19)$$

Now assume the common form $E_1(q_1) = Aq_1^r$:

$$= -\frac{\partial}{\partial \beta} \log \left(\int e^{-\beta Aq_1^r} dq_1 \right) \quad (20)$$

Make a change of variables to $x = \beta^{1/r} q_1$:

$$= -\frac{\partial}{\partial \beta} \log \left(\beta^{-1/r} \int e^{-Ax^r} dx \right) = -\frac{\partial}{\partial \beta} \log \left(\beta^{-1/r} \right) - \frac{\partial}{\partial \beta} \log \left(\int e^{-Ax^r} dx \right) \quad (21)$$

$$= \frac{1}{r} \frac{\partial}{\partial \beta} \log \beta - (0) = \frac{1}{r\beta} = \frac{1}{r} kT \quad (22)$$

Summarizing, if the energy of a system in thermal equilibrium with its surroundings has an energy which may be written as

$$E(q_1, q_2, \dots, q_n) = Aq_1^r + E'(q_2, \dots, q_n) \quad (23)$$

then we have

$$\langle E_1 \rangle = \langle Aq_1^r \rangle = \frac{1}{r} kT \quad (24)$$

For example, an idealized harmonic oscillator has energy given by

$$E = T + U = \frac{1}{2}mv^2 + \frac{1}{2}m\omega^2 x^2 \quad (25)$$

and so has average energy

$$\langle E \rangle = \langle T \rangle + \langle U \rangle = \left\langle \frac{1}{2}mv^2 \right\rangle + \left\langle \frac{1}{2}m\omega^2 x^2 \right\rangle = \frac{1}{2}kT + \frac{1}{2}kT = kT \quad (26)$$

In a gas there are three translational degrees of freedom, giving an average energy $\langle E \rangle = \frac{3}{2}kT$. At higher temperatures and a diatomic molecule the rotational modes may now be excited, giving an additional two degrees of freedom and an average energy $\langle E \rangle = \frac{5}{2}kT$. At still higher temperatures the diatomic molecules may be in excited vibrational modes. With both vibrational kinetic and potential energies, there are an additional two degrees of freedom, giving an average energy $\langle E \rangle = \frac{7}{2}kT$. Explicitly, at high energies the energy for a diatomic molecule would be of the form

$$E = \frac{1}{2}M (v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}I (\omega_1^2 + \omega_2^2) + \frac{1}{2}\mu\dot{\eta}^2 + \frac{1}{2}k\eta^2 \quad (27)$$

M is the molecule's mass, \mathbf{v} is the center of mass velocity, I is the moment of inertia about an axis perpendicular to the symmetry axis of the molecule, ω_i are the angular velocities about the two axes perpendicular to the symmetry axis of the molecule, μ is the reduced mass of the molecule, k is the effective spring constant for the bond and η is the deviation of the atomic separation distance from its natural length. The seven quadratic degrees of freedom are clearly visible.

6 Maxwell Relations

The equality of mixed partial derivatives gives rise to several Maxwell relations between common thermodynamic variables:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad (28)$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad (29)$$

A mnemonic for remembering these is the following square, along with the phrase **Good Physicists Have Studied Under Very Fine Teachers**.

$-S$	U	V
H		F
$-P$	G	T

This may be used to quickly express thermodynamic quantities in terms of conjugate variables, located in opposing corners. The two corners opposite the chosen potential are the coefficients for the differentials. For example, the Gibb's free energy, G is given by

$$dG = -S dT + V dP \quad (30)$$

Notice that the minus sign only appears for the coefficient S and not the differential dP . Since we could have written

$$dG = \left(\frac{\partial G}{\partial T} \right)_P dT + \left(\frac{\partial G}{\partial P} \right)_T dP \quad (31)$$

we conclude that

$$S = - \left(\frac{\partial G}{\partial T} \right)_P \quad V = \left(\frac{\partial G}{\partial P} \right)_T \quad (32)$$

Equating the mixed partial derivatives of G results in the following:

$$\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T} \right)_P = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \implies - \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P \quad (33)$$

The other Maxwell relations arise through similar analyses.

7 Statistical Mechanics

The partition function for a system is defined to be

$$Z = \sum_i e^{-\beta E_i} = \sum_E \Omega(E) e^{-\beta E} \quad (34)$$

In the first expression the sum is over all states, which may be degenerate in energy. In the second expression the sum is over all energies, with the degeneracy of these states denoted by $\Omega(E)$. Both methods give the same result.

If a system consists of subsystems, with individual partition functions ζ_i , which weakly interact then the partition function for the whole system is given by

$$Z = \prod_i \zeta_i \quad (35)$$

However, when consider a system of N indistinguishable particles we must include a combinatorial factor:

$$Z = \frac{\zeta^N}{N!} \quad (36)$$

Refined versions of this are found with a quantum mechanical foundation, giving rise to particle statistics, discussed below.

The partition function allows for a statistical calculation of thermodynamic quantities, such as

$$\langle E \rangle = - \frac{\partial \log Z}{\partial \beta} \quad (37)$$

$$S = k(\log Z + \beta \langle E \rangle) \quad (38)$$

$$C_V = \frac{1}{kT^2} \frac{\partial^2 \log Z}{\partial T^2} \quad (39)$$

8 Particle Statistics

The classical treatment of multi-particle systems where particles are distinguishable leads to Maxwell-Boltzmann statistics: the expected number of particles in a given state with energy E_i is

$$\langle n_i \rangle = N \cdot \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = N \cdot \frac{e^{-\beta E_i}}{Z} \quad (40)$$

When indistinguishability is introduced in the quantum mechanical treatment of a multiparticle system two distinct behaviours arise: Bose-Einstein statistics and Fermi-Dirac statistics. Bose-Einstein statistics describe systems of bosons, which have integral spin, where the total wavefunction

is unchanged after swapping two particles. This results in the expected number of particles in a state with energy E_i being

$$\langle n_i \rangle = \frac{1}{e^{(E_i - \mu)/kT} - 1} \quad (41)$$

where μ is the chemical potential. For large T this is

$$\langle n_i \rangle \approx \frac{kT}{E_i - \mu} \quad (42)$$

Fermi-Dirac statistics describe fermions, which have half-integral spin, where the total wavefunction changes sign upon swapping two particles. One consequence of this is that no two particles may be in the same quantum state, for then the wavefunction would vanish. The expected number of particles in a state with energy E_i here is

$$\langle n_i \rangle = \frac{1}{e^{(E_i - \mu)/kT} + 1} \quad (43)$$

Notice that for any temperature this is never greater than one.

In the case of photons there is no restriction on the number of particles and the expected number of particles in a state with energy E_i is

$$\langle n_i \rangle = \frac{1}{e^{E_i/kT} - 1} \quad (44)$$

For large T this is

$$\langle n_i \rangle \approx \frac{kT}{E_i} \quad (45)$$

9 Einstein & Debye Theories of Specific Heat

Einstein assumed that solids may be modelled as collections of identical, isotropic harmonic oscillators with three degrees of freedom per molecule. Using the appropriate quantum statistics, the average energy of a vibrational states is

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/kT} - 1} \quad (46)$$

The quantity $\frac{h\nu}{k}$ is referred to as the Einstein temperature. The total energy per mole is given by

$$\frac{E}{n} = \frac{3N_A h\nu}{e^{h\nu/kT} - 1} \quad (47)$$

and the specific heat is

$$c_V = \frac{1}{n} \frac{\partial E}{\partial T} = 3N_A k \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \quad (48)$$

At high temperatures we have the approximate expression

$$c_V \approx 3N_A k \left(1 + \frac{h\nu}{kT} \right) \approx 3N_A k = 3R \quad (49)$$

This matches the classically derived Law of Dulong and Petit:

$$E = 3nkTN_A = 3nRT \quad (50)$$

However, the low temperature behaviour does not match observation, where the specific heat is seen to go as T^3 . In contrast, the Debye model considers the normal modes of the solid, or “phonons”, and correctly matches both the high- and low-temperature limiting behaviours.

A Summary

Laws of Thermodynamics

$$\begin{aligned}T_1 = T_2 \quad \wedge \quad T_2 = T_3 &\implies T_1 = T_3 && (1^{\text{st}} \text{ Law}) \\dQ = dE + dW &&& (2^{\text{d}} \text{ Law}) \\\Delta S \geq 0 &&& (3^{\text{d}} \text{ Law}) \\T \rightarrow 0 &\implies S \rightarrow S_0 && (4^{\text{th}} \text{ Law})\end{aligned}$$

Thermodynamic Processes

$$\begin{aligned}S &= k \log \Omega && (\text{Entropy}) \\dS &= \frac{dQ}{T} \\ \beta &= \frac{1}{kT} = \frac{\partial \log \Omega}{\partial E} = \frac{1}{k} \frac{\partial S}{\partial E} && (\text{Temperature}) \\S + S' &= \text{maximal} \quad \wedge \quad T = T' && (\text{Thermal Equilibrium}) \\dQ &= 0 && (\text{Adiabatic Processes}) \\PV^\gamma &= \text{const.} \\TV^{\gamma-1} &= \text{const.} \\P^{1-\gamma}T^\gamma &= \text{const.} \\dT &= 0 && (\text{Isothermal Processes}) \\W &= nRT \log \left(\frac{V_2}{V_1} \right) \\dP &= 0 && (\text{Isobaric Processes}) \\W &= P\Delta V\end{aligned}$$

Ideal Gases

$$\begin{aligned}PV &= nRT = NkT && (\text{Ideal Gas Law}) \\dE &= \left(\frac{\partial E}{\partial T} \right)_V dT && (\text{Ideal Gas Energy}) \\ \left(P + \frac{n^2 a}{V^2} \right) (V - nb) &= nRT = NkT && (\text{Van der Waals Equation})\end{aligned}$$

Equipartition Theorem

$$\begin{aligned}E(q_1, q_2, \dots, q_n) &= E_1(q_1) + E'(q_2, \dots, q_n) = E_1 + E' && (\text{Assumptions}) \\E_1(q_1) &= Aq_1^r \\\langle E_1 \rangle &= \frac{1}{r} kT && (\text{Conclusion})\end{aligned}$$

Maxwell Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (\text{Maxwell Relations})$$

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

$$H = E + PV \quad (\text{Enthalpy})$$

$$G = H - TS \quad (\text{Gibb's Free Energy})$$

$$F = E - TS \quad (\text{Helmholtz Free Energy})$$

$-S$	U	V
H		F
$-P$	G	T

(Mnemonic)

Statistical Mechanics

$$Z = \sum_i e^{-\beta E_i} = \sum_E \Omega(E) e^{-\beta E} \quad (\text{Partition Function})$$

$$Z = \prod_i \zeta_i \quad (\text{Weakly Interacting Subsystems})$$

$$Z = \frac{\zeta^N}{N!} \quad (\text{Indistinguishable Subsystems})$$

$$\langle E \rangle = -\frac{\partial \log Z}{\partial \beta} \quad (\text{Average Energy})$$

$$S = k(\log Z + \beta \langle E \rangle) \quad (\text{Entropy})$$

$$C_V = \frac{1}{kT^2} \frac{\partial^2 \log Z}{\partial T^2} \quad (\text{Specific Heat})$$

Particle Statistics

$$\langle n_i \rangle = N \cdot \frac{e^{-\beta E_i}}{Z} \quad (\text{Maxwell-Boltzmann Statistics})$$

$$\langle n_i \rangle = \frac{1}{e^{(E_i - \mu)/kT} - 1} \quad (\text{Bose-Einstein Statistics})$$

$$\langle n_i \rangle = \frac{1}{e^{(E_i - \mu)/kT} + 1} \quad (\text{Fermi-Dirac Statistics})$$

$$\langle n_i \rangle = \frac{1}{e^{E_i/kT} - 1} \quad (\text{Photon Statistics})$$

Theories of Specific Heat

$$c_V = 3N_A k \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \quad (\text{Einstein Theory})$$

$$c_V \rightarrow \alpha T^3 \quad (\text{Debye Low Temperature})$$

$$c_V \rightarrow 3N_A k = 3R \quad (\text{Einstein \& Debye High Temperature})$$

(51)