Physics 176
Topics to Review For the Final Exam

Professor Henry Greenside
May 2, 2011

Thermodynamic Concepts and Facts

1. Practical criteria for identifying when a macroscopic system is in thermodynamic equilibrium: all macroscopic features are time independence, temperature same everywhere, pressure same everywhere unless there is an external spatially varying field, chemical potential same everywhere, properties independent of history, and no relative macroscopic motion (only rigid rotation and translation of the macroscopic system allowed).

2. Concept of a relaxation time τ, especially thermal, diffusive, and mechanical relaxation times. Know the fact that $\tau \propto L^2$ where L is some characteristic size of the system, and understand how the L^2 scaling is connected to a random walk arising from collisions.

3. The concepts of thermal energy U, heat Q and work W for some macroscopic equilibrium system, and that they are related by the first law of thermodynamics, $\Delta U = Q + W$. Make sure you understand how the signs of Q and W are chosen.

4. The concept of a state variable such as energy, volume, entropy, temperature, and chemical potential. However, heat and work are not state variables.

5. The concept of an equation of state that relates various state variables ($PV = NkT$ is an example).

   While most equations of state are discovered experimentally and known empirically, they can sometimes be discovered by calculating the pressure P in terms of some thermodynamic potential, e.g., $P = -(\partial F/\partial V)_{T,N}$, which in turn lets one compute P in terms of a partition function.

6. The concepts of intensive and extensive thermodynamic variables.

7. The definition and applications of heat capacity and specific heats, especially that $C_V = (\partial U/\partial T)_V$ and $C_P = (\partial H/\partial T_P$ where $H = U + PV$ is the enthalpy. One therefore has $C_P = C_V + P(\partial V/\partial T)_P$.

8. Detailed quantitative knowledge of the experimental heat capacities $C(T)$ of a solid, of a gas of identical diatomic molecules, and of a paramagnet as a function of temperature.

9. The concepts of quasistatic, reversible, and irreversible thermodynamic processes.

10. The concept of a quasistatic adiabatic process, which is also a constant-entropy process.

11. How to calculate changes in entropy: via $\Delta S = Q/T$ for a constant temperature process (phase transition or reservoir) and via integrals $\int C(T)/T\, dT$ over temperature ranges involving a known heat capacity $C(T)$.

12. The thermodynamic definition of temperature $1/T = (\partial S/\partial U)_{N,V}$ in terms of the entropy. From a given equation of state $S = S(U, V, N)$, how to derive the temperature T of the system, the energy dependence $U(T)$ and so the heat capacity $C = C(T)$.

13. How to calculate the changes in energy, heat, work, temperature, and entropy for an arbitrary process of an ideal gas (or of some other substance with a known equation of state) as parameters like temperature, pressure, and volume are changed in various ways. Familiarity with isothermal, adiabatic, isobaric, and isochoric processes.

14. The concept of the efficiency of a heat engine, and that a Carnot cycle is capable of achieving the maximum possible efficiency, although a Carnot cycle itself is impractical for engineering applications since it involves two isothermal processes.

15. How to show that the criterion of an isolated equilibrium system being in a state of maximum entropy implies that the temperature and chemical potentials must be the same for all macroscopic subsystems, and further be able to show that energy necessarily flows from high-temperature to low-temperature subsystems in order for the entropy to approach a maximum.

16. The third law of thermodynamics: that the entropy and heat capacity of a system go to zero as $T \to 0$.

17. The thermodynamic identity $dU = TdS - PdV + \sum_i \mu_i dN_i$ and how to use such an identity to derive relations such as $P/T = (\partial S/\partial V)_{V,N_i}$.

18. How to derive thermodynamic identities for other thermodynamic potentials such as the Helmholtz free energy $F = U - TS$ or Gibbs free energy $G = U - TS + PV$, and how to derive thermodynamic potentials that are functions of particular variables such as T, V, and μ.

19. The equipartition theorem as applied to gases and solids, and the range of validity of the equipartition theorem. The concept of "a degree of freedom" and the idea that degrees of freedom can freeze out with decreasing temperature. N. The degree of freedom can be determined experimentally through the adiabatic exponent $\gamma = (f + 2)/f$ via the relation $PV^\gamma = $ constant. How to use the equipartition theorem to estimate the order of magnitude of the heat capacity of a solid or gas.

    Note: A degree of freedom starts to freeze out when the thermal energy kT becomes comparable to or smaller than the spacings ΔE between adjacent low-level energy levels.

20. Elementary knowledge of phase transitions:

    (a) The qualitative features of a pressure-temperature phase diagram, say of water or of carbon dioxide: the qualitative locations of phases, phase lines, critical points, and triple points, and knowledge of the actual numerical values of these details for water or CO_2.

    (b) How the stability of a phase for given T and P is determined by the lowest value of the Gibbs free energy G and how G varies qualitatively with temperature and pressure (via the relations $\partial G/\partial P = V$ and $\partial G/\partial T = -S$).

    (c) What is the Clausius-Clapeyron equation, how to derive it, and how to use it.

    (d) The van der Waals model as an empirical insightful way to understand how a gas undergoes a phase transition to the liquid state. You should understand the physical meaning of the two terms $a(N/V)^2$ and $-Nb$ that are used to modify the ideal gas law to obtain the van der Waals equation. You should also understand the meaning of Figures 5.21 and 5.23, and how the Maxwell construction allows one to predict the change in volume of the gas to liquid at a given pressure. You should understand how to determine the location of the critical point of an equation of state like the van der Waals model, by the condition that $dP/dV = 0$ and that $d^2P/dV^2 = 0$.

Statistical Physics Concepts and Facts

1. Elementary kinetic theory of a gas, for the cases of anisotropic velocities (all velocities parallel or antiparallel to Cartesian axes) and of isotropic velocities, and for the cases of a constant speed and for a known speed distribution $\mathcal{D}(v)$. How to use the ideal gas law $PV = NkT$ and a kinetic argument to relate the temperature T in gas law to the average kinetic energy of molecules in the gas. Also how to use a simple kinetic theory to calculate the flux of particles through a tiny hole (effusion) or the rate at which energy or charge is delivered by molecular collisions to a small area of a wall per unit time. The concepts of a mean free path and mean collision time.

2. The concepts of microstates and macrostates, and the ability to identify and count microstates for representative systems.

3. The concept of multiplicity Ω of microstates and how to calculate the multiplicity of simple systems like a paramagnet or Einstein solid as a function of energy U, number of particles N, and volume V.

4. The definition of entropy via $S = k \ln \Omega$ and an understanding of why entropy is additive for weakly interacting subsystems.

5. How to deduce a specific heat C from a known multiplicity $\Omega(U)$: $\Omega \to S \to T \to U(T) \to C(T)$. How to deduce the qualitative graphical forms of $T(U)$ and $C(T)$ from a qualitative graph of the entropy $S(U)$ as a function of energy U.

6. How to derive and apply the Sackur-Tetrode equation for the entropy of an ideal equilibrium gas of atoms, and how to compute the entropy of mixing of two atomic gases.

7. How to derive the equipartition theorem for an energy with a quadratic degree of freedom.

8. The concept of a Boltzmann factor $e^{-\beta E_s}$ and partition function Z for a small system in equilibrium with a constant-temperature reservoir, and the concept of a Gibbs factor $e^{-\beta(E_s - \mu N_s)}$ and grand partition function $\mathcal{Z}$ for a small system in equilibrium with a constant-temperature, constant-chemical-potential reservoir.

9. How to use partition functions to calculate the statistical properties (average, variance) of some macroscopic variable X, and how to show that relative fluctuations $\Delta X / \overline{X}$ (standard deviation of a thermodynamic variable over its average) scale as $1/\sqrt{N}$ where N is the number of components.

10. How to calculate thermodynamic properties (U, S, P, μ, C, etc) of some equilibrium system in terms of its partition function Z via the relations $F = -kT \ln(Z)$, or in terms of the grand partition function $\mathcal{Z}$ via the relation $\Omega = -kT \ln(\mathcal{Z})$.

11. How to use partition functions to calculate the properties of three key systems:

   (a) a paramagnet of identical but distinguishable spins (not necessarily spin-1/2).

   (b) an ideal gas of identical molecules that can rotate and vibrate and that have internal electronic structure. This includes the Maxwell speed distribution.

   (c) and an Einstein solid consisting of N identical quantum harmonic oscillators.

   and how to apply this knowledge to other systems whose energy states are known.

12. Statistical mechanics of ideal quantum gases:

   (a) The criterion $Z_1 = (V/V_Q)Z_{\text{int}} > N$ that determines when a non-quantum approach is acceptable (so $Z_N \approx Z_1^N/N!$ for an ideal gas of identical particles). Here $V_Q = (h/\sqrt{2\pi mkT})^3$ is the thermal "quantum volume", Z_{int} is the partition function of internal molecular degrees of freedom (rotation, vibration, electronic).

   (b) The concepts of a fermion and boson in terms of how many particles can be in a given energy state, and how to determine conceptually and experimentally whether a particle is a boson or fermion.

   (c) How to derive and apply the Fermi-Dirac, Bose-Einstein, and Boltzmann distributions for the average occupancy $\overline{n}(\epsilon)$ of a given energy level ϵ.

   (d) How to use an expression of the form

   $$U = \alpha \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon(n_x, n_y, n_z) \, \overline{n}[\epsilon(n_x, n_y, n_z)], \tag{1}$$

   to analyze properties such as the pressure, entropy, and heat capacity of a quantum ideal gas. Here the sums go over quantum states (n_x, n_y, n_z) of free particles in a cubic box of side L. The constant α is the number of particles that can be in the same state or that have independent polarizations. One key trick is approximating the sums by integrals and then switching to spherical coordinates (n, θ, ϕ).

(e) How to use Eq. (1) to calculate properties of a zero-temperature ideal gas of electrons (fermions), and the concepts of a Fermi energy E_F and Fermi temperature T_F. An understanding of why the heat capacity of an electron gas is proportional to T for temperatures $T \ll T_F$.

(f) How to calculate properties of an equilibrium photon gas, in particular the Planck energy distribution, the pressure and entropy of a photon gas, and the Stefan-Boltzmann radiation law. Why the chemical potential $\mu = 0$ for a photon gas.

Mathematical Skills

The following are key mathematical skills related to thermal physics that you should be familiar with:

1. How to evaluate simple multivariate integrals.

2. How to evaluate definite integrals by differentiation with respect to a parameter, especially the definite integration of a Gaussian and moments of a Gaussian.

3. The definition of the Gamma function and how to evaluate the Gamma function for arguments in terms of a recursion relation.

4. How to change from Cartesian to spherical or cylindrical (polar) coordinates and evaluate integrals in the latter coordinate systems.

5. Elementary combinatorics related to the binomical coefficient, for example that allow one to calculate the number of microstates in a two-state paramagnet or in an Einstein solid.

6. Stirling's approximation $n! \approx \sqrt{2\pi n}(n/e)^n$, especially in the context of approximating binomial coefficients $\binom{n}{k}$ for integers $n, k \gg 1$.

7. How to approximate various expressions by the first few terms in a Taylor series without having to compute explicit derivatives for the coefficients of the Taylor series. An important example would be the ability to calculate the leading order behavior for the heat capacity $C(T)$ of some systems for regimes of small temperature and of large temperature.

8. How to show that any smooth function $f(x)$ with a single global maximum raised to a large power N can be accurately approximated by a Gaussian centered on that maximum whose width scales as $N^{-1/2}$.

9. The idea of approximating discrete sums with sufficiently many slowly varying terms by an integral:

$$\sum_{i=1}^{N} f(i) \approx \int_{1}^{N} f(x)\, dx. \tag{2}$$

This trick is used to approximate the high temperate partition function for the rotational states of a non-symmetric diatomic molecule AB.

10. How to calculate the probability density $\mathcal{D}(y)$ for a continuous variable $y = y(x)$ that is a known function of x, from a known probability density $\mathcal{D}(x)$. An example would be how to calculate the probability density of kinetic energies in an equilibrium gas from the Maxwell speed density. Also how to deduce a probability densitys $f(x)$ or $f(x, y)$ that depends on fewer variables than a given density $f(x, y, z)$.

Key Equations (Not a Complete List)

$$PV = NkT, \qquad \Delta U = Q + W, \qquad U = Nf\left(kT/2\right), \qquad v_{\text{rms}} = \sqrt{3kT/m}, \tag{3}$$

$$PV^\gamma = \text{const}, \qquad VT^{f/2} = \text{const}, \qquad \gamma = \frac{f+2}{f}. \tag{4}$$

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NkT \qquad \text{or} \qquad p = \frac{8t}{3v-1} - \frac{3}{v^2}, \tag{5}$$

where

$$V_c = 3NB, \quad P_c = \frac{1}{27}\frac{a}{b^2}, \quad kT_c = \frac{8}{27}\frac{a}{b}, \qquad T = tT_c, \quad P = pP_c, \quad V = vV_c. \tag{6}$$

$$C = \frac{Q}{\Delta T}, \qquad L = \frac{Q}{m}, \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V, \qquad C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P. \tag{7}$$

$$S = k\ln\Omega, \qquad S = \frac{Q}{T}, \qquad \Delta S = \int_{T_1}^{T_2} \frac{C(T)}{T}\,dT, \qquad S = Nk\left(\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right]\right). \tag{8}$$

$$\overline{E} = -\frac{\partial\ln(Z)}{\partial\beta}. \qquad C_V = \frac{1}{kT^2}\left(\overline{E^2} - \left(\overline{E}\right)^2\right), \qquad \overline{N} = -\frac{\partial\ln(\mathcal{Z})}{\partial x}, \qquad x = \beta(\epsilon - \mu). \tag{9}$$

$$\mathcal{D}(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{-mv^2/(2kT)}, \qquad \overline{v} = \sqrt{\frac{8kT}{\pi m}}, \qquad \overline{v^2} = \frac{3kT}{m}. \tag{10}$$

$$F = U - TS, \qquad dF = -S\,dT - P\,dV + \mu\,dN, \qquad Z = \sum_s e^{-\beta U(s)}, \qquad F = -kT\ln(Z). \tag{11}$$

$$G = U - TS + PV, \qquad dG = -S\,dT + V\,dP + \mu\,dN, \qquad G = N\mu. \tag{12}$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V, \qquad \left(\frac{\partial G}{\partial T}\right)_{T,N} = -S, \qquad \left(\frac{dP}{dT}\right)_{12} = \frac{S_1 - S_2}{V_1 - V_2} = \frac{L_{12}}{T(V_1 - V_2)}. \tag{13}$$

$$\Phi = U - TS - \mu N, \quad d\Phi = -S\,dT - P\,dV - N\,d\mu, \quad \mathcal{Z} = \sum_s e^{-\beta[U(s) - \mu N(s)]}, \quad \Phi = -kT\ln(\mathcal{Z}). \tag{14}$$

$$Z_{\text{total}} \approx \frac{1}{N!}Z_1^N, \qquad Z_1 = Z_{\text{trans}}Z_{\text{int}} = \frac{V}{V_Q}Z_{\text{int}}, \qquad V_Q = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3, \qquad \mu_{\text{gas}} = -k\,T\ln\left(\frac{V\,Z_{\text{int}}}{NV_Q}\right). \tag{15}$$

$$p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}, \qquad \epsilon_{\text{electron}} = \frac{p^2}{2m} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right), \qquad \epsilon_{\text{photon}} = pc = \frac{hcn}{2L}. \tag{16}$$

$$\epsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}, \qquad U = \frac{3}{5}N\epsilon_F, \qquad P = \frac{2}{3}\frac{U}{V}. \tag{17}$$

$$U_{\text{photon}} = 2 \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \epsilon(n) \, \overline{n}_{\text{Planck}}(\epsilon) = 2 \sum_{n_x, n_y, n_z} \frac{hcn}{2L} \frac{1}{e^{\beta hcn/(2L)} - 1} \tag{18}$$

$$\frac{\text{power}}{\text{area}} = \sigma T^4, \qquad I = \frac{\mathcal{L}}{4\pi d^2}, \qquad \mathcal{L} = \left(4\pi R^2\right) \times \sigma T^4. \tag{19}$$

$$\binom{n}{m} = \frac{n!}{m!(n-m)!}, \qquad n! \approx \sqrt{2\pi n} \left(\frac{n}{e}\right)^n, \qquad \ln(1+x) \approx x. \tag{20}$$

$$\int_0^{\infty} e^{-\alpha x^2} \, dx = \frac{\sqrt{\pi}}{2} \, \alpha^{-1/2}, \qquad \int_0^{\infty} x \, e^{-\alpha x^2} \, dx = \frac{1}{2}\alpha^{-1}, \tag{21}$$

$$\cosh(x) = \frac{e^x + e^{-x}}{2}, \qquad \sinh(x) = \frac{e^x - e^{-x}}{2}, \qquad \tanh(x) = \frac{\sinh(x)}{\cosh(x)}. \tag{22}$$

$$e^x = 1 + \frac{1}{1!}x + \frac{1}{2!}x^2 + \dots, \quad 1 + x + \dots + x^{N-1} = \frac{1 - x^N}{1 - x}, \quad (1+x)^{\alpha} \approx 1 + \frac{\alpha}{1!}x + \frac{\alpha}{1}\frac{\alpha-1}{2}x^2 + \dots. \tag{23}$$