

4.S: Summary

References

- F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1987) This has been perhaps the most popular undergraduate text since it first appeared in 1967, and with good reason.
- A. H. Carter, *Classical and Statistical Thermodynamics* (Benjamin Cummings, 2000) A very relaxed treatment appropriate for undergraduate physics majors.
- D. V. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley, 2000) This is the best undergraduate thermodynamics book I've come across, but only 40% of the book treats statistical mechanics.
- C. Kittel, *Elementary Statistical Physics* (Dover, 2004) Remarkably crisp, though dated, this text is organized as a series of brief discussions of key concepts and examples. Published by Dover, so you can't beat the price.
- M. Kardar, *Statistical Physics of Particles* (Cambridge, 2007) A superb modern text, with many insightful presentations of key concepts.
- M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* (3rd edition, World Scientific, 2006) An excellent graduate level text. Less insightful than Kardar but still a good modern treatment of the subject. Good discussion of mean field theory.
- E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics* (part I, 3rd edition, Pergamon, 1980) This is volume 5 in the famous Landau and Lifshitz *Course of Theoretical Physics*. Though dated, it still contains a wealth of information and physical insight.

Summary

- **Distributions:** Let $\varrho(\varphi)$ be a normalized distribution on phase space. Then

$$\langle f(\varphi) \rangle = \text{Tr} [\varrho(\varphi) f(\varphi)] = \int d\mu \varrho(\varphi) f(\varphi), \quad (4.S.1)$$

where $d\mu = W(\varphi) \prod_i d\varphi_i$ is the phase space measure. For a Hamiltonian system of N identical indistinguishable point particles in d space dimensions, we have

$$d\mu = \frac{1}{N!} \prod_{i=1}^N \frac{d^d p_i d^d q_i}{(2\pi\hbar)^d}. \quad (4.S.2)$$

The $\frac{1}{N!}$ prefactor accounts for indistinguishability. Normalization means $\text{Tr} \varrho = 1$.

- **Microcanonical ensemble (μ CE):** $\varrho(\varphi) = \delta(E - \hat{H}(\varphi)) / D(E)$, where $D(E) = \text{Tr} \delta(E - \hat{H}(\varphi))$ is the density of states and $\hat{H}(\varphi) = \hat{H}(\mathbf{q}, \mathbf{p})$ is the Hamiltonian. The energy E , volume V , and particle number N are held fixed. Thus, the density of states $D(E, V, N)$ is a function of all three variables. The statistical entropy is $S(E, V, N) = k_B \ln D(E, V, N)$, where k_B is Boltzmann's constant. Since D has dimensions of E^{-1} , an arbitrary energy scale is necessary to convert D to a dimensionless quantity before taking the log. In the thermodynamic limit, one has

$$S(E, V, N) = N k_B \phi\left(\frac{E}{N}, \frac{V}{N}\right). \quad (4.S.3)$$

The differential of E is defined to be $dE = T dS - p dV + \mu dN$, thus $T = \left(\frac{\partial E}{\partial S}\right)_{V, N}$ is the temperature, $p = -\left(\frac{\partial E}{\partial V}\right)_{S, N}$ is the pressure, and $\mu = \left(\frac{\partial E}{\partial N}\right)_{S, V}$ is the chemical potential. Note that E , S , V , and N are all extensive quantities, they are halved when the system itself is halved.

- **Ordinary canonical ensemble (OCE):** In the OCE, energy fluctuates, while V , N , and the temperature T are fixed. The distribution is $\varrho = Z^{-1} e^{-\beta \hat{H}}$, where $\beta = 1/k_B T$ and $Z = \text{Tr} e^{-\beta \hat{H}}$ is the partition function. Note that Z is the Laplace transform of the density of states: $Z = \int dE D(E) e^{-\beta E}$. The Boltzmann entropy is $S = -k_B \text{Tr} (\varrho \ln \varrho)$. This entails $F = E - TS$, where $F = -k_B T \ln Z$ is the Helmholtz free energy, a Legendre transform of the energy E . From this we derive $dF = -S dT - p dV + \mu dN$.
- **Grand canonical ensemble (GCE):** In the GCE, both E and N fluctuate, while T , V , and chemical potential μ remain fixed. Then $\varrho = \Xi^{-1} e^{-\beta(\hat{H} - \mu \hat{N})}$, where $\Xi = \text{Tr} e^{-\beta(\hat{H} - \mu \hat{N})}$ is the grand partition function and $\Omega = -k_B T \ln \Xi$ is the grand potential.

Assuming $[\hat{H}, \hat{N}] = 0$, we can label states $|n\rangle$ by both energy and particle number. Then $P_n = \Xi^{-1} e^{-\beta(E_n - \mu N_n)}$. We also have $\Omega = E - TS - \mu N$, hence $d\Omega = -S dT - p dV - N d\mu$.

• **Thermodynamics:** From $E = \text{Tr}(\rho \hat{H})$, we have $dE = \text{Tr}(\hat{H} d\rho) + \text{Tr}(\rho d\hat{H}) = dQ - dW$, where $dQ = T dS$ and

$$dW = -\text{Tr}(\rho d\hat{H}) = -\sum_n P_n \sum_i \frac{\partial E_n}{\partial X_i} dX_i = \sum_i F_i dX_i, \quad (4.S.4)$$

with $P_n = Z^{-1} e^{-E_n/k_B T}$. Here $F_i = -\langle \frac{\partial \hat{H}}{\partial X_i} \rangle$ is the generalized force conjugate to the generalized displacement X_i .

• **Thermal contact:** In equilibrium, two systems which can exchange energy satisfy $T_1 = T_2$. Two systems which can exchange volume satisfy $p_1/T_1 = p_2/T_2$. Two systems which can exchange particle number satisfy $\mu_1/T_1 = \mu_2/T_2$.

• **Gibbs-Duhem relation:** Since $E(S, V, N)$ is extensive, Euler's theorem for homogeneous functions guarantees that $E = TS - pV + \mu N$. Taking the differential, we obtain the equation $S dT - V dp + N d\mu = 0$, so there must be a relation among any two of the intensive quantities T , p , and μ .

• **Generalized susceptibilities:** Within the OCE¹, let $\hat{H}(\lambda) = \hat{H}_0 - \sum_i \lambda_i \hat{Q}_i$, where \hat{Q}_i are observables with $[\hat{Q}_i, \hat{Q}_j] = 0$. Then

$$Q_k(T, V, N; \lambda) = \langle \hat{Q}_k \rangle = -\frac{\partial F}{\partial \lambda_k}, \quad \chi_{kl}(T, V, N; \lambda) = \frac{1}{V} \frac{\partial Q_k}{\partial \lambda_l} = -\frac{1}{V} \frac{\partial^2 F}{\partial \lambda_k \partial \lambda_l}. \quad (4.S.5)$$

The quantities χ_{kl} are the generalized susceptibilities.

• **Ideal gases:** For $\hat{H} = \sum_{i=1}^N \frac{p_i^2}{2m}$, one finds $Z(T, V, N) = \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N$, where $\lambda_T = h/\sqrt{2\pi m k_B T}$

λ_T is the thermal wavelength. Thus $F = N k_B T \ln(N/V) - \frac{1}{2} d N k_B T \ln T + N a$, where a is a constant. From this one finds $p = -\left(\frac{\partial F}{\partial V} \right)_{T, N} = n k_B T$, which is the ideal gas law, with $n = \frac{N}{V}$ the number density. The distribution of velocities in $d = 3$ dimensions is given by

$$f(\mathbf{v}) = \left\langle \frac{1}{N} \sum_{i=1}^N \delta(\mathbf{v} - \mathbf{v}_i) \right\rangle = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-m\mathbf{v}^2/2k_B T}, \quad (4.S.6)$$

and this leads to a speed distribution $\bar{f}(v) = 4\pi v^2 f(v)$.

• **Example:** For N noninteracting spins in an external magnetic field H , the Hamiltonian is $\hat{H} = -\mu_0 H \sum_{i=1}^N \sigma_i$, where $\sigma_i = \pm 1$. The spins, if on a lattice, are regarded as distinguishable. Then $Z = \zeta^N$, where $\zeta = \sum_{\sigma=\pm 1} e^{\beta \mu_0 H \sigma} = 2 \cosh(\beta \mu_0 H)$. The magnetization and magnetic susceptibility are then

$$M = -\left(\frac{\partial F}{\partial H} \right)_{T, N} = N \mu_0 \tanh\left(\frac{\mu_0 H}{k_B T} \right), \quad \chi = \frac{\partial M}{\partial H} = \frac{N \mu_0^2}{k_B T} \text{sech}^2\left(\frac{\mu_0 H}{k_B T} \right). \quad (4.S.7)$$

• **Example:** For noninteracting particles with kinetic energy $\frac{p^2}{2m}$ and internal degrees of freedom, $Z_N = \frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N \xi^N(T)$, where

$\xi(T) = \text{Tr} e^{-\beta \hat{h}_{int}}$ is the partition function for the internal degrees of freedom, which include rotational, vibrational, and electronic excitations. One still has $pV = N k_B T$, but the heat capacities at constant V and p are

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_{V, N} = \frac{1}{2} d N k_B - N T \varphi''(T), \quad C_p = T \left(\frac{\partial S}{\partial T} \right)_{p, N} = C_V + N k_B, \quad (4.S.8)$$

where $\varphi(T) = -k_B T \ln \xi(T)$.

1. The generalization to the GCE is straightforward.[↩]

Endnotes

1. We write the Hamiltonian as \hat{H} (classical or quantum) in order to distinguish it from magnetic field (H) or enthalpy (\mathcal{H}).[↩]
2. More on this in chapter 5.[↩]

3. The factor of $\frac{1}{2}$ preceding Ω_M in Equation [nrdos] appears because $\delta(u^2 - 1) = \frac{1}{2} \delta(u - 1) + \frac{1}{2} \delta(u + 1)$. Since $u = |\mathbf{u}| \geq 0$, the second term can be dropped.↩
4. Note that for integer argument, $\Gamma(k) = (k - 1)!$ ↩
5. See §2.7.4.↩
6. See T.-C. Lu and T. Grover, arXiv 1709.08784.↩
7. In applying Equation [EminusTS] to the denominator of Equation [PEOCE], we shift \mathcal{E}' by E and integrate over the difference $\delta\mathcal{E}' \equiv \mathcal{E}' - E$, retaining terms up to quadratic order in $\delta\mathcal{E}'$ in the argument of the exponent.↩
8. In deriving Equation [thermforce], we have used the so-called Feynman-Hellman theorem of quantum mechanics:

$$d\langle n | \hat{H} | n \rangle = \langle n | d\hat{H} | n \rangle, \text{ if } |n\rangle \text{ is an energy eigenstate.} \leftarrow$$
9. *Nota bene* we are concerned with classical spin configurations only – there is no superposition of states allowed in this model!
 ↩
10. Note that while we cannot simultaneously specify the eigenvalues of two components of \mathbf{L} along axes fixed in space, we can simultaneously specify the components of \mathbf{L} along one axis fixed in space and one axis rotating with a body. See Landau and Lifshitz, *Quantum Mechanics*, §103.↩
11. See §72 of Landau and Lifshitz, *Quantum Mechanics*, which, in my humble estimation, is the greatest physics book ever written.↩
12. See Landau and Lifshitz, *Quantum Mechanics*, §86.↩
13. Note that there is no prime on the \mathbf{k} sum for F , as we have divided the logarithm of Z by two and replaced the half sum by the whole sum.↩
14. The hyperfine splitting in hydrogen is on the order of $(m_e/m_p) \alpha^4 m_e c^2 \sim 10^{-6}$ eV, which is on the order of 0.01 K. Here $\alpha = e^2/\hbar c$ is the fine structure constant.↩

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