

4.6: Exercise problems

? Exercise 4.6.1

Compare the third virial coefficient $C(T)$ that follows from the van der Waals equation, with its value for the hardball model of particle interactions (whose calculation was the subject of Problem 3.28), and comment.

? Exercise 4.6.2

Calculate the entropy and the internal energy of the van der Waals gas, and discuss the results.

? Exercise 4.6.3

Use two different approaches to calculate the so-called *Joule-Thomson coefficient* $(\partial E/\partial V)_T$ for the van der Waals gas, and the change of temperature of such a gas, with a temperature-independent C_V , at its fast expansion.

? Exercise 4.6.4

Calculate the difference $C_P - C_V$ for the van der Waals gas, and compare the result with that for an ideal classical gas.

? Exercise 4.6.5

Calculate the temperature dependence of the phase-equilibrium pressure $P_0(T)$ and the latent heat $\Lambda(T)$, for the van der Waals model, in the low-temperature limit $T \ll T_c$.

? Exercise 4.6.6

Perform the same tasks as in the previous problem in the opposite limit – in close vicinity of the critical point T_c .

? Exercise 4.6.7

$$P + \frac{a}{V(V + Nb)T^{1/2}} = \frac{NT}{V - Nb},$$

with constant parameters a and b .

Hint: Be prepared to solve a cubic equation with particular (numerical) coefficients.

? Exercise 4.6.8

$$P = \frac{NT}{V - b} \exp \left\{ -\frac{a}{NTV} \right\},$$

with constant parameters a and b . Compare the value of the dimensionless factor $P_c V_c / NT_c$ with those given by the van der Waals and Redlich-Kwong models.

? Exercise 4.6.9

In the crude sketch shown in Figure 4.1.3b the derivatives dP/dT of the phase transitions liquid gas (“vaporization”) and solid-gas (“sublimation”), at the triple point, are different, with

$$\left(\frac{dP_v}{dT} \right)_{T=T_t} < \left(\frac{dP_s}{dT} \right)_{T=T_t}.$$

Is this occasional? What relation between these derivatives can be obtained from thermodynamics?

? Exercise 4.6.10

Use the Clapeyron-Clausius formula (4.1.17) to calculate the latent heat Λ of the Bose-Einstein condensation, and compare the result with that obtained in the solution of Problem 3.21.

? Exercise 4.6.11

- (i) Write the effective Hamiltonian for that the usual single-particle stationary Schrödinger equation coincides with the Gross-Pitaevski equation (4.3.19).
- (ii) Use this *Gross-Pitaevskii Hamiltonian*, with the trapping potential $U(\mathbf{r}) = m\omega^2 r^2/2$, to calculate the energy E of $N \gg 1$ trapped particles, assuming the trial solution $\psi \propto \exp\{-r^2/2r_0^2\}$, as a function of the parameter r_0 .⁵⁴
- (iii) Explore the function $E(r_0)$ for positive and negative values of the constant b , and interpret the results.
- (iv) For small $b < 0$, estimate the largest number N of particles that may form a metastable Bose Einstein condensate.

? Exercise 4.6.12

Superconductivity may be suppressed by a sufficiently strong magnetic field. In the simplest case of a bulk, long cylindrical sample of a type-I superconductor, placed into an external magnetic field \mathcal{H}_{ext} parallel to its surface, this suppression takes a simple form of a simultaneous transition of the whole sample from the superconducting state to the “normal” (non-superconducting) state at a certain value $\mathcal{H}_c(T)$ of the field's magnitude. This *critical field* gradually decreases with temperature from its maximum value $\mathcal{H}_c(0)$ at $T \rightarrow 0$ to zero at the critical temperature T_c . Assuming that the function $\mathcal{H}_c(T)$ is known, calculate the latent heat of this phase transition as a function of temperature, and spell out its values at $T \rightarrow 0$ and $T = T_c$.

Hint: In this context, “bulk sample” means a sample much larger than the intrinsic length scales of the superconductor (such as the London penetration depth δ_L and the coherence length ξ).⁵⁵ For such bulk superconductors, magnetic properties of the superconducting phase may be well described just as the perfect diamagnetism, with $\mathcal{B} = 0$ inside it.

? Exercise 4.6.13

In some textbooks, the discussion of thermodynamics of superconductivity is started with displaying, as self-evident, the following formula:

$$F_n(T) - F_s(T) = \frac{\mu_0 \mathcal{H}_c^2(T)}{2} V,$$

where F_s and F_n are the free energy values in the superconducting and non-superconducting (“normal”) phases, and $\mathcal{H}_c(T)$ is the critical value of the magnetic external field. Is this formula correct, and if not, what qualification is necessary to make it valid? Assume that all conditions of the simultaneous field induced phase transition in the whole sample, spelled out in the previous problem, are satisfied.

? Exercise 4.6.14

In Sec. 4, we have discussed Weiss' molecular-field approach to the Ising model, in which the average $\langle s_j \rangle$ plays the role of the order parameter η . Use the results of that analysis to calculate the coefficients a and b in the corresponding Landau expansion (4.3.6) of the free energy. List the critical exponents α and β , defined by Eqs. (4.2.6) and (4.2.8), within this approach.

? Exercise 4.6.15

Consider a ring of $N = 3$ Ising “spins” ($s_k = \pm 1$), with similar ferromagnetic coupling J between all sites, in thermal equilibrium.

- Calculate the order parameter η and the low-field susceptibility $\chi \equiv \partial\eta/\partial h|_{h=0}$.
- Use the low-temperature limit of the result for χ to predict it for a ring with an arbitrary N , and verify your prediction by a direct calculation (in this limit).
- Discuss the relation between the last result, in the limit $N \rightarrow \infty$, and Equation (4.5.15).

? Exercise 4.6.16

Calculate the average energy, entropy, and heat capacity of a three-site ring of Ising-type “spins” ($s_k = \pm 1$), with *anti*-ferromagnetic coupling (of magnitude J) between the sites, in thermal equilibrium at temperature T , with no external magnetic field. Find the asymptotic behavior of its heat capacity for low and high temperatures, and give an interpretation of the results.

? Exercise 4.6.17

Using the results discussed in Sec. 5, calculate the average energy, free energy, entropy, and heat capacity (all per spin) as functions of temperature T and external field h , for the infinite 1D Ising model. Sketch the temperature dependence of the heat capacity for various values of ratio h/J , and give a physical interpretation of the result.

? Exercise 4.6.18

Use the molecular-field theory to calculate the critical temperature and the low-field susceptibility of a d -dimensional cubic lattice of spins, described by the so-called *classical Heisenberg model*.⁵⁶

$$E_m = -J \sum_{\{k,k'\}} \mathbf{s}_k \cdot \mathbf{s}_{k'} - \sum_k \mathbf{h} \cdot \mathbf{s}_k.$$

Here, in contrast to the (otherwise, very similar) Ising model (4.2.3), the spin of each site is modeled by a classical 3D vector $\mathbf{s}_k = \{s_{xk}, s_{yk}, s_{zk}\}$ of unit length: $s_k^2 = 1$.

- The plasma phase, in which atoms are partly or completely ionized, is frequently mentioned on one more phase, on equal footing with the three phases listed above, but one has to remember that in contrast to them, a typical electroneutral plasma consists of particles of two very different sorts – positive ions and electrons.
- Such classification schemes, started by Paul Ehrenfest in the early 1930s, have been repeatedly modified to accommodate new results for particular systems, and by now only the “first-order phase transition” is still a generally accepted term, but with a definition different from the original one.
- For example, for water the latent heat of vaporization at the ambient pressure is as high as $\sim 2.2 \times 10^6$ J/kg, i.e. ~ 0.4 eV per molecule, making this ubiquitous liquid indispensable for effective fire fighting. (The latent heat of water ice’s melting is an order of magnitude lower.)
- Due to the phenomenological character of the van der Waals model, one cannot say for sure whether the condensed phase it predicts corresponds to a liquid or a solid. However, in most real substances at ambient conditions, gas coexists with liquid, hence the name.
- The special choice of numerical coefficients in Equation (4.1.3) makes the border between these two regions to take place exactly at $t = 1$, i.e. at the temperature equal to T_c , with the critical point’s coordinates equal to P_c and V_c .
- Actually, this assumption is not crucial for our analysis of mechanical stability, because if a fluctuation takes place in a small part of the total volume V , its other parts play the role of pressure-fixing environment.
- Frequently, $P_0(T)$ is called the *saturated vapor pressure*.
- A natural question: is the two-phase state with $P = P_0(T)$ the only state existing between points 1 and 2? Indeed, the branches 1-1' and 2-2' of the single-phase isotherm also have negative derivatives $(\partial P/\partial V)_T$ and hence are mechanically stable with respect to small perturbations. However, these branches are actually *metastable*, i.e. have larger Gibbs energy per particle (i.e.

μ) than the counterpart phase and are hence unstable to *larger* perturbations – such as foreign microparticles (say, dust), protrusions on the confining walls, etc. In very controlled conditions, these single-phase “superheated” and “supercooled” states can survive almost all the way to the zero-derivative points 1' and 2', leading to sudden jumps of the system into the counterpart phase. (At fixed pressure, such jumps go as shown by dashed lines in Figure 4.1.2.) In particular, at the atmospheric pressure, purified water may be supercooled to almost -50°C , and superheated to nearly $+270^\circ\text{C}$. However, at more realistic conditions, perturbations result in the two-phase coexistence formation close to points 1 and 2.

9. This *Maxwell equal-area rule* (also called “Maxwell’s construct”) was suggested by J. C. Maxwell in 1875 using more complex reasoning.
10. It is fascinating how well is this Arrhenius exponent hidden in the polynomial van der Waals equation (4.1.2)!
11. $(\text{CH}_3-\text{CH}_2)-\text{O}-(\text{CH}_2-\text{CH}_3)$, historically the first popular general anesthetic.
12. It is interesting that very close to the critical point the substance suddenly becomes opaque – in the case of ether, whitish. The qualitative explanation of this effect, called the *critical opalescence*, is simple: at this point, the difference of the Gibbs energies per particle (i.e. the chemical potentials) of the two phases becomes so small that unavoidable thermal fluctuations lead to spontaneous appearance and disappearance of relatively large (a few- μm -scale) single-phase regions in all the volume. A large concentration of boundaries of such randomly shaped regions leads to strong light scattering.
13. Please note that for water, P_t is much lower than the normal atmospheric pressure (101.325 kPa).
14. Note the recent (2018) re-definition of the “legal” kelvin via joule (see, appendix CA: *Selected Physical Constants*); however, the new definition is compatible, within experimental accuracy, with that mentioned above.
15. Perhaps the most practically important example is the air/water system. For its detailed discussion, based on Equation (4.1.19), the reader may be referred, e.g., to Sec. 3.9 in F. Schwabl, *Statistical Mechanics*, Springer (2000). Other important applications include liquid solutions, and metallic *alloys* – solid solutions of metal elements.
16. For ferromagnets, this point is usually referred to at the *Curie temperature*, and for antiferromagnets, as the *Néel temperature*.
17. Unfortunately, I will have no time/space for these interesting (and practically important) generalizations, and have to refer the interested reader to the famous monograph by R. Stratonovich, *Topics in the Theory of Random Noise*, in 2 vols., Gordon and Breach, 1963 and 1967, and/or the influential review by H. Haken, *Ferstkörperprobleme* **10**, 351 (1970).
18. See, e.g., QM Sec. 4.4.
19. At $J < 0$, the first term of Equation (4.2.1) gives a reasonable model of an antiferromagnet, but in this case, the external magnetic field effects are more subtle; I will not have time to discuss them.
20. See, e.g., QM Equation (4.163).
21. Named after Ernst Ising who explored the 1D version of the model in detail in 1925, though a similar model was discussed earlier (in 1920) by Wilhelm Lenz.
22. For more detailed discussions of phase transition theories (including other popular models of the ferromagnetic phase transition, e.g., the *Potts model*), see, e.g., either H. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford U. Press, 1971; or A. Patashinskii and V. Pokrovskii, *Fluctuation Theory of Phase Transitions*, Pergamon, 1979; or B. McCoy, *Advanced Statistical Mechanics*, Oxford U. Press, 2010. For a very concise text, I can recommend J. Yeomans, *Statistical Mechanics of Phase Transitions*, Clarendon, 1992.
23. The forms of this and other functions of τ are selected to make all critical exponents non-negative.
24. In most models of ferromagnetic phase transitions, this variable is proportional to the genuine low-field magnetic susceptibility χ_m of the material – see, e.g., EM Equation (5.111).
25. As was already discussed in Secs. 1.4 and 2.4, there is some dichotomy of terminology for free energies in literature. In models (4.2.1) and (4.2.3), the magnetic field effects are accounted for at the microscopic level, by the inclusion of the corresponding term into each particular value E_m . From this point of view, the list of macroscopic variables in these systems does not include either P and V or their magnetic analogs, so that we may take $G \equiv F + PV = F + \text{const}$, and the equilibrium (at fixed h , T and N) corresponds to the minimum of the *Helmholtz* free energy F .
26. Historically, the last term belongs to the later (1950) extension of the theory by V. Ginzburg and L. Landau – see below.
27. According to Equation (4.2.10), the correlation radius may be interpreted as the distance at that the order parameter η relaxes to its equilibrium value, if it is deflected from that value at some point. Since the law of such spatial change may be obtained by a variational differentiation of F , for the actual relaxation law, all major terms of (4.3.6) have to be comparable.
28. As an immediate elementary sanity check of this relation, resulting from the analogy of Eqs. (1.1.1) and (1.1.5), the minimization of Δg in the absence of superconductivity ($\psi = 0$) gives the correct result $\mathcal{B} = \mu_0 \mathcal{H}$. Note that this account of the difference between Δf and Δg is necessary here because (unlike Eqs. (4.2.1) and (4.2.3)), the Ginzburg Landau free energy (4.3.16) does not take into account the effect of the field on each particle directly.

29. It is discussed in EM Sec. 6.5.
30. See, e.g., QM Sec. 3.1.
31. See, e.g., EM Sec. 6.5.
32. See, e.g., M. Tinkham, *Introduction to Superconductivity*, 2nd ed., McGraw-Hill, 1996. A short discussion of the Josephson effects and Abrikosov vortices may be found in QM Sec. 1.6 and EM Sec. 6.5 of this series.
33. See, e.g., Sec. 45 in E. Lifshitz and L. Pitaevskii, *Statistical Physics*, Part 2, Pergamon, 1980.
34. Since in this naïve approach we neglect the fluctuations of spin, i.e. their disorder, the assumption of full ordering implies $S = 0$, so that $F \equiv E - TS = E$, and we may use either notation for the system's energy.
35. The fact that the stable states always correspond to $\eta = \pm 1$, partly justifies the treatment, in this crude approximation, of the order parameter η as a continuous variable.
36. Since these magnetization jumps are accompanied by (negative) jumps of the free energy F , they are sometimes called the first-order phase transitions. Note, however, that in this simple theory, these transitions are between two physically similar *fully-ordered* phases.
37. For me, it was always shocking how little my graduate students knew about this fascinating (and very important) field of modern engineering, which involves so much interesting physics and fantastic electromechanical technology. For getting acquainted with it, I may recommend, for example, the monograph by C. Mee and E. Daniel, *Magnetic Recording Technology*, 2nd ed., McGraw-Hill, 1996.
38. In some texts, this approximation is called the “mean-field theory”. This terminology may lead to confusion, because the molecular-field theory belongs to a different, deeper level of the theoretical hierarchy than, say, the (more phenomenological) Landau-style mean-field theories. For example, for a given microscopic model, the molecular-field approach may be used for the (approximate) calculation of the parameters a , b , and T_c participating in Equation (4.3.6) – the starting point of the Landau theory.
39. Named after Pierre Curie, rather than his (more famous) wife Marie Skłodowska-Curie.
40. It was developed in 1941 by H. Kramers and G. Wannier. I am following this method here because it is very close to the one used in quantum mechanics (see, e.g., QM Sec. 2.5), and may be applied to other problems as well. For a simpler approach to the 1D Ising problem, which gives an explicit solution even for an “open-end” system with a finite number of spins, see the model solution of Problem 5.5.
41. This is a result of the “translational” (or rather rotational) symmetry of the system, i.e. its invariance to the index replacement $k \rightarrow k + 1$ in all terms of Equation (4.5.2).
42. Named after Felix Bloch who was the first one to discuss such excitations in ferromagnetism.
43. For the closed-ring model (Figure 4.5.1) such analysis gives an almost similar prediction, with the difference that in that system, the Bloch walls may appear only in pairs, so that $E_W = 4J$, and $S_W = \ln[N(N-1)] \approx 2 \ln N$.
44. This is a very vivid application of one of the core results of thermodynamics. If the reader is still uncomfortable with it, they are strongly encouraged to revisit Equation (1.4.19) and its discussion.
45. For that, the interested reader may be referred to either Sec. 151 in the textbook by Landau and Lifshitz, or Chapter 15 in the text by Huang, both cited above.
46. Discussion of such laws in the task of *physical kinetics*, which will be briefly reviewed in Chapter 6.
47. The calculation of these rates for several particular cases is described in QM Secs. 6.6, 6.7, and 7.6 – see, e.g., QM Equation (7.196), which is valid for a very general model of a quantum system.
48. Note that a flip of a single spin changes the signs of only $(2d + 1)$ terms in the sum (4.2.3), i.e. does not require the recalculation of all $(2d + 1)N$ terms of the sum, so that the computation of Δ takes just a few multiply-and accumulate operations even at $N \gg 1$.
49. The latter step is necessary to avoid the system's trapping in local minima of its multidimensional energy profile $E_m(s_1, s_2, \dots, s_N)$.
50. Initially developed in the quantum field theory in the 1950s, it was adapted to statistics by L. Kadanoff in 1966, with a spectacular solution of the so-called *Kubo problem* by K. Wilson in 1972, later awarded with a Nobel Prize.
51. This might be expected because physically C is just a certain constant addition to the system's energy. However, the introduction of that constant is mathematically necessary, because Eqs. (4.5.31) and (4.5.32) may be reconciled only if $C' \neq C$.
52. This equation of state, suggested in 1948, describes most real gases better than not only the original van der Waals model, but also other two-parameter alternatives, such as the *Berthelot*, *modified-Berthelot*, and *Dieterici* models, though some approximations with more fitting parameters (such as the *Soave-Redlich-Kwong model*) work even better.

53. This model is currently less popular than the Redlich-Kwong one (also with two fitting parameters), whose analysis was the task of the previous problem.
54. This task is essentially the first step of the variational method of quantum mechanics – see, e.g., QM Sec. 2.9.
55. A discussion of these parameters, as well as of the difference between the type-I and type-II superconductivity, may be found in EM Secs. 6.4-6.5. However, those details are not needed for the solution of this problem.
56. This classical model is formally similar to the generalization of the genuine (quantum) Heisenberg model (4.2.1) to arbitrary spin s , and serves as its infinite-spin limit.

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