Cambridge University Press
978-1-107-18038-3 — String Theory Methods for Condensed Matter Physics
Horatiu Nastase
Excerpt
More Information

1 Lightning Review of Statistical Mechanics, Thermodynamics, Phases, and Phase Transitions

In Part I, I will describe various condensed matter models and problems of interest. In other words, we will study the condensed matter issues that can be described in one way or another using string theory methods.

To set up the notation, in Chapter 1, I will make a lightning review of thermodynamics, phase transitions, and statistical mechanics. These are issues that are supposed to be known, but we will review them in a way that will be useful for us later and in order to have a common starting point.

1.1 Note on Conventions

In most of this book, I will use field theorists, conventions, with $\hbar = c = 1$, unless needed to emphasize some quantum or (non)relativistic issues. We can always reintroduce $\hbar$ and c by dimensional analysis, if needed. In these conventions, there is only one dimensionful unit, namely $mass = 1/length = energy = 1/time = \cdots$. When I speak of dimension of a quantity, I refer to mass dimension.

For the Minkowski metric $\eta^{\mu\nu}$ I use the mostly plus signature convention, so in the most relevant case of 3+1 dimensions the signature is $(-+++)$, for $\eta^{\mu\nu} = diag(-1, +1, +1, +1)$.

I also use the Einstein summation convention, i.e. repeated indices are summed over. The repeated indices will be one up and one down, unless we are in Euclidean space, when it doesn't matter, so we can put all indices down.

1.2 Thermodynamics

In thermodynamics, we use two types of quantities:

- *Intensive quantities*, which are quantities that are independent of the size of the system. The relevant examples for us are

$$T, P, \vec{E}, \vec{H}, \mu_\alpha, \{P_j\}. \tag{1.1}$$

Here T is the temperature, P is the pressure, $\vec{E}$ is the electric field, $\vec{H}$ is the magnetic field, μ_α are chemical potentials for the particle species α, i.e. the increase in energy required to add one particle to the system, and P_j are generalized pressures (such that $P_0 = P$).

Cambridge University Press
978-1-107-18038-3 — String Theory Methods for Condensed Matter Physics
Horatiu Nastase
Excerpt
More Information

- *Extensive quantities*, which are quantities which increase with the size of the system, usually with the volume (though it can also be with the surface area, for example). The relevant examples for us are

$$S, V, V\vec{D}, V\vec{B}, N_\alpha, \{X_j\}, \tag{1.2}$$

respectively; i.e. these are the conjugate quantities corresponding to the intensive quantities above. Here S is the entropy, V the volume, $\vec{D}$ is the electric induction, $\vec{B}$ is the magnetic induction, N_α are numbers of particles of species α, and X_j are generalized volumes (such that $X_0 = -V$).

1. The *first law of thermodynamics* is then the following statement about the energy differential:

$$dU = TdS - PdV + \sum_j P_j dX_j + \vec{E}\cdot d(V\vec{D}) + \vec{H}\cdot d(V\vec{B}) + \sum_\alpha \mu_\alpha N_\alpha . \tag{1.3}$$

For the electro-magnetic quantities, we need to add the *material relations* that relate the inductions to the fields:

- Electric case:

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} = \epsilon \vec{E}, \tag{1.4}$$

where ϵ_0 is the vacuum electric permittivity, ϵ is the electric permittivity in the material, and $\vec{P}$ is the polarization.

- Magnetic case:

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) = \mu\vec{H}, \tag{1.5}$$

where μ_0 is the vacuum magnetic permeability, μ is the magnetic permeability in the material, and $\vec{M}$ is the magnetization.

From the first law and the material relations we can deduce the electric and magnetic energy densities (or reversely from the energy densities and material relations we can deduce the first law for the electro-magnetic case):

- in the vacuum:

$$\begin{aligned} \rho_e &= \frac{\epsilon_0 \vec{E}^2}{2} \\ \rho_m &= \frac{\mu_0 \vec{H}^2}{2}. \end{aligned} \tag{1.6}$$

- in the material:

$$\begin{aligned} \rho_e &= \frac{\epsilon \vec{E}^2}{2} = \frac{\vec{D}^2}{2\epsilon} \\ \rho_m &= \frac{\mu \vec{H}^2}{2} = \frac{\vec{B}^2}{2\mu}. \end{aligned} \tag{1.7}$$

2. The *second law of thermodynamics* is the statement that the entropy always increases in a process, i.e. its variation is positive or zero:

$$\Delta S \geq 0. \tag{1.8}$$

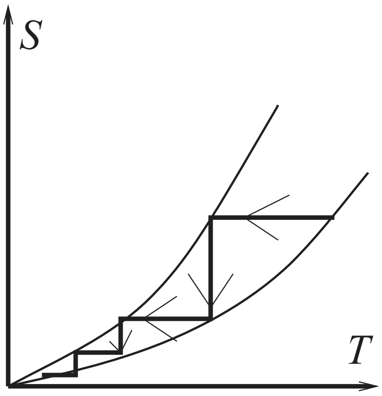

Fig. 1.1 Third law of thermodynamics.

3. The *third law of thermodynamics* is usually less known in its correct form. The statement is that as the temperature goes to zero, $T \to 0$, then the entropy goes to a constant, $S \to S_0$. Often it is stated as the fact that $S \to 0$, but there are in fact examples with nonzero entropy $S_0 \neq 0$, i.e. with a degenerate ground state, at zero temperature. One very important example for us will be the case of black holes, which later will be embedded in string theory.

An equivalent statement of the third law is that *It is impossible to reach* $T = 0$ *in a finite number of steps from* $T \neq 0$. To understand the equivalence, consider the (S, T) diagram, and two curves for the system, reaching the same $(S_0, 0)$ point, as in Figure 1.1. The most efficient cooling process is the Carnot process, i.e. an isothermal line ($T =$ const.), followed by an isentropic line ($S =$ const.), i.e. a vertical line, followed by a horizontal line. To reach $T = 0$ by moving on verticals and horizontals between the two curves, we can see that we need an infinite number of steps.

For expediency, we will include formally $\{\vec{E}, \vec{H}, \mu_\alpha\}$ into $\{P_j\}$ and $\{V\vec{D}, V\vec{B}, N_\alpha\}$ into $\{X_j\}$.

- Then the *Euler equation* (obtained from the homogeneity properties of T and S) says that for a system with extensive quantities S and $\{X_j\}$, for $j = 1, \ldots, r$, we have

$$U = TS + \sum_{j=1}^{r} P_j X_j. \tag{1.9}$$

- Together with the first law, the Euler equation implies the *Gibbs-Duhem equation*:

$$SdT + \sum_{j=1}^{r} X_j dP_j = 0. \tag{1.10}$$

Thermodynamic Potentials

For many systems, it is useful to work with variables that include only part of the extensive quantities and the rest of the intensive quantities, i.e. with $\{P_l\}$, $l = 1, \ldots, m$ and

Cambridge University Press
978-1-107-18038-3 — String Theory Methods for Condensed Matter Physics
Horatiu Nastase
Excerpt
More Information

$\{X_{l'}\}$, $l' = m+1, \dots, r$. As always, that is done by performing a *Legendre transform* over X_l; i.e. one uses the following *thermodynamic potentials*:

$$\bar{U} = \bar{U}[P_1, \dots, P_m] = U - \sum_{l=1}^{m} P_l X_l. \tag{1.11}$$

Their differentials, i.e. the first law of thermodynamics for systems at constant $P_1, \dots, P_m$, are given by

$$d\bar{U} = -\sum_{l=1}^{m} X_l dP_l + \sum_{l'=m+1}^{r} P_{l'} dX_{l'}. \tag{1.12}$$

This is the general formalism, but there are special cases of thermodynamic potentials that are important and have been named before:

- The *free energy*, or *Helmholtz potential*,

$$F = U - TS. \tag{1.13}$$

- The *enthalpy*,

$$H = U + PV, \tag{1.14}$$

and we can also define a *generalized enthalpy*,

$$H^* = U - P_j X_j, \tag{1.15}$$

where $j \neq 0$ and $j \neq$ chemical potential.

- The *free enthalpy*, or *Gibbs potential*,

$$G = U - TS + PV, \tag{1.16}$$

and we can also define a *generalized Gibbs potential*,

$$G^* = U - TS - \sum_{l=1}^{m} P_l X_l. \tag{1.17}$$

- The *grand-canonical potential*,

$$\Omega = U - TS - \sum_{\alpha=1}^{n} \mu_\alpha N_\alpha. \tag{1.18}$$

The reason for considering the thermodynamic potentials is that *at equilibrium, for a system in contact with a reservoir that fixes* $T, P_1, \dots, P_n$, i.e. the situation that we will denote by

$$\mathcal{S} \cup \mathcal{R}_{T,P_1,\dots,P_n}, \tag{1.19}$$

the equilibrium is obtained for the minimum of the thermodynamic potential $\bar{U}[T, P_1, \dots, P_n]$.

1.3 Phase Transitions

One of the quantities that we are interested in, in order to describe a phase transition, is the dimensionality of the phase manifold. In order to obtain it, we have the *Gibbs phase rule*:

Consider a system with f phases, n chemical (nonreacting) components, and q nonchemical degrees of freedom, whose intensive parameters we fix (e.g., T, P). Then the *number of effective degrees of freedom = dimensionality of the phase manifold* is

$$v = n + q - f. \tag{1.20}$$

Example To understand it, consider the simplest case, of a system with two phases ($f = 2$), one component ($n = 1$), and we fix T and P, i.e. $q = 2$, then $v = 1 + 2 - 2 = 1$, i.e. the separation between the two phases is a line (1-dimensional) that can be, for instance, drawn in the (T, P) plane.

Phase transition types

There are two important classifications of phase transitions, the first being developed by **Ehrenfest**. It is based on the thermodynamic potential $\bar{U}$ for the system under consideration. According to it, we have phase transitions of

- *first order*, which means that the thermodynamic potential $\bar{U}$ is constant (continuous) across the phase transition, but its first derivatives are not, i.e. they are discontinuous across the phase transition, $\partial\bar{U}/\partial a_j \neq$ const.
- *second order*, which means that the thermodynamic potential $\bar{U}$ is constant across the phase transition, as are its first derivatives $\partial\bar{U}/\partial a_j =$ const., but its second derivatives are discontinuous across the phase transition, $\partial^2\bar{U}/\partial a_i \partial a_j \neq$ const.

In principle, we could go on and define third order (only the third order derivative of the thermodynamic potential being discontinuous), etc., but no such phase transition was found until now, so most likely there is no other type of phase transition.

The other important classification is due to **Landau**, who showed that the first and second order phase transitions have a different interpretation, and the difference between them can be described as follows.

- *first order* is when the phases differ only quantitatively, but not qualitatively.
- *second order* is when the phases also differ qualitatively. Specifically, there exists a so-called *order parameter* that we will denote by ψ, such that $\psi = 0$ in one phase that is symmetric under some symmetry, and $\psi \neq 0$ in the other phase, where we have no such symmetry, i.e. in the asymmetric phase.

Example of first order phase transition

Consider a system in contact with a (T, P) reservoir, i.e. $\mathcal{S} \cup \mathcal{R}_{T,P}$. Then the thermodynamic potential is the Gibbs potential $G = G(T, P) = U - TS + PV$, with $dG = -SdT + VdP + \cdots$. If the phase transition is first order, $G(T, P)$ is continuous across the phase transition, but its first derivatives,

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P}\right)_T , \tag{1.21}$$

are discontinuous, i.e. we have nonzero ΔV and ΔS, thus nonzero $\Lambda_{12} \equiv T\Delta S$. They are in fact related by the *Clausius-Clapeyron relation*: Across the coexistence line of the two phases (i.e. for $V_1 \leq V \leq V_2$), we have

$$\left.\frac{\partial P}{\partial T}\right|_{\text{phase trans.}} = \frac{\Delta S}{\Delta V} = \frac{\Lambda_{12}}{T(V_2 - V_1)}. \tag{1.22}$$

Example of second order phase transition
For the same system in contact with a (T, P) reservoir, the Gibbs potential $G(T, P)$ is again the relevant thermodynamic potential, and it and its first derivatives, S and V, are continuous, but its second derivatives are discontinuous, thus the *specific heat*,

$$C_P = \frac{T}{\nu}\left(\frac{\partial S}{\partial T}\right)_P = -\frac{T}{\nu}\left(\frac{\partial^2 G}{\partial T^2}\right)_P \tag{1.23}$$

is discontinuous. Here ν is the number of moles, actually defining the molar specific heat.

We can also consider a system in contact with a reservoir of magnetic and/or electric field $\vec{H}$, $\vec{E}$. In that case, the second derivatives of the thermodynamic potential are the following susceptibilities:

- the *magnetic susceptibility* χ_m, defined as

$$\chi_m = \frac{\partial M}{\partial H} = \frac{1}{\mu_0}\frac{\partial B}{\partial H} - 1 = -\frac{1}{\mu_0}\left(\frac{\partial^2 \bar{U}}{\partial H^2}\right) \tag{1.24}$$

is discontinuous, and

- the *electric susceptibility*

$$\kappa_e = \frac{1}{\epsilon_0}\frac{\partial P}{\partial E} = \frac{1}{\epsilon_0}\frac{\partial D}{\partial E} = -\frac{1}{\epsilon_0}\left(\frac{\partial^2 \bar{U}}{\partial E^2}\right) \tag{1.25}$$

is also discontinuous.

1.4 Statistical Mechanics and Ensembles

Statistical Mechanics
We now review the basics of statistical mechanics. We consider first the classical case, when there is a distribution function in the N-particle phase space. The one-particle phase space is $\{\vec{r}_k, \vec{p}_k\}$, and the N-particle phase space is shortened as $\vec{r}^N \equiv \{\vec{r}_1\vec{r}_2, \ldots, \vec{r}_N\}$.

The infinitesimal probability to be in phase space (around the point $(\vec{r}^N, \vec{p}^N)$) at time t is

$$dP(\vec{r}^N, \vec{p}^N, t) = \mathcal{P}(\vec{r}^N, \vec{p}^N, t)d\Gamma_N = \frac{d\mathcal{N}}{\mathcal{N}}, \tag{1.26}$$

Cambridge University Press
978-1-107-18038-3 — String Theory Methods for Condensed Matter Physics
Horatiu Nastase
Excerpt
More Information

where $\mathcal{N}$ is the number of particles (out of which $d\mathcal{N}$ are in the given state), $\mathcal{P}$ (or also ρ later) is the *distribution function of the statistical ensemble*, and $d\Gamma_N = d\vec{r}^N d\vec{p}^N$ is the infinitesimal volume element of phase space.

We also define the quantities:

- The phase space volume for maximum energy E,

$$\Gamma_N(E) = \int_0^E d\Gamma_N(E), \tag{1.27}$$

- the phase space volume between E and $E + \Delta E$,

$$\Omega_N(E, \Delta E) = \Gamma_N(E + \Delta E) - \Gamma_N(E), \tag{1.28}$$

- and the density of states,

$$\omega(E) = \frac{\partial \Gamma(E)}{\partial E}. \tag{1.29}$$

Actually, to obtain the correct *number of states*, we should divide the phase space volume by $(N!h^{3N})$, the quantum unit of phase space times the symmetry factor for N particles.

In fact, above, when we called $\mathcal{P}$ the distribution function of the statistical ensemble, we have implicitly used the *ergodic hypothesis*, stating that the temporal average should equal the ensemble average,

$$\langle f \rangle_{\text{temporal}} = \langle f \rangle_{\text{ensemble}}. \tag{1.30}$$

This is an ergodic postulate, associated with Gibbs and Tollman (who formalized statistical mechanics by basing it on postulates from which one can find everything else).

The next important assumption is the one of equilibrium, when there is no time dependence. While there are many interesting things about systems out of equilibrium, like in the case of heavy ion collisions, for instance, in this course we will stick with the assumption of equilibrium. We then have the *postulate of a priori equal probabilities*, which states that: The probability density is constant in the allowed domain $\mathcal{D}$ in phase space and zero outside it.

From the above postulates, we can obtain that the distribution function depends explicitly only on the total energy of the system E, and depends on phase space only implicitly, i.e. that

$$\mathcal{P}(\vec{r}^N, \vec{p}^N) = f\left(E(\vec{r}^N, \vec{p}^N)\right). \tag{1.31}$$

Statistical Ensembles

We now review the most important statistical ensembles.

Microcanonical

The first one can be immediately derived from the above statement that the distribution function depends explicitly only on E. We consider then a constant energy $E = E_0$, thus having a probability $P(E(\ldots))$ constant for $E = E_0$ and zero for $E \neq E_0$. It is in fact correct to consider a *quasi-microcanonical ensemble*, with energy $E \in (E_0, E_0 + \Delta E)$.

Cambridge University Press
978-1-107-18038-3 — String Theory Methods for Condensed Matter Physics
Horatiu Nastase
Excerpt
More Information

Boltzmann Formula

The next step is in some sense a postulate, meaning that it cannot be truly derived, but must be postulated, and in fact there might be alternatives to it for some systems. The postulate is Boltzmann's formula relating entropy with the distribution function. We can relate S to the logarithm of the number of states (remembering that, up to the factor of $1/(N!h^{3N})$, the total volume of phase space for the quasi-microcanonical case, Ω, is the number of states). The result is

$$S = k_B \ln \Omega, \tag{1.32}$$

where k_B is Boltzmann's constant. In the thermodynamical large N limit, we have also the equivalent formulas

$$S = k_B \ln \omega = k_B \ln \Gamma(E) = -k_B \langle \ln \rho \rangle. \tag{1.33}$$

The entropy is $S = S(E, V, N, \ldots)$. Note that the above equality is a bit counter-intuitive, but correct, since in the large N limit, the volume of the $3N$-dimensional space bounded by E is approximately equal to the volume of the space between E and $E + dE$, as we can check.

Since the first law is written as (renaming U as E)

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN + \cdots \tag{1.34}$$

by combining it with the Boltzmann formula, we obtain the relations ($\beta \equiv 1/(k_B T)$):

$$\beta = \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}; \quad \beta P = \left(\frac{\partial \ln \Omega}{\partial V}\right)_{E,N}; \quad -\beta\mu = \left(\frac{\partial \ln \Omega}{\partial N}\right)_{E,V}. \tag{1.35}$$

Canonical

Consider the system in contact with a reservoir of temperature, $\mathcal{S} \cup \mathcal{R}_T$, in which case the distribution function is

$$\rho(\mathcal{H}) = \frac{e^{-\beta \mathcal{H}}}{Z(\beta, V, N, \ldots)}, \tag{1.36}$$

where the $\mathcal{H}$ is the Hamiltonian and the *partition function* Z is simply the sum over states of the numerator,

$$Z = \sum_n g_n e^{-\beta E_n}, \tag{1.37}$$

where g_n is the degeneracy of the energy E_n.

The thermodynamical potential is the free energy and is given in terms of the partition function as

$$F(\beta, V, N) = -k_B T \ln Z. \tag{1.38}$$

Grand-Canonical

Consider a system in contact with a temperature and a particle (chemical potential) reservoir, $\mathcal{S} \cup \mathcal{R}_{T,\mu}$. The distribution function is then

$$\rho(\mathcal{H}) = \frac{e^{-\beta(\mathcal{H}-\mu N)}}{Z(\beta, \beta\mu, \ldots)}, \tag{1.39}$$

and the partition function is

$$Z(\beta, \beta\mu, V, \ldots) = \sum_{N \geq 0} e^{-\beta(\mathcal{H}-\mu N)} \frac{Z_1^N}{f}. \tag{1.40}$$

Here Z_1 is a single-particle partition function, and $f = N!$ for free particles and $f = 1$ for interacting particles.

Isothermal-Isobaric

For the case $\mathcal{S} \cup \mathcal{R}_{T,P}$, the distribution function is

$$\rho = \frac{e^{-\beta(\mathcal{H}+PV)}}{Z(\beta, \beta P, \ldots)} \tag{1.41}$$

and the partition function is given as an integration over the volume (which is a continuous variable, thus integrated instead of summed)

$$Z(\beta, \beta P) = \int_0^\infty dV e^{-\beta PV} Z_{\text{can}}(\beta, V, N), \tag{1.42}$$

and $Z_{\text{can}}(\beta, V, N)$ is the canonical partition function.

The thermodynamic potential is the Gibbs potential and is again given in terms of the partition function as

$$G(T, P, N) = -k_B T \ln Z. \tag{1.43}$$

Generalized Canonical

The distribution function is

$$\rho = \frac{e^{-\beta\mathcal{H}+\sum_{j=1}^{n} \beta P_j X_j (-\beta PV + \beta\mu N)}}{Z}, \tag{1.44}$$

where in brackets we have considered the case that we write explicitly the P and μ variables, and the partition function is

$$\begin{aligned} Z &= \left(\int_0^\infty dV \sum_{N \geq 0} e^{-\beta PV + \beta\mu N} \right) \int d\Gamma_{V,N} e^{-\beta\mathcal{H}_{V,N} + \sum_{j=1}^{n} \beta P_j X_j} \\ &= Z(\beta, (\beta P, \beta\mu), \beta P_1, \ldots, \beta P_n, X_{n+1}, \ldots, X_r). \end{aligned} \tag{1.45}$$

Note that if we don't put the P and μ in the reservoir, Z depends on V and N instead.

Then the thermodynamic potential is again given in terms of the partition function as before:

$$\bar{U} = -k_B T \ln Z(\beta, \beta P_1, \ldots, \beta P_n, X_{n+1}, \ldots, X_r). \tag{1.46}$$

Cambridge University Press
978-1-107-18038-3 — String Theory Methods for Condensed Matter Physics
Horatiu Nastase
Excerpt
More Information

The total energy is the statistical average of the sum of the energies, $U = \langle E \rangle$, and by writing it explicitly in terms of the distribution function, we see that we can write it in terms of the derivative of $\ln Z$:

$$U = \langle E \rangle = -\frac{\partial \ln Z}{d\beta}. \tag{1.47}$$

Similarly, the extensive quantity X_j is the average of some A_j, $X_j = \langle A_j \rangle$, and by writing it explicitly in terms of the distribution function, we see that we can write is as a derivative,

$$X_j = \langle A_j \rangle = \frac{\partial \ln Z}{\partial \beta P_j}, \tag{1.48}$$

for $j = 1, \dots, n$. For the other values, $l = n+1, \dots, r$, we obtain

$$P_l = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial X_l}. \tag{1.49}$$

1.5 Distributions

Classical Distribution: Maxwell-Boltzmann

We now analyze the standard distributions, starting with the classical distribution of Maxwell-Boltzmann. The total probability is the product of the individual probabilities, so the same holds for the distributions functions $\mathcal{P}$ (or ρ),

$$\mathcal{P} = \prod_i \mathcal{P}(\vec{r}_i, \vec{p}_i), \tag{1.50}$$

and the partition function is $Z = Z_1^N/N!$.

The distribution function for a single particle is

$$\mathcal{P}(\vec{r}, \vec{p}) = \frac{e^{-\beta E}}{\int \dots \int d\vec{r} d\vec{p} e^{-\beta E}}. \tag{1.51}$$

Quantum Distributions

Consider one-particle states α, with occupation number n_α. Then the energy is

$$E = \sum_\alpha \epsilon_\alpha n_\alpha \tag{1.52}$$

and the number of particles is

$$N = \sum_\alpha n_\alpha. \tag{1.53}$$

The quantum distribution function is then $\langle n_\alpha \rangle$. The partition function is

$$Z = \prod_\alpha Z_\alpha, \tag{1.54}$$