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Chapter 6

Classical Interacting Systems

6.1 References

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  A superb modern text, with many insightful presentations of key concepts.

- L. E. Reichl, *A Modern Course in Statistical Physics* (2nd edition, Wiley, 1998)
  A comprehensive graduate level text with an emphasis on nonequilibrium phenomena.

- M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* ($3^{\rm rd}$ 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, $3^{\rm rd}$ 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.

- J.-P Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, 1990)
  An advanced, detailed discussion of liquid state physics.

6.2 Nonideal Classical Gases

Let's switch gears now and return to the study of continuous classical systems described by a Hamiltonian $\hat{H}\big(\{\boldsymbol{x}_i\},\{\boldsymbol{p}_i\}\big)$. In the next chapter, we will see how the critical properties of classical fluids can in fact be modeled by an appropriate *lattice gas* Ising model, and we'll derive methods for describing the liquid-gas phase transition in such a model.

6.2.1 The configuration integral

Consider the ordinary canonical partition function for a nonideal system of identical point particles interacting via a central two-body potential $u(r)$. We work in the ordinary canonical ensemble. The N-particle partition function is

$$\begin{aligned} Z(T,V,N) &= \frac{1}{N!}\int\prod_{i=1}^{N}\frac{d^dp_i\,d^dx_i}{h^d}\,e^{-\hat{H}/k_BT} \\ &= \frac{\lambda_T^{-Nd}}{N!}\int\prod_{i=1}^{N}d^dx_i\,\exp\bigg(-\frac{1}{k_BT}\sum_{i<j}u\big(|\boldsymbol{x}_i-\boldsymbol{x}_j|\big)\bigg) \quad . \end{aligned} \tag{6.1}$$

Here, we have assumed a many body Hamiltonian of the form

$$\hat{H}=\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{2m}+\sum_{i<j}u\big(|\boldsymbol{x}_i-\boldsymbol{x}_j|\big) \quad , \tag{6.2}$$

in which massive nonrelativistic particles interact via a two-body central potential. As before, $\lambda_T=\sqrt{2\pi\hbar^2/mk_BT}$ is the thermal wavelength. We can now write

$$Z(T,V,N)=\lambda_T^{-Nd}\,Q_N(T,V) \quad , \tag{6.3}$$

where the *configuration integral* $Q_N(T,V)$ is given by

$$Q_N(T,V)=\frac{1}{N!}\int d^dx_1\cdots\int d^dx_N\,\prod_{i<j}e^{-\beta u(r_{ij})} \quad . \tag{6.4}$$

There are no general methods for evaluating the configurational integral exactly.

6.2.2 One-dimensional Tonks gas

The Tonks gas is a one-dimensional generalization of the hard sphere gas. Consider a one-dimensional gas of indistinguishable particles of mass m interacting via the potential

$$u(x-x')=\begin{cases}\infty & \text{if } |x-x'|<a \\ 0 & \text{if } |x-x'|\geq a \quad .\end{cases} \tag{6.5}$$

Thus, the Tonks gas may be considered to be a gas of *hard rods*. The above potential guarantees that the portion of configuration space in which any rods overlap is *forbidden* in this model. Let the gas be placed in a finite volume L. The hard sphere nature of the particles means that no particle can get within a distance $\frac{1}{2}a$ of the ends at $x = 0$ and $x = L$. That is, there is a one-body potential $v(x)$ acting as well, where

$$v(x) = \begin{cases} \infty & \text{if } x < \frac{1}{2}a \\ 0 & \text{if } \frac{1}{2}a \le x \le L - \frac{1}{2}a \\ \infty & \text{if } x > L - \frac{1}{2}a \quad . \end{cases} \tag{6.6}$$

The configuration integral of the 1D Tonks gas is given by

$$Q_N(T,L) = \frac{1}{N!} \int\limits_0^L dx_1 \cdots \int\limits_0^L dx_N \, \chi(x_1, \ldots, x_N) \quad , \tag{6.7}$$

where $\chi = e^{-U/k_{\rm B}T}$ is zero if any two 'rods' (of length a) overlap, or if any rod overlaps with either boundary at $x = 0$ and $x = L$, and $\chi = 1$ otherwise. Note that χ does not depend on the temperature. Due to permutation symmetry, we may integrate over the subspace where $x_1 < x_2 < \cdots < x_N$ and then multiply the result by $N!$. Clearly x_j must lie to the right of $x_{j-1} + a$ as well as to the left of $Y_j \equiv L - Na + (j - \frac{1}{2})a$. Note that since $Y_j - a = Y_{j-1}$. Thus, the configurational integral is

$$\begin{aligned} Q_N(T,L) &= \int\limits_{a/2}^{Y_1} dx_1 \int\limits_{x_1+a}^{Y_2} dx_2 \cdots \int\limits_{x_{N-1}+a}^{Y_N} dx_N = \int\limits_{a/2}^{Y_1} dx_1 \int\limits_{x_1+a}^{Y_2} dx_2 \cdots \int\limits_{x_{N-2}+a}^{Y_{N-1}} dx_{N-1} \left(Y_{N-1} - x_{N-1}\right) \\ &= \frac{1}{2} \int\limits_{a/2}^{Y_1} dx_1 \int\limits_{x_1+a}^{Y_2} dx_2 \cdots \int\limits_{x_{N-3}+a}^{Y_{N-2}} dx_{N-2} \left(Y_{N-2} - x_{N-2}\right)^2 = \cdots = \frac{1}{k!} \int\limits_{a/2}^{Y_1} dx_1 \int\limits_{x_1+a}^{Y_2} dx_2 \cdots \int\limits_{x_{N-k-1}+a}^{Y_{N-k}} dx_{N-k} \left(Y_{N-k} - x_{N-k}\right)^k \\ &= \frac{1}{N!} \left(Y_1 - \tfrac{1}{2}a\right)^N = \frac{1}{N!} \left(L - Na\right)^N \quad . \end{aligned} \tag{6.8}$$

The partition function is $Z(T,L,N) = \lambda_T^{-N} \, Q_N(T,L)$, and so the free energy is

$$F = -k_{\rm B}T \log Z = -Nk_{\rm B}T \left\{ -\log \lambda_T + 1 + \log\left(\frac{L}{N} - a\right) \right\} \quad , \tag{6.9}$$

where we have used Stirling's rule to write $\log N! \approx N \log N - N$. The pressure is

$$p = -\frac{\partial F}{\partial L} = \frac{nk_{\rm B}T}{1 - na} \quad , \tag{6.10}$$

where $n = N/L$ is the one-dimensional density. Note that the pressure diverges as n approaches $1/a$. The usual one-dimensional ideal gas law, $pL = Nk_{\rm B}T$, is replaced by $pL_{\rm eff} = Nk_{\rm B}T$, where $L_{\rm eff} = L - Na$ is the 'free' volume obtained by subtracting the total "excluded volume" Na from the original volume L.

Note the similarity here to the van der Waals equation of state, $(p+av^{-2})(v-b) = RT$, where $v = N_{\mathrm{A}} V/N$ is the molar volume. Defining $\tilde{a} \equiv a/N_{\mathrm{A}}^2$ and $\tilde{b} \equiv b/N_{\mathrm{A}}$, we have

$$p + \tilde{a} n^2 = \frac{n k_{\mathrm{B}} T}{1 - \tilde{b} n} \quad , \tag{6.11}$$

where $n = N_{\mathrm{A}}/v$ is the number density. The term involving the constant $\tilde{a}$ is due to the long-ranged attraction of atoms due to their mutual polarizability. The term involving $\tilde{b}$ is an excluded volume effect. The Tonks gas models only the latter.

6.2.3 Mayer cluster expansion

Let us return to the general problem of computing the configuration integral. Consider the function $e^{-\beta u_{ij}}$, where $u_{ij} \equiv u(|\boldsymbol{x}_i - \boldsymbol{x}_j|)$. We assume that at very short distances there is a strong repulsion between particles, *i.e.* $u_{ij} \to \infty$ as $r_{ij} = |\boldsymbol{x}_i - \boldsymbol{x}_j| \to 0$, and that $u_{ij} \to 0$ as $r_{ij} \to \infty$. Thus, $e^{-\beta u_{ij}}$ vanishes as $r_{ij} \to 0$ and approaches unity as $r_{ij} \to \infty$. For our purposes, it will prove useful to define the function

$$f(r) = e^{-\beta u(r)} - 1 \quad , \tag{6.12}$$

called the *Mayer function* after Josef Mayer. We may now write

$$Q_N(T,V) = \frac{1}{N!} \int \! d^d\!x_1 \cdots \int \! d^d\!x_N \prod_{i<j} \big(1 + f_{ij}\big) \quad . \tag{6.13}$$

A typical potential we might consider is the semi-phenomenological Lennard-Jones potential,

$$u(r) = 4\,\epsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right\} \quad . \tag{6.14}$$

This accounts for a long-distance attraction due to mutually induced electric dipole fluctuations, and a strong short-ranged repulsion, phenomenologically modelled with a r^{-12} potential, which mimics a hard core due to overlap of the atomic electron distributions. Setting $u'(r) = 0$ we obtain $r^* = 2^{1/6}\,\sigma \approx 1.12246\,\sigma$ at the minimum, where $u(r^*) = -\epsilon$. In contrast to the Boltzmann weight $e^{-\beta u(r)}$, the Mayer function $f(r)$ vanishes as $r \to \infty$, behaving as $f(r) \sim -\beta u(r)$. The Mayer function also depends on temperature. Sketches of $u(r)$ and $f(r)$ for the Lennard-Jones model are shown in fig. 6.1.

The Lennard-Jones potential is realistic for certain simple fluids, but it leads to a configuration integral which is in general impossible to evaluate. Indeed, even a potential as simple as that of the hard sphere gas is intractable in more than one space dimension. We can however make progress by deriving a series expansion for the equation of state in powers of the particle density. This is known as the *virial expansion*. As was the case when we investigated noninteracting quantum statistics, it is convenient to work in the grand canonical ensemble and to derive series expansions for the density $n(T,z)$ and the pressure $p(T,z)$ in terms of the fugacity z, then solve for $z(T,n)$ to obtain $p(T,n)$. These expansions in terms of fugacity have a nifty diagrammatic interpretation, due to Mayer.

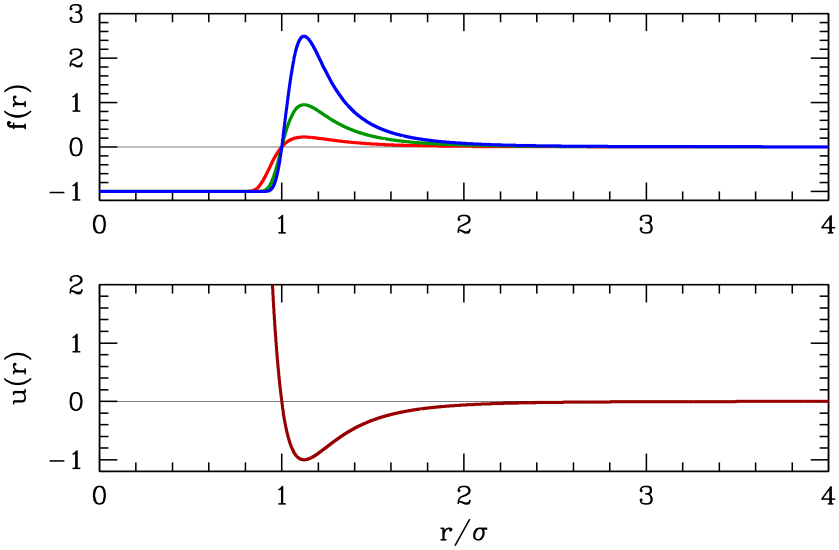

Figure 6.1: Bottom panel: Lennard-Jones potential $u(r) = 4\epsilon\left(x^{-12} - x^{-6}\right)$, with $x = r/\sigma$ and $\epsilon = 1$. Note the weak attractive tail and the strong repulsive core. Top panel: Mayer function $f(r,T) = e^{-u(r)/k_{\rm B}T} - 1$ for $k_{\rm B}T = 0.8\,\epsilon$ (blue), $k_{\rm B}T = 1.5\,\epsilon$ (green), and $k_{\rm B}T = 5\,\epsilon$ (red).

We begin by expanding the product in eqn. 6.13 as

$$\prod_{i<j}\left(1+f_{ij}\right) = 1 + \sum_{i<j} f_{ij} + \sum_{\substack{i<j\,,\,k<l\\(ij)\neq(kl)}} f_{ij}\,f_{kl} + \ldots \quad . \tag{6.15}$$

As there are $\frac{1}{2}N(N-1)$ possible pairings, there are $2^{N(N-1)/2}$ terms in the expansion of the above product. Each such term may be represented by a graph, as shown in fig. 6.2. For each such term, we draw a connection between dots representing different particles i and j if the factor f_{ij} appears in the term under consideration. The contribution for any given graph may be written as a product over contributions from each of its disconnected component clusters. For example, in the case of the term in fig. 6.2, the contribution to the configurational integral would be

$$\begin{aligned}\Delta Q = \frac{V^{N-11}}{N!}&\int\! d^dx_1\,d^dx_4\,d^dx_7\,d^dx_9\;f_{1,4}\,f_{4,7}\,f_{4,9}\,f_{7,9}\\&\times\int\! d^dx_2\,d^dx_5\,d^dx_6\;f_{2,5}\,f_{2,6}\times\int\! d^dx_3\,d^dx_{10}\;f_{3,10}\times\int\! d^dx_8\,d^dx_{11}\;f_{8,11} \quad .\end{aligned} \tag{6.16}$$

We will refer to a given product of Mayer functions which arises from this expansion as a *term*.

The particular labels we assign to each vertex of a given graph don't affect the overall value of the graph. Now a given unlabeled graph consists of a certain number of connected subgraphs. For a system with N particles, we may then write

$$N = \sum_\gamma m_\gamma\,n_\gamma \quad , \tag{6.17}$$

$$\big(f_{1,4}\, f_{4,7}\, f_{4,9}\, f_{7,9}\big)\,\big(f_{2,5}\, f_{2,6}\big)\,\big(f_{3,10}\big)\,\big(f_{8,11}\big)$$

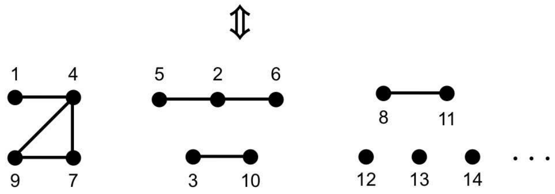

Figure 6.2: Diagrammatic interpretation of a term involving a product of eight Mayer functions.

where γ ranges over all possible connected subgraphs, and

$$\begin{aligned} m_\gamma &= \text{number of connected subgraphs of type } \gamma \text{ in the unlabeled graph} \\ n_\gamma &= \text{number of vertices in the connected subgraph } \gamma \quad . \end{aligned}$$

Note that the single vertex • counts as a connected subgraph, with $n_\bullet = 1$. We now ask: how many ways are there of assigning the N labels to the N vertices of a given unlabeled graph? One might first thing the answer is simply $N!$, however this is too big, because different assignments of the labels to the vertices may not result in a distinct graph. To see this, consider the examples in fig. 6.3. In the first example, an unlabeled graph with four vertices consists of two identical connected subgraphs. Given any assignment of labels to the vertices, then, we can simply exchange the two subgraphs and get the same term. So we should divide $N!$ by the product $\prod_\gamma m_\gamma!$. But even this is not enough, because within each connected subgraph γ there may be permutations which leave the integrand unchanged, as shown in the second and third examples in fig. 6.3. We define the *symmetry factor* s_γ as the number of permutations of the labels which leaves a given connected subgraphs γ invariant. Examples of symmetry factors are shown in fig. 6.4. Consider, for example, the third subgraph in the top row. Clearly one can rotate the figure about its horizontal symmetry axis to obtain a new labeling which represents the same term. This twofold axis is the only symmetry the diagram possesses, hence $s_\gamma = 2$. For the first diagram in the second row, one can rotate *either* of the triangles about the horizontal symmetry axis. One can also rotate the figur e in the plane by 180° so as to exchange the two triangles. Thus, there are $2 \times 2 \times 2 = 8$ symmetry operations which result in the same term, and $s_\gamma = 8$. Finally, the last subgraph in the second row consists of five vertices each of which is connected to the other four. Therefore any permutation of the labels results in the same term, and $s_\gamma = 5! = 120$. In addition to dividing by the product $\prod_\gamma m_\gamma!$, we must then also divide by $\prod_\gamma s_\gamma^{m_\gamma}$.

We can now write the partition function as

$$\begin{aligned} Z &= \frac{\lambda_T^{-Nd}}{N!} \sum_{\{m_\gamma\}} \frac{N!}{\prod m_\gamma!\, s_\gamma^{m_\gamma}} \cdot \prod_\gamma \bigg(\int \! d^d\!x_1 \cdots d^d\!x_{n_\gamma} \prod_{i<j}^{\gamma} f_{ij} \bigg)^{m_\gamma} \delta_{N\, , \sum m_\gamma n_\gamma} \\ &= \sum_{\{m_\gamma\}} \prod_\gamma \frac{1}{m_\gamma!} \bigg(\frac{V b_\gamma(T)}{\lambda_T^d} \bigg)^{m_\gamma} \delta_{N\, , \sum m_\gamma n_\gamma} \end{aligned} \tag{6.18}$$

where the product $\prod_{i<j}^{\gamma} f_{ij}$ is over all links in the subgraph γ. The final Kronecker delta enforces the

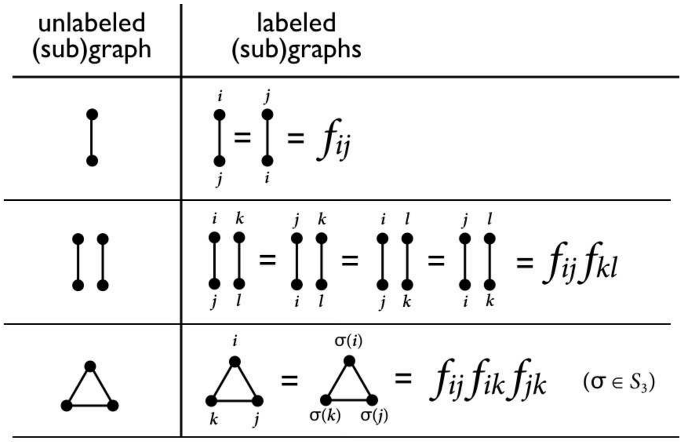

Figure 6.3: Different assignations of labels to vertices may not result in a distinct term in the expansion of the configuration integral.

constraint $N = \sum_\gamma m_\gamma \, n_\gamma$. We have defined the *dimensionless cluster integrals* b_γ as

$$b_\gamma(T) \equiv \frac{1}{s_\gamma} \int \frac{d^d\!x_1}{\lambda_T^d} \cdots \int \frac{d^d\!x_{n_\gamma - 1}}{\lambda_T^d} \prod_{i<j}^{\gamma} f_{ij} \quad , \tag{6.19}$$

where we assume the limit $V \to \infty$. Since $f_{ij} = f\big(|\boldsymbol{x}_i - \boldsymbol{x}_j|\big)$, the product $\prod_{i<j}^{\gamma} f_{ij}$ is invariant under simultaneous translation of all the coordinate vectors by any constant vector, and hence the integral over the n_γ position variables contains exactly one factor of the volume, which yields factor of V within the round brackets in the second line of eqn. 6.18. Thus, each cluster integral is *intensive*[1], scaling as V^0.

If we compute the grand partition function, then the fixed N constraint is relaxed, and we can do the sums:

$$\begin{aligned} \Xi(T,V,\mu) &= \sum_{\{m_\gamma\}} \big(e^{\beta\mu}\big)^{\sum m_\gamma n_\gamma} \prod_\gamma \frac{1}{m_\gamma!} \left(\frac{V b_\gamma(T)}{\lambda_T^d}\right)^{m_\gamma} \\ &= \prod_\gamma \sum_{m_\gamma = 0}^{\infty} \frac{1}{m_\gamma!} \left(\frac{V z^{n_\gamma} \, b_\gamma(T)}{\lambda_T^d}\right)^{m_\gamma} = \exp\!\bigg(V \lambda_T^{-d} \sum_\gamma z^{n_\gamma} \, b_\gamma\bigg) \quad , \end{aligned} \tag{6.20}$$

where $z = \exp(\beta\mu)$ is the fugacity. Thus, since $\Omega = -k_\mathrm{B} T \log \Xi$,

$$\Omega(T,V,\mu) = -\frac{V k_\mathrm{B} T}{\lambda_T^d} \sum_\gamma z^{n_\gamma} \, b_\gamma(T) \quad , \tag{6.21}$$

and we can write

$$\begin{aligned} p &= k_\mathrm{B} T \, \lambda_T^{-d} \sum_\gamma z^{n_\gamma} \, b_\gamma(T) \\ n &= \lambda_T^{-d} \sum_\gamma n_\gamma \, z^{n_\gamma} \, b_\gamma(T) \quad , \end{aligned} \tag{6.22}$$

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[1] We assume that the long-ranged behavior of $f(r) \approx -\beta u(r)$ is integrable.

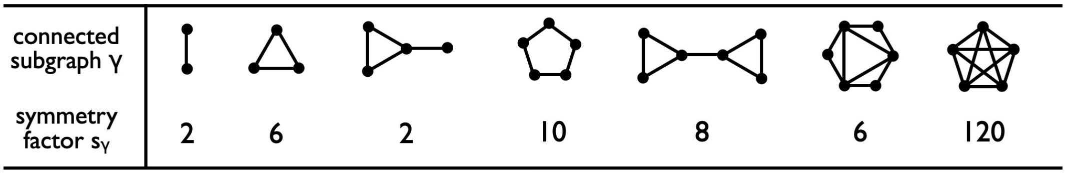

Figure 6.4: The symmetry factor s_γ for a connected subgraph γ is the number of permutations of its indices which leaves the term $\prod_{(ij)\in\gamma} f_{ij}$ invariant.

where $b_\bullet \equiv 1$. As in the case of ideal quantum gas statistical mechanics, we can systematically invert the relation $n = n(z,T)$ to obtain $z = z(n,T)$, and then insert this into the equation for $p(z,T)$ to obtain the equation of state $p = p(n,T)$. This yields the *virial expansion* of the equation of state,

$$p = nk_{\rm B}T\,\Big\{1 + B_2(T)\,n + B_3(T)\,n^2 + \ldots\Big\} \quad . \tag{6.23}$$

Lowest order expansion

We may rather easily obtain

$$B_2(T) = -\lambda_T^d\, b_{-}(T) \qquad , \qquad B_3(T) = 2\lambda_T^{2d}\, b_{\triangle}(T) \quad , \tag{6.24}$$

with

$$b_{-}(T) = \tfrac{1}{2}\!\int\!\frac{d^d\!x_1}{\lambda_T^d}\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_2|\big) = \tfrac{1}{2}\!\int\!\frac{d^d\!r}{\lambda_T^d}\, f(r) \tag{6.25}$$

and

$$\begin{aligned} b_{\wedge}(T) &= \tfrac{1}{2}\!\int\!\frac{d^d\!x_1}{\lambda_T^d}\!\int\!\frac{d^d\!x_2}{\lambda_T^d}\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_2|\big)\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_3|\big) \\ &= \tfrac{1}{2}\!\int\!\frac{d^d\!r}{\lambda_T^d}\!\int\!\frac{d^d\!r'}{\lambda_T^d}\, f(r)\, f(r') = 2\big(b_{-}\big)^2 \end{aligned} \tag{6.26}$$

and

$$\begin{aligned} b_{\triangle}(T) &= \tfrac{1}{6}\!\int\!\frac{d^d\!x_1}{\lambda_T^d}\!\int\!\frac{d^d\!x_2}{\lambda_T^d}\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_2|\big)\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_3|\big)\, f\big(|\boldsymbol{x}_2 - \boldsymbol{x}_3|\big) \\ &= \tfrac{1}{6}\!\int\!\frac{d^d\!r}{\lambda_T^d}\!\int\!\frac{d^d\!r'}{\lambda_T^d}\, f(r)\, f(r')\, f\big(|\boldsymbol{r} - \boldsymbol{r}'|\big) \quad . \end{aligned} \tag{6.27}$$

Cookbook recipe

Just follow these simple steps:

- The pressure and number density are written as sums over unlabeled connected clusters γ, *viz.*

$$\begin{aligned} p &= k_{\rm B}T\,\lambda_T^{-d}\sum_\gamma z^{n_\gamma}\,b_\gamma(T) \\ n &= \lambda_T^{-d}\sum_\gamma n_\gamma\,z^{n_\gamma}\,b_\gamma(T) \quad , \end{aligned} \tag{6.28}$$

  where $z=\exp(\beta\mu)$ is the fugacity.

- To compute the dimensionless cluster integral $b_\gamma(T)$, first draw the connected cluster γ with *unlabeled* vertices.

- Next, assign labels $1\,,\,2\,,\,\ldots\,,\,n_\gamma$ to the vertices, where n_γ is the total number of vertices in the cluster γ. It doesn't matter how you assign the labels.

- Write down the product $\prod_{i<j}^\gamma f_{ij}$. The factor f_{ij} appears in the product if there is a link in your (now labeled) cluster between sites i and j.

- The symmetry factor s_γ is the number of elements of the symmetric group S_{n_γ} which leave the product $\prod_{i<j}^\gamma f_{ij}$ invariant. The identity permutation leaves the product invariant, so $s_\gamma \geq 1$.

- The dimensionless cluster integral $b_\gamma(T)$ is given by

$$b_\gamma(T) \equiv \frac{1}{s_\gamma}\int\!\frac{d^d\!x_1}{\lambda_T^d}\cdots\int\!\frac{d^d\!x_{n_\gamma-1}}{\lambda_T^d}\prod_{i<j}^{\gamma} f_{ij} \quad , \tag{6.29}$$

  Due to translation invariance, $b_\gamma(T)\propto V^0$. One can therefore set $\boldsymbol{x}_{n_\gamma}\equiv 0$, eliminate the volume factor from the denominator, and perform the integral over the remaining $n_\gamma - 1$ coordinates.

- This procedure generates expansions for $p(T,z)$ and $n(T,z)$ in powers of the fugacity $z=\exp(\beta\mu)$. To obtain something useful like $p(T,n)$, we mut invert the equation $n=n(T,z)$ to find $z=z(T,n)$, and then substitute into the equation $p=p(T,z)$ to obtain $p=p\big(T,z(T,n)\big)=p(T,n)$. The result is the virial expansion,

$$p = nk_{\rm B}T\left\{1+B_2(T)\,n+B_3(T)\,n^2+\ldots\right\} \quad , \tag{6.30}$$

  where

$$B_k(T) = -(k-1)\,\lambda_T^{(k-1)d}\sum_{\gamma\in\Gamma_k} b_\gamma(T) \quad , \tag{6.31}$$

  with Γ_k the set of all one-particle irreducible (1PI) k-site clusters. A 1PI cluster remains connected if any of its sites and all that site's connecting links are removed.

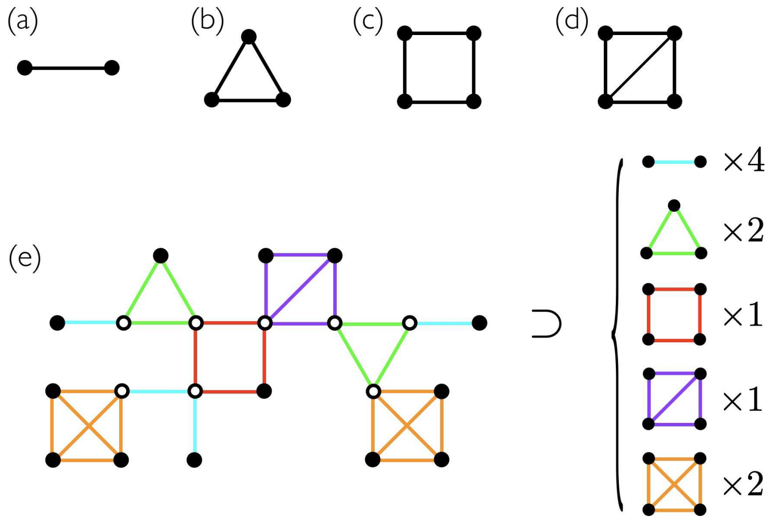

Figure 6.5: Connected *versus* irreducible clusters. Clusters (a) through (d) are *irreducible* in that they remain connected if any component site and its connecting links are removed. Cluster (e) is connected, but is *reducible*. Its integral b_γ is proportional to a product over its irreducible components, each shown in a unique color, and occurring with various multiplicities. The open circles denote *articulation points*. Removal of an articulation point and all the links connected to it results in a disconnected diagram. Removal of any of the closed circles and its associated links does not result in a disconnected diagram.

6.2.4 Examples

Hard sphere gas in three dimensions

The hard sphere potential is given by

$$u(r) = \begin{cases} \infty & \text{if } r \le a \\ 0 & \text{if } r > a \end{cases} \quad . \tag{6.32}$$

Here a is the *diameter* of the spheres. The corresponding Mayer function is then temperature independent, and given by

$$f(r) = \begin{cases} -1 & \text{if } r \le a \\ 0 & \text{if } r > a \end{cases} \quad . \tag{6.33}$$

We can change variables to obtain

$$\mathsf{b}_2(T) = \tfrac{1}{2} \int \frac{d^3\!r}{\lambda_T^3}\, f(r) = -\tfrac{2}{3}\pi a^3 \lambda_T^{-3} \quad . \tag{6.34}$$

The calculation of b_3 is more challenging. We have

$$\mathsf{b}_3 = \tfrac{1}{6} \int \frac{d^3\!\rho}{\lambda_T^3} \int \frac{d^3\!r}{\lambda_T^3}\, f(\rho)\, f(r)\, f\big(|\boldsymbol{r} - \boldsymbol{\rho}|\big) \quad . \tag{6.35}$$

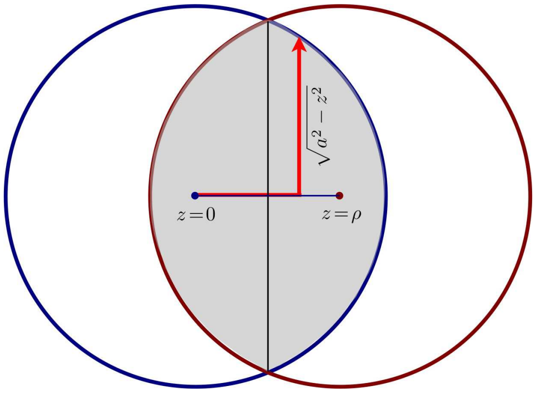

Figure 6.6: The overlap of hard sphere Mayer functions. The shaded volume is $\mathcal{V}$.

We must first compute the volume of overlap for spheres of *radius* a (recall a is the *diameter* of the constituent hard sphere particles) centered at 0 and at $\boldsymbol{\rho}$:

$$\begin{aligned}\mathcal{V} &= \int d^3\!r\, f(r)\, f\big(|\boldsymbol{r}-\boldsymbol{\rho}|\big) \\ &= 2\int\limits_{\rho/2}^{a} dz\, \pi(a^2-z^2) = \tfrac{4\pi}{3}a^3 - \pi a^2\rho + \tfrac{\pi}{12}\,\rho^3 \quad .\end{aligned} \tag{6.36}$$

We then integrate over region $|\boldsymbol{\rho}| < a$, to obtain

$$\mathsf{b}_3 = -\tfrac{1}{6}\cdot 4\pi\lambda_T^{-6}\int\limits_0^a d\rho\,\rho^2\cdot\Big\{\tfrac{4\pi}{3}a^3 - \pi a^2\rho + \tfrac{\pi}{12}\,\rho^3\Big\} = -\tfrac{5\pi^2}{36}\,a^6\lambda_T^{-6} \quad . \tag{6.37}$$

Thus, we have

$$B_2 = -\lambda_T^3\,\mathsf{b}_2(T) = \tfrac{2\pi}{3}a^3 = 4\,v_0 \qquad , \qquad B_3 = -2\lambda_T^6\,\mathsf{b}_3(T) = \tfrac{5\pi^2}{18}a^6 = 10\,v_0^2 \quad , \tag{6.38}$$

where $v_0 = \pi a^3/6$ is the hard sphere volume. The equation of state is then

$$p = nk_{\mathrm{B}}T\,\Big\{1 + B_2\,n + B_3\,n^2 + \mathcal{O}(n^3)\Big\} \quad . \tag{6.39}$$

B_4 for the three-dimensional hard sphere gas was calculated in by van Laar[2] and is given by

$$B_4 = \Big(\tfrac{2707}{70} + \tfrac{219\sqrt{2}}{35\pi} - \tfrac{4131}{70\pi}\cos^{-1}(1/3)\Big)v_0^3 \quad . \tag{6.40}$$

The coefficients beyond B_4 require numerical evaluation. The *packing fraction* of hard spheres is given by $\varphi = nv_0$. There is a first order, entropy-driven phase transition as a function of pressure at $\beta p_{\mathrm{c}} a^3 = 11.6$, *i.e.* $p_{\mathrm{c}}(T) = 11.6\,k_{\mathrm{B}}T a^{-3}$. The coexistence region (see fig. 6.7) lies between the packing fraction for

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[2] J. J. Van Laar, Koninklijke Nederlandse Akademie van Wetenschappen Amsterdam *Prov. Sec. Sci.* **1**, 273 (1899).

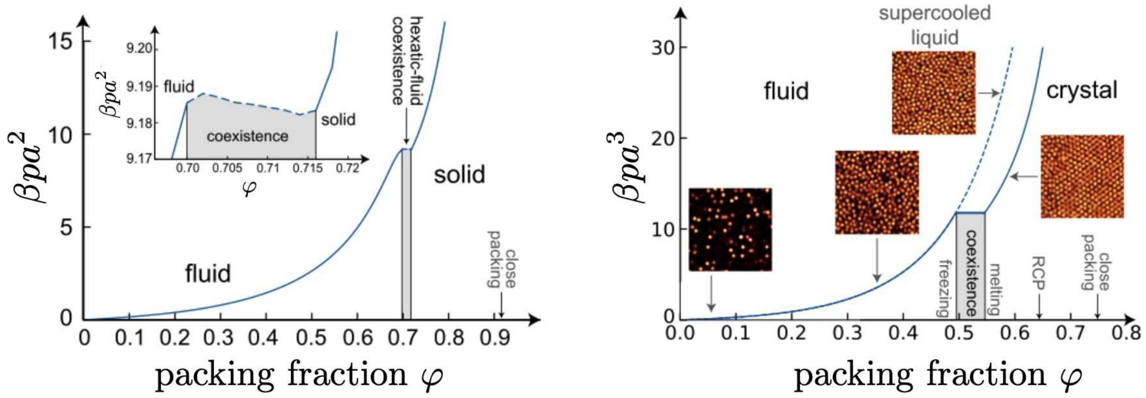

Figure 6.7: Phase diagram of the hard disk (left) and hard sphere gas (right), from G. P. Royall *et al.*, *Rev. Mod. Phys.* **96**, 045003 (2024).

freezing, $\varphi_{\mathsf{f}} = 0.492$, and the packing fraction for melting, $\varphi_{\mathsf{m}} = 0.543$. The critical volume fraction for dense random packing is $\varphi_{\mathsf{drp}} \approx 0.64$, and the maximum possible packing occurs for crystalline close packing (face-centered cubic or hexagonal close-packed structures) at $\varphi_{\mathsf{ccp}} = \frac{\pi}{3\sqrt{2}} \approx 0.740$.

For the hard disk gas in $d = 2$, one has $v_0 = \frac{1}{4}\pi a^2$ where a again is the diameter, and

$$B_2 = 2\,v_0 \qquad , \qquad B_3 = \Big(\tfrac{16}{3} - \tfrac{4\sqrt{3}}{\pi}\Big) v_0^2 \qquad , \qquad B_4 = \Big(16 - \tfrac{36\sqrt{3}}{\pi} + \tfrac{80}{\pi^2}\Big) v_0^3 \quad . \tag{6.41}$$

Weakly attractive tail

Suppose

$$u(r) = \begin{cases} \infty & \text{if } r \le a \\ -u_0(r) & \text{if } r > a \quad . \end{cases} \tag{6.42}$$

Then the corresponding Mayer function is

$$f(r) = \begin{cases} -1 & \text{if } r \le a \\ e^{\beta u_0(r)} - 1 & \text{if } r > a \quad . \end{cases} \tag{6.43}$$

Thus,

$$\mathsf{b}_2(T) = \tfrac{1}{2}\int \frac{d^3\!r}{\lambda_T^3}\, f(r) = -\tfrac{2\pi}{3} a^3 \lambda_T^{-3} + 2\pi\lambda_T^{-3} \int\limits_a^\infty \! dr\, r^2 \left[e^{\beta u_0(r)} - 1 \right] \quad . \tag{6.44}$$

Thus, the second virial coefficient is

$$B_2(T) = -\lambda_T^3\, \mathsf{b}_2(T) \approx \tfrac{2\pi}{3} a^3 - \frac{2\pi}{k_{\mathrm{B}} T} \int\limits_a^\infty \! dr\, r^2\, u_0(r) \quad , \tag{6.45}$$

where we have assumed $k_{\mathrm{B}}T \ll u_0(r)$. We see that the second virial coefficient *changes sign* at some temperature T_0, from a negative low temperature value to a positive high temperature value.

Spherical potential well

Consider an attractive spherical well potential with an infinitely repulsive core,

$$u(r) = \begin{cases} \infty & \text{if } r \le a \\ -\epsilon & \text{if } a < r < R \\ 0 & \text{if } r > R \quad . \end{cases} \tag{6.46}$$

Then the corresponding Mayer function is

$$f(r) = \begin{cases} -1 & \text{if } r \le a \\ e^{\beta\epsilon} - 1 & \text{if } a < r < R \\ 0 & \text{if } r > R \quad . \end{cases} \tag{6.47}$$

Writing $s \equiv R/a$, we have

$$\begin{aligned} B_2(T) = -\lambda_T^3 \, \mathsf{b}_2(T) &= -\tfrac{1}{2}\int d^3\!r \, f(r) \\ &= -\frac{1}{2}\left\{(-1)\cdot\tfrac{4\pi}{3}a^3 + \big(e^{\beta\epsilon}-1\big)\cdot\tfrac{4\pi}{3}a^3(s^3-1)\right\} \\ &= \tfrac{2\pi}{3}a^3\left\{1 - (s^3-1)\big(e^{\beta\epsilon}-1\big)\right\} \quad . \end{aligned} \tag{6.48}$$

To find the temperature T_0 where $B_2(T)$ changes sign, we set $B_2(T_0) = 0$ and obtain

$$k_{\mathrm{B}} T_0 = \epsilon \bigg/ \log\!\left(\frac{s^3}{s^3-1}\right) \quad . \tag{6.49}$$

Recall in our study of the thermodynamics of the Joule-Thompson effect in §2.10.7 that the throttling process is *isenthalpic*. The temperature change, when a gas is pushed (or escapes) through a porous plug from a high pressure region to a low pressure one is

$$\Delta T = \int\limits_{p_1}^{p_2} dp \left(\frac{\partial T}{\partial p}\right)_{\!H} \quad , \tag{6.50}$$

where

$$\left(\frac{\partial T}{\partial p}\right)_{\!H} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_{\!p} - V\right] \quad . \tag{6.51}$$

Appealing to the virial expansion, and working to lowest order in corrections to the ideal gas law, we have

$$p = \frac{N}{V}\, k_{\mathrm{B}} T + \frac{N^2}{V^2}\, k_{\mathrm{B}} T \, B_2(T) + \ldots \tag{6.52}$$

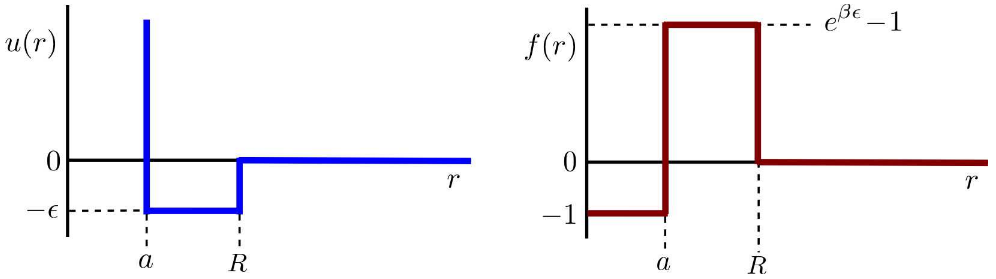

Figure 6.8: An attractive spherical well with a repulsive core $u(r)$ and its associated Mayer function $f(r)$.

and we compute $\big(\frac{\partial V}{\partial T}\big)_p$ by setting

$$0 = dp = -\frac{Nk_{\rm B}T}{V^2}\,dV + \frac{Nk_{\rm B}}{V}\,dT - \frac{2N^2}{V^3}\,k_{\rm B}T\,B_2(T)\,dV + \frac{N^2}{V^2}\,d\big(k_{\rm B}T\,B_2(T)\big) + \ldots \quad . \tag{6.53}$$

Dividing by dT, we find

$$T\bigg(\frac{\partial V}{\partial T}\bigg)_p - V = N\bigg[T\,\frac{\partial B_2}{\partial T} - B_2\bigg] \quad . \tag{6.54}$$

The temperature where $\big(\frac{\partial T}{\partial p}\big)_H$ changes sign is called the *inversion temperature* T^*. To find the inversion point, we set $T^*\,B_2'(T^*) = B_2(T^*)$, *i.e.*

$$\frac{d\log B_2}{d\log T}\bigg|_{T^*} = 1 \quad . \tag{6.55}$$

If we approximate $B_2(T) \approx A - \frac{B}{T}$, then the inversion temperature follows simply:

$$\frac{B}{T^*} = A - \frac{B}{T^*} \qquad \Longrightarrow \qquad T^* = \frac{2B}{A} \quad . \tag{6.56}$$

6.3 Coulomb Systems : Plasmas and the Electron Gas

6.3.1 Electrostatic potential

Coulomb systems are particularly interesting in statistical mechanics because of their long-ranged forces, which result in the phenomenon of *screening*. Long-ranged forces wreak havoc with the Mayer cluster expansion, since the Mayer function is no longer integrable. Thus, the virial expansion fails, and new techniques need to be applied to reveal the physics of plasmas.

The potential energy of a Coulomb system is

$$U = \tfrac{1}{2}\int d^d\!r \int d^d\!r'\,\rho(\boldsymbol{r})\,u(\boldsymbol{r}-\boldsymbol{r}')\,\rho(\boldsymbol{r}') \quad , \tag{6.57}$$

where $\rho(\boldsymbol{r})$ is the charge density and $u(\boldsymbol{r})$, which has the dimensions of (energy)/(charge)^2, satisfies

$$\nabla^2 u(\boldsymbol{r}-\boldsymbol{r}') = -4\pi\,\delta(\boldsymbol{r}-\boldsymbol{r}') \quad . \tag{6.58}$$

Thus,

$$u(\boldsymbol{r}) = \begin{cases} -2\pi\,|x-x'| & , \quad d=1 \\ -2\,\log|\boldsymbol{r}-\boldsymbol{r}'| & , \quad d=2 \\ |\boldsymbol{r}-\boldsymbol{r}'|^{-1} & , \quad d=3 \quad . \end{cases} \tag{6.59}$$

For discete particles, the charge density $\rho(\boldsymbol{r})$ is given by

$$\rho(\boldsymbol{r}) = \sum_i q_i\,\delta(\boldsymbol{r}-\boldsymbol{x}_i) \quad , \tag{6.60}$$

where q_i is the charge of the i^{th} particle. We will assume two types of charges: $q=\pm e$, with $e>0$. The electric potential is

$$\phi(\boldsymbol{r}) = \int\! d^d\!r'\; u(\boldsymbol{r}-\boldsymbol{r}')\,\rho(\boldsymbol{r}') = \sum_i q_i\,u(\boldsymbol{r}-\boldsymbol{x}_i) \quad . \tag{6.61}$$

This satisfies the Poisson equation, $\nabla^2\phi(\boldsymbol{r}) = -4\pi\rho(\boldsymbol{r})$. The total potential energy can be written as

$$U = \tfrac{1}{2}\int\! d^d\!r\;\phi(\boldsymbol{r})\,\rho(\boldsymbol{r}) = \tfrac{1}{2}\sum_i q_i\,\phi(\boldsymbol{x}_i) \quad , \tag{6.62}$$

where it is understood that we omit self-interaction terms.

6.3.2 Debye-Hückel theory

A simple derivation

For a gas of noninteracting classical particles with dispersion $\varepsilon(\boldsymbol{k})$, the number density in the GCE is given by

$$n(T,z) = z\int\!\frac{d^d k}{(2\pi)^d}\; e^{-\varepsilon(\boldsymbol{k})/k_{\rm B}T} \equiv z\lambda_T^{-d} \quad . \tag{6.63}$$

For the ballistic dispersion $\varepsilon(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$ one has $\lambda_T = \sqrt{2\pi\hbar^2/mk_{\rm B}T}$. Suppose the particles each have charge q, and are in the presence of a constant external potential ϕ. Then the internal energy of each particle is $q\phi$ and $n(T,z) = z\lambda_T^{-d}\exp(-q\phi/k_{\rm B}T)$, which is obvious after replacing $\varepsilon(\boldsymbol{k}) \to \varepsilon(\boldsymbol{k}) + q\phi$. Now let us suppose $\phi(\boldsymbol{r})$ varies smoothly in space. We then have that the *local* number density is

$$n(\boldsymbol{r}) = z\lambda_T^{-d}\exp\!\big(-q\,\phi(\boldsymbol{r})/k_{\rm B}T\big) \quad . \tag{6.64}$$

If there are two species of charges, with $q=\pm\varepsilon$, then the local charge density is

$$\rho(\boldsymbol{r}) = en_+(\boldsymbol{r}) - en_-(\boldsymbol{r}) + \rho_{\rm ext}(\boldsymbol{r}) \quad , \tag{6.65}$$

where $n_\pm(\boldsymbol{r}) = z_\pm \lambda_\pm^{-d} \exp(\mp e\phi(\boldsymbol{r})/k_\mathrm{B}T)$ and where ρ_ext is a fixed external charge density[3]. Now we close the loop and acknowledge that the total charge density $\rho(\boldsymbol{r})$ is the *source* of the electric potential $\phi(\boldsymbol{r})$, which entails Poisson's equation. We then arrive at the coupled system of equations,

$$\begin{aligned} \rho(\boldsymbol{r}) &= e z_+ \lambda_+^{-d}\, e^{-e\phi(\boldsymbol{r})/k_\mathrm{B}T} - e z_- \lambda_-^{-d}\, e^{+e\phi(\boldsymbol{r})/k_\mathrm{B}T} + \rho_\mathrm{ext}(\boldsymbol{r}) \\ \nabla^2 \phi(\boldsymbol{r}) &= -4\pi \rho(\boldsymbol{r}) \quad . \end{aligned} \tag{6.66}$$

These are the equations of Debye-Hückel theory.

Mean field approach

Formally, the grand partition function for our plasma is given by

$$\Xi(T,V,\mu_+,\mu_-) = \sum_{N_+=0}^{\infty} \sum_{N_-=0}^{\infty} \frac{(z_+\lambda_+^{-d})^{N_+}}{N_+!} \cdot \frac{(z_-\lambda_-^{-d})^{N_-}}{N_-!} \cdot \int\! d^d\!x_1 \cdots \int\! d^d\!x_N\, e^{-\beta U(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)} \quad , \tag{6.67}$$

where $z_\pm = \exp(\mu_\pm/k_\mathrm{B}T)$ are the fugacities, $\lambda_\pm = (2\pi\hbar^2/m_\pm k_\mathrm{B}T)^{1/2}$ are the thermal wavelengths, $N = N_+ + N_-$ is the total number of particles in the (N_+, N_-) sector of the double sum, and

$$U(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N) = \sum_{i<j}^{N} q_i\, q_j\, u(\boldsymbol{x}_i - \boldsymbol{x}_j) \tag{6.68}$$

is the total potential energy. The many body integral in position space is in general intractable. What's more, the Mayer function

$$f_{ij} = e^{-\beta\, q_i q_j u(r_{ij})} - 1 \tag{6.69}$$

behaves as $f_{ij} \approx -\beta\, q_i q_j u(r_{ij})$ as $r_{ij} \to \infty$, which is not integrable. Thus it would prove a tricky business indeed to attempt to derive a cluster expansion as we did in §6.2.3 for the equation of state[4].

Here we adopt a *mean field* approach, writing

$$\rho(\boldsymbol{r}) = \bar\rho(\boldsymbol{r}) + \delta\rho(\boldsymbol{r}) \qquad , \qquad \phi(\boldsymbol{r}) = \bar\phi(\boldsymbol{r}) + \delta\phi(\boldsymbol{r}) \quad . \tag{6.70}$$

We then have

$$\begin{aligned} U &= \tfrac{1}{2}\!\int\! d^d\!r\, \big[\bar\rho(\boldsymbol{r}) + \delta\rho(\boldsymbol{r})\big] \cdot \big[\bar\phi(\boldsymbol{r}) + \delta\phi(\boldsymbol{r})\big] \\ &= \tfrac{1}{2}\!\int\! d^d\!r\, \bar\phi(\boldsymbol{r})\, \bar\rho(\boldsymbol{r}) + \overbrace{\tfrac{1}{2}\!\int\! d^d\!r\, \bar\phi(\boldsymbol{r})\, \delta\rho(\boldsymbol{r}) + \tfrac{1}{2}\!\int\! d^d\!r\, \bar\rho(\boldsymbol{r})\, \delta\phi(\boldsymbol{r})}^{\text{these two terms are the same}} + \tfrac{1}{2}\!\int\! d^d\!r\, \delta\rho(\boldsymbol{r})\, \delta\phi(\boldsymbol{r}) \\ &= -\tfrac{1}{2}\!\int\! d^d\!r\, \bar\phi(\boldsymbol{r})\, \bar\rho(\boldsymbol{r}) + \int\! d^d\!r\, \bar\phi(\boldsymbol{r})\, \rho(\boldsymbol{r}) + \overbrace{\tfrac{1}{2}\!\int\! d^d\!r\, \delta\rho(\boldsymbol{r})\, \delta\phi(\boldsymbol{r})}^{\text{ignore fluctuation term}} \\ &= -U_0 + \int\! d^d\!r\, \bar\phi(\boldsymbol{r})\, \rho(\boldsymbol{r}) + (\text{flucts})^2 \quad , \end{aligned} \tag{6.71}$$

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[3] Note that there are two separate chemical potentials $\mu_\pm$ and in principle two independent thermal wavelengths $\lambda_\pm$ But there is one temperature T to rule them all.

[4] One can make progress in this direction, but it requires resumming infinite classes of diagrams.

where $U_0 \equiv \frac{1}{2}\int d^d\!r\;\bar{\phi}(\boldsymbol{r})\,\bar{\rho}(\boldsymbol{r})$, and where we have used $\delta\rho = \rho - \bar{\rho}$. Thus we have

$$\Xi = e^{U_0/k_{\rm B}T}\exp\bigg(z_+\lambda_+^{-d}\int\!d^d\!r_+\;e^{-e\,\bar{\phi}(\boldsymbol{r}_+)/k_{\rm B}T}\bigg)\exp\bigg(z_-\lambda_-^{-d}\int\!d^d\!r_-\;e^{e\,\bar{\phi}(\boldsymbol{r}_-)/k_{\rm B}T}\bigg) \tag{6.72}$$

whence

$$\Omega(T,V,\mu_+,\mu_-) = -U_0 - k_{\rm B}T z_+\lambda_+^{-d}\!\int\!d^d\!r\;\exp\bigg(-\frac{e\,\bar{\phi}(\boldsymbol{r})}{k_{\rm B}T}\bigg) - k_{\rm B}T z_-\lambda_-^{-d}\!\int\!d^d\!r\;\exp\bigg(+\frac{e\,\bar{\phi}(\boldsymbol{r})}{k_{\rm B}T}\bigg)\quad, \tag{6.73}$$

where

$$\lambda_\pm = \bigg(\frac{2\pi\hbar^2}{m_\pm k_{\rm B}T}\bigg)\qquad,\qquad z_\pm = \exp\bigg(\frac{\mu_\pm}{k_{\rm B}T}\bigg)\quad. \tag{6.74}$$

Note that since $\bar{\phi}(\boldsymbol{r}) = \int d^d\!r'\;u(\boldsymbol{r}-\boldsymbol{r}')\,\bar{\rho}(\boldsymbol{r}')$ is a linear functional of $\bar{\rho}(\boldsymbol{r})$, we have

$$\frac{\delta U_0}{\delta\bar{\phi}(\boldsymbol{r})} = \bar{\rho}(\boldsymbol{r})\quad. \tag{6.75}$$

We next demand that the free energy Ω is extremized with respect to the mean field $\bar{\phi}(\boldsymbol{r})$, *viz.*

$$0 = \frac{\delta\Omega}{\delta\bar{\phi}(\boldsymbol{r})} = -\bar{\rho}(\boldsymbol{r}) + e\,\lambda_+^{-d}\,z_+\;\exp\bigg(-\frac{e\,\bar{\phi}(\boldsymbol{r})}{k_{\rm B}T}\bigg) - e\,\lambda_-^{-d}\,z_-\;\exp\bigg(+\frac{e\,\bar{\phi}(\boldsymbol{r})}{k_{\rm B}T}\bigg)\quad. \tag{6.76}$$

This yields a mean field charge density $\bar{\rho}(\boldsymbol{r})$ which agrees with that in eqn. 6.66. At $r\to\infty$, we assume charge neutrality and $\phi(\infty) = 0$. Thus

$$\lambda_+^{-d}\,z_+ = n_+(\infty) = \lambda_-^{-d}\,z_- = n_-(\infty) \equiv n_\infty\quad, \tag{6.77}$$

where n_∞ is the ionic density of either species at infinity. Therefore,

$$\rho(\boldsymbol{r}) = -2e\,n_\infty\sinh\bigg(\frac{e\,\phi(\boldsymbol{r})}{k_{\rm B}T}\bigg)\quad, \tag{6.78}$$

where we have dropped the bars on $\bar{\phi}$ and $\bar{\rho}$ for convenience. We now invoke Poisson's equation,

$$\nabla^2\phi = 8\pi e n_\infty\sinh(\beta e\phi) - 4\pi\rho_{\rm ext}\quad, \tag{6.79}$$

where $\rho_{\rm ext}$ is an externally imposed charge density.

If $|e\phi| \ll k_{\rm B}T$, we can expand the sinh function and obtain

$$\nabla^2\phi = \kappa_{\rm D}^2\,\phi - 4\pi\rho_{\rm ext}\quad, \tag{6.80}$$

where

$$\kappa_{\rm D} = \bigg(\frac{8\pi n_\infty e^2}{k_{\rm B}T}\bigg)^{1/2}\qquad,\qquad \lambda_{\rm D} = \bigg(\frac{k_{\rm B}T}{8\pi n_\infty e^2}\bigg)^{1/2}\quad. \tag{6.81}$$

The quantity $\lambda_{\rm D}$ is known as the *Debye screening length*. Consider, for example, a point charge Q located at the origin. We then solve Poisson's equation in the weak field limit,

$$\nabla^2\phi = \kappa_{\rm D}^2\,\phi - 4\pi Q\,\delta(\boldsymbol{r})\quad. \tag{6.82}$$

Fourier transforming, we obtain

$$-\boldsymbol{q}^2\,\hat{\phi}(\boldsymbol{q}) = \kappa_{\rm D}^2\,\hat{\phi}(\boldsymbol{q}) - 4\pi Q \qquad \Rightarrow \qquad \hat{\phi}(\boldsymbol{q}) = \frac{4\pi Q}{\boldsymbol{q}^2 + \kappa_{\rm D}^2} \quad . \tag{6.83}$$

Transforming back to real space, we obtain, in three dimensions, the Yukawa potential,

$$\phi(\boldsymbol{r}) = \int\!\frac{d^3\!q}{(2\pi)^3}\,\frac{4\pi Q\, e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{\boldsymbol{q}^2 + \kappa_{\rm D}^2} = \frac{Q}{r}\, e^{-\kappa_{\rm D} r} \quad . \tag{6.84}$$

For the charge density,

$$\hat{\rho}(\boldsymbol{q}) = \frac{\boldsymbol{q}^2}{4\pi}\,\hat{\phi}(\boldsymbol{q}) = \frac{Q\,\boldsymbol{q}^2}{\boldsymbol{q}^2+\kappa_{\rm D}^2} \quad \Rightarrow \quad \rho(\boldsymbol{r}) = Q\left(\delta(\boldsymbol{r}) - \frac{\kappa_{\rm D}^2}{4\pi r}\, e^{-\kappa_{\rm D} r}\right) \quad . \tag{6.85}$$

Note that $\hat{\rho}(0) = 0$, which says there is total charge neutrality: $\int\! d^3\!r\; \rho(\boldsymbol{r}) = \hat{\rho}(0) = 0$. Thus, the plasma perfectly screens the external charge. This solution must however break down sufficiently close to $r=0$, where the assumption $e\phi(r) \ll k_{\rm B}T$ is not valid. For larger r, the Yukawa form is increasingly accurate.

For another example, consider an electrolyte held between two conducting plates, one at an electric potential (*i.e.* voltage) $\phi(x=0)=0$ and the other at potential $\phi(x=L)=V$, where $\hat{\boldsymbol{x}}$ is normal to the plane of the plates. Again assuming a weak field $e\phi \ll k_{\rm B}T$, we solve $\nabla^2\phi = \kappa_{\rm D}^2\,\phi$ and obtain

$$\phi(x) = A\, e^{\kappa_{\rm D} x} + B\, e^{-\kappa_{\rm D}\, x} \quad . \tag{6.86}$$

We fix the constants A and B by invoking the boundary conditions, which results in

$$\phi(x) = \frac{V \sinh(\kappa_{\rm D} x)}{\sinh(\kappa_{\rm D} L)} \quad . \tag{6.87}$$

Debye-Hückel theory is valid provided $n_\infty\, \lambda_{\rm D}^3 \gg 1$, so that the statistical assumption of many charges in a screening volume is justified.

6.3.3 The electron gas : Thomas-Fermi screening

Assuming $k_{\rm B}T \ll \varepsilon_{\rm F}$, thermal fluctuations are unimportant and we may assume $T=0$. In the same spirit as the Debye-Hückel approach, we assume a slowly varying mean electrostatic potential $\phi(\boldsymbol{r})$. Locally, we can write

$$\varepsilon_{\rm F} = \frac{\hbar^2 k_{\rm F}^2}{2m} - e\phi(\boldsymbol{r}) \quad . \tag{6.88}$$

Thus, the Fermi wavevector $k_{\rm F}$ is spatially varying, according to the relation

$$k_{\rm F}(\boldsymbol{r}) = \left[\frac{2m}{\hbar^2}\Big(\varepsilon_{\rm F} + e\phi(\boldsymbol{r})\Big)\right]^{1/2} \quad . \tag{6.89}$$

The local electron number density is

$$n(\boldsymbol{r}) = \frac{k_{\rm F}^3(\boldsymbol{r})}{3\pi^2} = n_\infty\bigg(1 + \frac{e\phi(\boldsymbol{r})}{\varepsilon_{\rm F}}\bigg)^{3/2} \quad . \tag{6.90}$$

In the presence of a uniform compensating positive background charge $\rho_+ = en_\infty$, Poisson's equation takes the form

$$\nabla^2\phi = 4\pi e\, n_\infty \left[\left(1 + \frac{e\phi(\boldsymbol{r})}{\varepsilon_\text{F}}\right)^{3/2} - 1\right] - 4\pi\rho_\text{ext}(\boldsymbol{r}) \quad . \tag{6.91}$$

If $|e\phi| \ll \varepsilon_\text{F}$, we may expand in powers of the ratio, obtaining

$$\nabla^2\phi = \frac{6\pi n_\infty e^2}{\varepsilon_\text{F}}\,\phi - 4\pi\rho_\text{ext} \equiv \kappa^2_\text{TF}\,\phi - 4\pi\rho_\text{ext} \quad , \tag{6.92}$$

where κ_TF is the *Thomas-Fermi wavevector,*

$$\kappa_\text{TF} = \left(\frac{6\pi n_\infty e^2}{\varepsilon_\text{F}}\right)^{1/2} \quad . \tag{6.93}$$

Thomas-Fermi theory is valid provided $n_\infty\,\lambda^3_\text{TF} \gg 1$, where $\lambda_\text{TF} = \kappa^{-1}_\text{TF}$, so that the statistical assumption of many electrons in a screening volume is justified.

One important application of Thomas-Fermi screening is to the theory of metals. In a metal, the outer, valence electrons of each atom are stripped away from the positively charged ionic core and enter into itinerant, plane-wave-like states. These states disperse with some $\varepsilon(\boldsymbol{k})$ function (that is periodic in the Brillouin zone, *i.e.* under $\boldsymbol{k} \to \boldsymbol{k} + \boldsymbol{G}$, where $\boldsymbol{G}$ is a reciprocal lattice vector), and at $T = 0$ this *energy band* is filled up to the Fermi level ε_F, as Fermi statistics dictates. (In some cases, there may be several bands at the Fermi level, as we saw in the case of yttrium.) The set of ionic cores then acts as a neutralizing positive background. In a perfect crystal, the ionic cores are distributed periodically, and the positive background is approximately uniform. A charged impurity in a metal, such as a zinc atom in a copper matrix, has a different nuclear charge and a different valency than the host. The charge of the ionic core, when valence electrons are stripped away, differs from that of the host ions, and therefore the impurity acts as a *local charge impurity*. For example, copper has an electronic configuration of $[\text{Ar}]\,3d^{10}\,4s^1$. The 4s electron forms an energy band which contains the Fermi surface. Zinc has a configuration of $[\text{Ar}]\,3d^{10}\,4s^2$, and in a Cu matrix the Zn gives up its two $4s$ electrons into the $4s$ conduction band, leaving behind a charge $+2$ ionic core. The Cu cores have charge $+1$ since each copper atom contributed only one $4s$ electron to the conduction band. The conduction band electrons neutralize the uniform positive background of the Cu ion cores. What is left is an extra $Q = +e$ nuclear charge at the Zn site, and one extra $4s$ conduction band electron. The $Q = +e$ impurity is, however, *screened* by the electrons, and at distances greater than an atomic radius the potential that a given electron sees due to the Zn core is of the Yukawa form,

$$\phi(\boldsymbol{r}) = \frac{Q}{r}\,e^{-\kappa_\text{TF} r} \quad . \tag{6.94}$$

We should take care, however, that the dispersion $\varepsilon(\boldsymbol{k})$ for the conduction band in a metal is not necessarily of the free electron form $\varepsilon(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$. To linear order in the potential, however, the change in the local electronic density is

$$\delta n(\boldsymbol{r}) = e\phi(\boldsymbol{r})\,g(\varepsilon_\text{F}) \quad , \tag{6.95}$$

where $g(\varepsilon_\text{F})$ is the density of states at the Fermi energy. Thus, in a metal, we should write

$$\nabla^2\phi = (-4\pi)(-e\,\delta n) = 4\pi e^2 g(\varepsilon_\text{F})\,\phi = \kappa^2_\text{TF}\,\phi \quad , \tag{6.96}$$

where

$$\kappa_{\text{TF}} = \sqrt{4\pi e^2\, g(\varepsilon_{\text{F}})} \quad . \tag{6.97}$$

The value of $g(\varepsilon_{\text{F}})$ will depend on the form of the dispersion. For ballistic bands with an effective mass m^*, the formula in eqn. 6.92 still applies.

The Thomas-Fermi atom

Consider an ion formed of a nucleus of charge $+Ze$ and an electron cloud of charge $-Ne$. The net ionic charge is then $(Z-N)e$. Since we will be interested in atomic scales, we can no longer assume a weak field limit and we must retain the full nonlinear screening theory, for which

$$\nabla^2\phi(\boldsymbol{r}) = 4\pi e \cdot \frac{(2m)^{3/2}}{3\pi^2\hbar^3}\Big(\varepsilon_{\text{F}} + e\phi(\boldsymbol{r})\Big)^{3/2} - 4\pi Ze\,\delta(\boldsymbol{r}) \quad . \tag{6.98}$$

We assume an isotropic solution. It is then convenient to define

$$\varepsilon_{\text{F}} + e\phi(\boldsymbol{r}) = \frac{Ze^2}{r}\cdot\chi(r/r_0) \quad , \tag{6.99}$$

where r_0 is yet to be determined. As $r\to 0$ we expect $\chi\to 1$ since the nuclear charge is then unscreened. We then have

$$\nabla^2\bigg\{\frac{Ze^2}{r}\cdot\chi(r/r_0)\bigg\} = \frac{1}{r_0^2}\,\frac{Ze^2}{r}\,\chi''(r/r_0) \quad , \tag{6.100}$$

thus we arrive at the *Thomas-Fermi equation*,

$$\chi''(t) = \frac{1}{\sqrt{t}}\,\chi^{3/2}(t) \quad , \tag{6.101}$$

with $r = t\,r_0$, provided we take

$$r_0 = \frac{\hbar^2}{2me^2}\bigg(\frac{3\pi}{4\sqrt{Z}}\bigg)^{2/3} = 0.885\,Z^{-1/3}\,a_{\text{B}} \quad , \tag{6.102}$$

where $a_{\text{B}} = \hbar^2/me^2 = 0.529\,\text{Å}$ is the Bohr radius. The TF equation is subject to the following boundary conditions:

- At short distances, the nucleus is unscreened, *i.e.* $\chi(0)=1$.
- For positive ions, with $N<Z$, there is perfect screening at the ionic boundary $R = t^*\,r_0$, where $\chi(t^*)=0$. This requires

$$\boldsymbol{E} = -\boldsymbol{\nabla}\phi = \bigg[-\frac{Ze^2}{R^2}\,\chi(R/r_0) + \frac{Ze^2}{R\,r_0}\,\chi'(R/r_0)\bigg]\,\hat{\boldsymbol{r}} = \frac{(Z-N)\,e}{R^2}\,\hat{\boldsymbol{r}} \quad . \tag{6.103}$$

This requires

$$-t^*\,\chi'(t^*) = 1 - \frac{N}{Z} \quad . \tag{6.104}$$

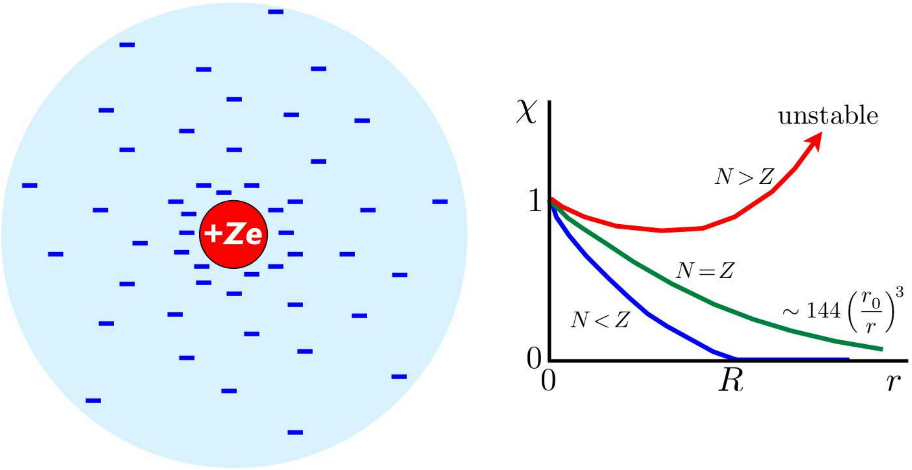

Figure 6.9: The Thomas-Fermi atom consists of a nuclear charge $+Ze$ surrounded by N electrons distributed in a cloud. The electric potential $\phi(\boldsymbol{r})$ felt by any electron at position $\boldsymbol{r}$ is screened by the electrons within this radius, resulting in a self-consistent potential $\phi(\boldsymbol{r}) = \phi_0 + (Ze^2/r)\,\chi(r/r_0)$.

For an atom, with $N = Z$, the asymptotic solution to the TF equation is a power law, and by inspection is found to be $\chi(t) \sim C\,t^{-3}$, where C is a constant. The constant follows from the TF equation, which yields $12\,C = C^{3/2}$, hence $C = 144$. Thus, a neutral TF atom has a density with a power law tail, with $\rho \sim r^{-6}$. TF ions with $N > Z$ are unstable.

6.4 The Ising Model

The simplest model of an interacting system consists of a lattice $\mathcal{L}$ of N sites, each of which hosts a spin σ_i which may be either up ($\sigma_i = +1$) or down ($\sigma_i = -1$). The Hamiltonian is

$$\hat{H} = -J \sum_{\langle ij \rangle} \sigma_i\,\sigma_j - \mu_0 H \sum_i \sigma_i \quad . \tag{6.105}$$

The energy J accounts for an interaction between sites i and j, here taken to be nearest neighbors on $\mathcal{L}$. When $J = 0$, the model describes N noninteracting spins. The geometry is then irrelevant, and as we saw in §4.8.1, for each spin we have $\langle \sigma_i \rangle = \mu_0 \tanh(\mu_0 H / k_{\rm B} T)$.

In zero external field (*i.e.* $H = 0$), energetic considerations dictate that the interaction term on each link $\langle ij \rangle$ prefers neighboring spins to be *ferromagnetically* aligned in a $|\!\uparrow\uparrow\,\rangle$ or $|\!\downarrow\downarrow\,\rangle$ configuration (*i.e.* $\sigma_i\,\sigma_j = +1$) when $J > 0$, and *antiferromagnetically* aligned in a $|\!\uparrow\downarrow\,\rangle$ or $|\!\downarrow\uparrow\,\rangle$ configuration (*i.e.* $\sigma_i\,\sigma_j = -1$) when $J < 0$.

This model is not exactly solvable in general. In one dimension, the solution is quite straightforward. In two dimensions, Onsager's solution of the model (with $H = 0$) is among the most celebrated results in statistical physics. In higher dimensions the system has been studied by numerical simulations (the Monte Carlo method), by series expansions, and by field theoretic calculations (renormalization group), but no exact solutions exist.

One important aspect of interacting systems is the emergence of *correlations*. We define the *correlation matrix* of the Ising model $C_{ij}(T,H) \equiv \langle \sigma_i \sigma_j \rangle$, which is the average of the product $\sigma_i \sigma_j$[5]. When $J=0$ the system is noninteracting, and the average of the product is the product of the averages for all $i \neq j$, *i.e.* $C_{ij}(T,H) = m_i m_j$, where $m_i \equiv \langle \sigma_i \rangle$. Thus the *connected correlator*,

$$\widetilde{C}_{ij}(T,H) \equiv \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \quad , \tag{6.106}$$

which is the average of the product *minus* the product of the averages, vanishes identically for $J=0$ whenever $i \neq j$.

The general expression for the *thermal density matrix* at temperature T is

$$\varrho(T,N,H) = \frac{\sum_{\boldsymbol{\sigma}} e^{-E(\boldsymbol{\sigma})/k_{\rm B}T} \, |\boldsymbol{\sigma}\rangle\langle\boldsymbol{\sigma}|}{\sum_{\boldsymbol{\sigma}'} e^{-E(\boldsymbol{\sigma}')/k_{\rm B}T}} = \frac{1}{Z(T,N,H)} \sum_{\boldsymbol{\sigma}} e^{-E(\boldsymbol{\sigma})/k_{\rm B}T} \, |\boldsymbol{\sigma}\rangle\langle\boldsymbol{\sigma}| \quad . \tag{6.107}$$

where

$$Z(T,N,H) = \mathsf{Tr}\, e^{-\hat{H}/k_{\rm B}T} = \sum_{\boldsymbol{\sigma}} e^{-E(\boldsymbol{\sigma})/k_{\rm B}T} \tag{6.108}$$

is the partition function. Here N is the number of sites, which is the volume $|\mathcal{L}|$ of the lattice (*i.e.* the total number of sites). Thermodynamic averages of any quantity $\mathcal{O}(\boldsymbol{\sigma})$ are computed via

$$\langle \mathcal{O} \rangle = \mathsf{Tr}\,(\mathcal{O}\varrho) = \frac{1}{Z(T,N,H)} \sum_{\boldsymbol{\sigma}} \mathcal{O}(\boldsymbol{\sigma})\, e^{-E(\boldsymbol{\sigma})/k_{\rm B}T} \quad . \tag{6.109}$$

When $J \neq 0$, there are nontrivial correlations between different sites. Consider, for example, the case $H=0$. In this case the model has what we call a $\mathbb{Z}_2$ symmetry, which means that for any spin configuration $\boldsymbol{\sigma} = \{\sigma_1, \ldots, \sigma_N\}$, the energy $E(\boldsymbol{\sigma})$ is invariant under reversing the direction of all the spins[6] . *I.e.* if $\varepsilon\boldsymbol{\sigma} \equiv \{-\sigma_1, \ldots, -\sigma_N\}$, we have $E(\varepsilon\boldsymbol{\sigma}) = E(\boldsymbol{\sigma})$ for each of the 2^N possible spin configurations $\boldsymbol{\sigma}$. This means that $\langle \sigma_i \rangle = 0$ for all i . At $T=0$ there are two ground states, $|\Uparrow\rangle \equiv |\uparrow\uparrow\uparrow\cdots\rangle$ and $|\Downarrow\rangle \equiv |\downarrow\downarrow\downarrow\cdots\rangle$, each with energy $E_0 = -N_{\rm nn} J$, where $N_{\rm nn}$ is the number of nearest neighbor links[7] on $\mathcal{L}$. The thermal density matrix as $T \to 0$ is given by $\varrho(T=0, H=0) = \frac{1}{2}|\Uparrow\rangle\langle\Uparrow| + \frac{1}{2}|\Downarrow\rangle\langle\Downarrow|$, from which we obtain $\langle \sigma_i \rangle = 0$ and $\widetilde{C}_{ij}(T=0,H=0) = 1$. If we apply an external field $H>0$, then the two ground states are no longer degenerate in energy, and $E_{\Uparrow} = -N_{\rm nn}J - N\mu_0 H$ while $E_{\Downarrow} = -N_{\rm nn}J + N\mu_0 H$. Thus, as $T \to 0$, even for very small $H>0$, in the thermodynamic limit the $|\Uparrow\rangle$ state is selected. and we obtain a very different density matrix: $\varrho(T=0,H>0) = |\Uparrow\rangle\langle\Uparrow|$. Using this density matrix, we obtain $\langle \sigma_i \rangle = +1$ and $\langle \sigma_i \sigma_j \rangle = +1$ $(i \neq j)$, hence $\widetilde{C}_{ij}(T=0,H>0) = 0$.

6.4.1 Spontaneous symmetry breaking

In quantum mechanics, the eigenstates of a Hamiltonian $\hat{H}_0$ which commutes with all the *generators* of a symmetry group G may be classified according to the *representations* of that group. Typically this

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[5] The correlation matrix $C_{ij}(T,H)$ is defined for arbitrary sites i and j. In the thermodynamic limit, it is independent of the system size N.

[6] The group $\mathbb{Z}_2$ contains two elements, $\{1,\varepsilon\}$, and the multiplication table is $1\times 1 = 1$, $1\times\varepsilon = \varepsilon\times 1 = \varepsilon$, and $\varepsilon\times\varepsilon = 1$.

[7] On a lattice with coordination number z and with periodic boundary conditions, $N_{\rm nn} = \frac{1}{2}zN$.

entails the appearance of degeneracies in the eigenspectrum, with degenerate states transforming into each other under the group operations, as we saw above. Adding a perturbation V to the Hamiltonian which breaks G down to a subgroup H will accordingly split these degeneracies, and the new multiplets of $\hat{H} = \hat{H}_0 + \hat{V}$ are characterized by representations of the lower symmetry group H.

In quantum field theory, or in the thermodynamic limit of a classical system, as a consequence of the infinite number of degrees of freedom, symmetries may be *spontaneously broken*. This means that even if the Hamiltonian H (or action S) for the field theory is invariant under a group G of symmetry transformations, the ground state or thermodynamic density matrix may not be invariant under the full symmetry group G. The presence or absence of spontaneous symmetry breaking (SSB), and its detailed manifestations, will in general depend on the couplings, or the temperature in the case of quantum statistical mechanics. SSB is usually associated with the presence of a local *order parameter* which transforms nontrivially under some group operations, and whose whose quantum statistical average vanishes in a fully symmetric phase, but takes nonzero values in symmetry-broken phase[8]. The parade example is the Ising model, $\hat{H} = -\sum_{i<j} J_{ij}\, \sigma_i\, \sigma_j$, where each $\sigma_i = \pm 1$, the subscript i indexes a physical location in space, such as a site $\boldsymbol{R}_i$ on a particular lattice. The model is explicitly $\mathbb{Z}_2$ symmetric under $\sigma_i \to \varepsilon \sigma_i$ for all i, where $\varepsilon \in \{+1, -1\}$, yet if the interaction matrix $J_{ij} = J(\boldsymbol{R}_i - \boldsymbol{R}_j)$ is short-ranged and the space dimension d is greater than one, there is a *critical temperature* $T_{\rm c}$ below which SSB sets in, and the system develops a spontaneous magnetization $m = \langle \sigma_i \rangle$. You know how in quantum mechanics, the eigenstates of a particle moving in one-dimensional double-well potential $V(x) = V(-x)$ can be classified by their parity eigenvalues P, and the lowest two energy states are respectively symmetric ($\mathsf{P} = +1$) and antisymmetric ($\mathsf{P} = -1$) , and are delocalized among both wells. For a quantum field theory, however, with (Euclidean) Lagrangian density $\mathcal{L}_{\rm E} = \frac{1}{2}(\boldsymbol{\nabla}\phi)^2 + V(\phi)$, for $d > 1$ and $T < T_{\rm c}$, the system actually picks the left or the right well, so that $\langle \phi(\boldsymbol{r}) \rangle \neq 0$. Another example is the spontaneously broken $\mathsf{O}(2)$ invariance of superfluids, where the boson annihilation operator $\psi(\boldsymbol{r})$ develops a spontaneous average $\big\langle \psi(\boldsymbol{r}) \big\rangle = \sqrt{n_0}\, e^{i\theta}$, where n_0 is the condensate density and θ the condensate phase.

But this is an obvious swindle, because, as we have seen, $\langle \sigma_i \rangle = 0$ in zero external field, due to the $\mathbb{Z}_2$ symmetry of the model. Rather, we may understand the phenomenon of spontaneous symmetry breaking in either of the following ways:

- First, rather than defining the order parameter of the Ising model, for example, to be the expected value $m = \langle \sigma_i \rangle$ of the local spin[9], consider instead the behavior of the correlator $C_{ij} = \langle \sigma_i\, \sigma_j \rangle$ in the limit $d_{ij} = |\boldsymbol{R}_i - \boldsymbol{R}_j| \to \infty$. In a disordered phase, there is no correlation between infinitely far separated spins, hence $\lim_{d_{ij} \to \infty} C_{ij} = 0$. In the ordered phase, this is no longer true, and we define the *spontaneous magnetization* m from the long distance correlator: $m^2 \equiv \lim_{d_{ij} \to \infty} \langle \sigma_i\, \sigma_j \rangle$. In this formulation, SSB is associated with the emergence of *long-ranged order* in the correlators of operators which transform nontrivially under the symmetry group.

- Second, we could impose an external field which *explicitly* breaks the symmetry, such as a Zeeman term $\hat{V} = -\mu_0 H \sum_i \sigma_i$ in the Ising model. We compute the magnetization per site $m(T, N, H) =$

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[8] While SSB is generally associated with the existence of a phase transitions, not all phase transitions involve SSB. Exceptions include the Kosterlitz-Thouless transition, and also those topological phases which have no local order parameter.

[9] We assume translational invariance, which means $\langle \sigma_i \rangle$ is independent of the site index i.

$\langle\sigma_i\rangle$ as a function of temperature T, the external field H, *and* the system volume (*i.e.* number of sites) N. The order parameter $m(T)$ in zero field is then defined as

$$m(T)=\lim_{H\to 0}\lim_{N\to\infty} m(T,N,H) \quad . \tag{6.110}$$

The order of limits here is crucially important. The thermodynamic limit $N\to\infty$ is taken first, which means that the energy difference between $|\Uparrow\rangle$ and $|\Downarrow\rangle$ diverges, being proportional to N, thus infinitely suppressing the $|\Downarrow\rangle$ state if $H>0$ (and the $|\Uparrow\rangle$ state if $H<0$). The magnitude of the order parameter will be independent on the way in which we take $H\to 0$, but its sign will depend on whether $H\to 0^+$ or $H\to 0^-$, with $\mathsf{sgn}(m)=\mathsf{sgn}(H)$. Physically, the direction in which a system orders can be decided by the presence of small stray fields or impurities.

Note that in both formulations, SSB is necessarily associated with the existence of a local operator $\mathcal{O}_i$ which is identified as the order parameter field. In the first scheme, the correlations $\langle\mathcal{O}_i\,\mathcal{O}_j\rangle$ exhibit long-ranged order in the symmetry-broken phase. In the second scheme, $\mathcal{O}_i$ is the operator to which the local external field H_i couples. We will discuss the mean field theory of phase transitions and spontaneous symmetry breaking in chapter 7.

6.4.2 Solution in $d=1$ dimension

Consider a one-dimensional ring of L sites. The ordinary canonical partition function is then

$$Z_{\mathsf{PBC}}(T,L,H)=\mathsf{Tr}\,e^{-\beta\hat{H}}=\sum_{\{\sigma_n\}}\prod_{n=1}^{L} e^{\beta J\sigma_n\sigma_{n+1}}\,e^{\beta\mu_0 H\sigma_n} \quad , \tag{6.111}$$

where $\sigma_{L+1}\equiv\sigma_1$ owing to periodic (ring) boundary conditions (PBC). We can replace the factor $e^{\beta\mu_0 H\sigma_n}$ in the above expression with $e^{\beta\mu_0 H(\sigma_n+\sigma_{n+1})/2}$, since the product over n yields the same result. We then obtain $Z=\mathsf{Tr}\,\big(R^L\big)$, where R is a 2×2 matrix with entries

$$R_{\sigma\sigma'}=e^{\beta J\sigma\sigma'}\,e^{\beta\mu_0 H(\sigma+\sigma')/2}=\begin{pmatrix} e^{\beta J}\,e^{\beta\mu_0 H} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J}\,e^{-\beta\mu_0 H}\end{pmatrix}_{\sigma\sigma'} \quad , \tag{6.112}$$

called the *transfer matrix*. Expressed in terms of the Pauli matrices, we have[10]

$$R=e^{\beta J}\cosh(\beta\mu_0 H)\,I+e^{-\beta J}X+e^{\beta J}\sinh(\beta\mu_0 H)\,Z \quad , \tag{6.113}$$

where I, X, and Z are the 2×2 identity, Pauli X, and Pauli Z matrices.

Since the trace of a matrix is invariant under a similarity transformation, we have

$$Z(T,L,H)=\lambda_+^L+\lambda_-^L \quad , \tag{6.114}$$

where $\lambda_\pm$ are the eigenvalues of R, *viz.*

$$\lambda_\pm(T,H)=e^{\beta J}\cosh(\beta\mu_0 H)\pm\sqrt{e^{2\beta J}\sinh^2(\beta\mu_0 H)+e^{-2\beta J}} \quad . \tag{6.115}$$

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[10] Take care not to confuse Pauli Z with the partition function!

When $H = 0$, we have $\lambda_+ = 2\cosh(\beta J)$ and $\lambda_- = 2\sinh(\beta J)$. In the thermodynamic limit, $L \to \infty$, and the larger λ_+^L term dominates exponentially. We them have

$$F(T, L, H) = -L k_{\rm B} T \log \lambda_+(T, H) \quad . \tag{6.116}$$

From the free energy, we can compute the magnetization,

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,L} = \frac{L\mu_0 \sinh(\beta\mu_0 H)}{\sqrt{\sinh^2(\beta\mu_0 H) + e^{-4\beta J}}} \tag{6.117}$$

and the zero field isothermal susceptibility,

$$\chi(T) = \frac{1}{L}\frac{\partial M}{\partial H}\bigg|_{H=0} = \frac{\mu_0^2}{k_{\rm B} T}\, e^{2J/k_{\rm B}T} \quad . \tag{6.118}$$

Note that in the noninteracting limit $J \to 0$ we recover the familiar result for a free spin. The effect of the interactions at low temperature is to vastly increase the susceptibility. Rather than a set of independent single spins, the system effectively behaves as if it were composed of large blocks of spins, where the block size ξ is the *correlation length*, to be derived below.

The physical properties of the system are often elucidated by evaluation of various correlation functions. Accordingly, we define $C(n) \equiv \langle \sigma_1\, \sigma_{n+1} \rangle$, where

$$\big\langle \sigma_1\, \sigma_{n+1} \big\rangle = \frac{\mathsf{Tr}\left(\sigma_1\, R_{\sigma_1\sigma_2} \cdots R_{\sigma_n\sigma_{n+1}}\, \sigma_{n+1}\, R_{\sigma_{n+1}\sigma_{n+2}} \cdots R_{\sigma_L\sigma_1}\right)}{\mathsf{Tr}\left(R^L\right)} = \frac{\mathsf{Tr}\left(Z\, R^n\, Z\, R^{L-n}\right)}{\mathsf{Tr}\left(R^L\right)} \quad , \tag{6.119}$$

with $0 < n < L$, and where Z is the Pauli matrix. To compute this ratio, we decompose R in terms of its eigenvectors, writing $R = \lambda_+\, |+\rangle\langle+| + \lambda_-\, |-\rangle\langle-|$. Then

$$C(n) = \frac{\lambda_+^L\, Z_{++} Z_{++} + \lambda_-^L\, Z_{--} Z_{--} + \left(\lambda_+^{L-n}\, \lambda_-^n + \lambda_+^n\, \lambda_-^{L-n}\right) Z_{+-} Z_{-+}}{\lambda_+^L + \lambda_-^L} \quad , \tag{6.120}$$

with $Z_{\mu\mu'} = \langle\, \mu \,|\, Z \,|\, \mu' \,\rangle$ being the matrix elements of Z in the eigenbasis of R.

Zero external field

Consider $H = 0$, where $R = e^{\beta J} + e^{-\beta J}\, X$. Then $|\pm\rangle = \frac{1}{\sqrt{2}}\big(|\uparrow\rangle \pm |\downarrow\rangle\big)$, *i.e.* the eigenvectors of R are

$$\psi_\pm = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \quad , \tag{6.121}$$

which entails $Z_{++} = Z_{--} = 0$, while $Z_{+-} = Z_{-+} = 1$. The corresponding eigenvalues are given by $\lambda_+ = 2\cosh(\beta J)$ and $\lambda_- = 2\sinh(\beta J)$. The correlation function is then found to be

$$\begin{aligned} C(n) \equiv \big\langle \sigma_1\, \sigma_{n+1} \big\rangle &= \frac{\lambda_+^{L-|n|}\, \lambda_-^{|n|} + \lambda_+^{|n|}\, \lambda_-^{L-|n|}}{\lambda_+^L + \lambda_-^L} \\ &= \frac{\tanh^{|n|}(\beta J) + \tanh^{L-|n|}(\beta J)}{1 + \tanh^L(\beta J)} \approx \tanh^{|n|}(\beta J) \quad \text{for } L \to \infty \quad . \end{aligned} \tag{6.122}$$

This result is also valid for $n < 0$, provided $|n| \le L$. We see that we may write $C(n) = e^{-|n|/\xi(T)}$, where the *correlation length* is

$$\xi(T) = \frac{1}{\log \mathrm{ctnh}(J/k_{\mathrm{B}}T)} \quad . \tag{6.123}$$

Note that $\xi(T)$ grows as $T \to 0$ as $\xi \approx \frac{1}{2}\, e^{2J/k_{\mathrm{B}}T}$.

Chain with free ends

When the chain has free ends, *i.e.* open boundary conditions (OBC), there are $(L-1)$ links and the partition function is

$$Z_{\mathsf{OBC}}(T,L,H) = \sum_{\sigma,\sigma'} \big(R^{L-1}\big)_{\sigma\sigma'} = \sum_{\sigma,\sigma'} \Big\{ \lambda_+^{L-1}\, \psi_+(\sigma)\, \psi_+(\sigma') + \lambda_-^{L-1}\, \psi_-(\sigma)\, \psi_-(\sigma') \Big\} \quad , \tag{6.124}$$

where $\psi_\pm(\sigma) = \langle\, \sigma \,|\, \pm \,\rangle$. When $H=0$, we make use of eqn. 6.121 to obtain

$$R^{L-1} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \big(2\cosh\beta J\big)^{L-1} + \frac{1}{2}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \big(2\sinh\beta J\big)^{L-1} \quad , \tag{6.125}$$

and therefore $Z_{\mathsf{OBC}} = 2^L \cosh^{L-1}(\beta J)$. There's a simple trick to obtain the zero field partition function which amounts to a change of variables. We define $\nu_n \equiv \sigma_n$ for $l \le n < L$. Thus, $\nu_1 = \sigma_1\sigma_2$, $\nu_2 = \sigma_2\sigma_3$, *etc.* Note that each ν_j takes the values ± 1. The Hamiltonian for the chain is

$$H_{\mathsf{OBC}} = -J \sum_{n=1}^{L-1} \sigma_n\, \sigma_{n+1} = -J \sum_{n=1}^{L-1} \nu_n \quad . \tag{6.126}$$

The state of the system is defined by the L Ising variables $\{\sigma_1\,,\,\nu_1\,,\,\ldots\,,\,\nu_{L-1}\}$. Note that σ_1 doesn't appear in the Hamiltonian. Thus, the interacting model is recast as $L-1$ noninteracting Ising spins, and the partition function is

$$\begin{aligned} Z_{\mathsf{OBC}}(T,L,H) = \mathrm{Tr}\, e^{-\beta H_{\mathsf{OBC}}} &= \sum_{\sigma_1}\sum_{\nu_1}\cdots\sum_{\nu_{L-1}} e^{\beta J\nu_1} e^{\beta J \nu_2} \cdots e^{\beta J \nu_{L-1}} \\ &= \sum_{\sigma_1}\Bigg(\sum_{\nu} e^{\beta J \nu}\Bigg)^{L-1} = 2^L \cosh^{L-1}(\beta J) \quad . \end{aligned} \tag{6.127}$$

6.4.3 Domain walls

We have just seen how in one dimension, the Ising model never achieves long-ranged spin order. That is, the spin-spin correlation function decays asymptotically as an exponential function of the distance with a correlation length $\xi(T)$ which is finite for all > 0. Only for $T = 0$ does the correlation length diverge. At $T = 0$, there are two ground states, $|\Uparrow\rangle$ and $|\Downarrow\rangle$. To choose between these ground states, we can specify a boundary condition at the ends of our one-dimensional chain, where we demand that the spins are up. Equivalently, we can apply a magnetic field H of order $1/L$, which vanishes in the thermodynamic limit, but which at zero temperature will select the 'all up' ground state. At finite temperature, there is always a finite probability for any consecutive pair of sites $(n, n{+}1)$ to be in a high energy state, *i.e.* either $|\uparrow\downarrow\,\rangle$ or $|\downarrow\uparrow\,\rangle$. Such a configuration is called a *domain wall*, and in one-dimensional systems domain walls live on individual links. Relative to the configurations $|\uparrow\uparrow\,\rangle$ and $|\downarrow\downarrow\,\rangle$, a domain wall costs energy $2J$. For a system with $M = xL$ domain walls, the free energy in the thermodynamic limit is

$$F = E_0 + 2MJ - k_\mathrm{B}T \log \binom{L}{M} = L \cdot \bigg\{ (2x-1)J + k_\mathrm{B}T\Big[x\log x + (1-x)\log(1-x)\Big]\bigg\} \quad , \qquad (6.128)$$

where $E_0 = -LJ$ is the ground state energy. Minimizing the free energy with respect to x, one finds $x = 1\big/\big(e^{2J/k_\mathrm{B}T} + 1\big)$, so the equilibrium concentration of domain walls is finite,meaning there can be no long-ranged spin order. In one dimension, entropy wins and there is always a thermodynamically large number of domain walls in equilibrium. And since the correlation length for $T > 0$ is finite, any boundary conditions imposed at spatial infinity will have no thermodynamic consequences since they will only be 'felt' over a finite range.

As we shall discuss in the following chapter, this consideration is true for any system with sufficiently short-ranged interactions and a discrete global symmetry. Another example is the q-state Potts model,

$$H = -J \sum_{\langle ij\rangle} \delta_{\sigma_i,\sigma_j} - h \sum_i \delta_{\sigma_i,1} \quad . \qquad (6.129)$$

Here, the spin variables σ_i take values in the set $\{1, 2, \ldots, q\}$ on each site. The equivalent of an external magnetic field in the Ising case is a field h which prefers a particular value of σ ($\sigma = 1$ in the above Hamiltonian). See the appendix in §**??** for a transfer matrix solution of the one-dimensional Potts model.

In dimensions $d > 1$ the Ising model exhibits spontaneous symmetry breaking below a critical temperature T_c. Consider the two-dimensional Ising model on a square lattice. We'll impose periodic boundary conditions on a $L \times L$ region and later imagine taking the thermodynamic limit. Each spin configuration $|\,\boldsymbol{\sigma}\,\rangle$ can be represented as an L^2-digit binary number $\boldsymbol{n}$, with $n_{\boldsymbol{r}} = 0$ if $\sigma_{\boldsymbol{r}} = -1$ and $n_{\boldsymbol{r}} = 1$ if $\sigma_{\boldsymbol{r}} = +1$. Thus $n_{\boldsymbol{r}} = \frac{1}{2}(1 + \sigma_{\boldsymbol{r}})$; $\boldsymbol{r}$ labels a plaquette. We can also label each spin configuration by a configuration of *closed loops* in the following way. Let $\varGamma$ represent a set of closed loops, represented by the thick black lines in fig. 6.10. Start with each $\sigma_{\boldsymbol{r}} = +1$ and in each plaquette $\boldsymbol{r}$ flip the spin to $\sigma_{\boldsymbol{r}} = -1$ if $\boldsymbol{r}$ is enclosed by an odd number of loops. The energy of this configuration $|\,\varGamma\,\rangle$ is given by $E_\varGamma = 2JL_\varGamma$, where $L_\varGamma$ is the total perimeter of all the individual loops comprising $\varGamma$. This is because spins lying on opposite sides of a loop contribute an energy $-J\sigma_{\boldsymbol{r}}\sigma_{\boldsymbol{r}'} = +J$ instead of $-J$, which is their energy in the fiducial configuration with all spins up[11]. Thus the partition sum may be written as

$$Z = \mathrm{Tr}\; e^{-\beta\hat{H}} = 2\sum_{\varGamma} e^{-2\beta J L_\varGamma} = 2\sum_{P=0}^{\infty} N_P\, e^{-2\beta J P} \quad . \qquad (6.130)$$

Here we have subtracted off the ground state energy from the start, setting $E_0 \equiv 0$. The second sum is over the total perimeter P, with N_P the number of loop configurations with total perimeter P. But what is N_P? For a very crude approximation, we might take $N_P \sim (z-1)^P$, where $z = 4$ is the coordination

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[11] For each $\varGamma$ there are in fact *two* corresponding spin configurations, the second obtained by flipping all the spins of the first.

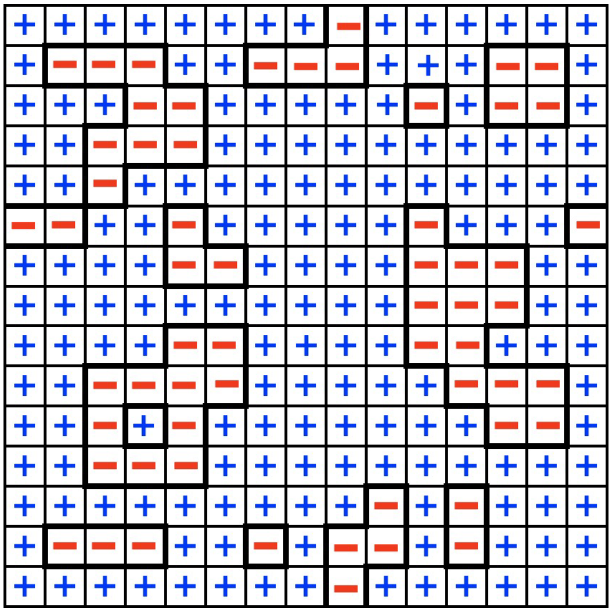

Figure 6.10: Domain walls (thick black lines) in the $d = 2$ Ising model.

number of the square lattice[12]. This is because at each step of an individual loop, if we rule out retracing our previous step, the number of possible directions in which the domain wall can be continued is $z - 1$. If we approximate $N_P \sim (z-1)^P$, then we have

$$N_P\, e^{-2\beta JP} \sim \exp\Big(\big[\log(z-1) - 2\beta J\big]P\Big) \tag{6.131}$$

and the argument of the exponential starts to increase with P when $T > T_{\rm c}$, where $k_{\rm B}T_{\rm c} = 2J/\log(z-1)$. Thus, below $T_{\rm c}$ the loops are suppressed, while above $T_{\rm c}$ the loops proliferate. This provides us a very rough picture of the phase transition and an estimate of where it occurs. For the square lattice, where $z = 4$, we obtain an estimate of $k_{\rm B}T_{\rm c}/J \approx 2/\log 3 = 1.8205$. The exact location of the phase transition, as we will derive below, is given by $k_{\rm B}T_{\rm c}/J = 2/\log(1+\sqrt{2}) = 2.2692$.

6.4.4 Kramers-Wannier duality

Consider an Ising model on a square lattice of size $L_x \times L_y$, with periodic boundary conditions, and let us set $H = 0$, so there is no explicit symmetry breaking. We label each plaquette on the square lattice by a vector $\boldsymbol{R}$ which may be taken to be the position of its center. We write the Ising model Hamiltonian as

$$\hat{H}(J_x, J_y) = -J_x \sum_{\boldsymbol{R}} \sigma_{\boldsymbol{R}}\, \sigma_{\boldsymbol{R}+\hat{\boldsymbol{x}}} - J_y \sum_{\boldsymbol{R}} \sigma_{\boldsymbol{R}}\, \sigma_{\boldsymbol{R}+\hat{\boldsymbol{y}}} \quad , \tag{6.132}$$

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[12] A better approximation for the asymptotic behavior of N_P is $N_P = CP^{-theta}(z-1)^P$, *i.e.* including a power law prefactor in addition to the exponential.

taking $J_{x,y} > 0$.[13] The ground state $|\Uparrow\rangle$ satisfies $\hat{H}\,|\Uparrow\rangle = E_0\,|\Uparrow\rangle$, where $E_0 = -N(J_x + J_y)$. Note that $|\Downarrow\rangle$ is also a ground state, obtained from $|\Uparrow\rangle$ by a $\mathbb{Z}_2$ transformation which flips all the plaquette spins and leaves the Hamiltonian invariant. Starting from $|\Uparrow\rangle$, let the state $|\,\Gamma\,\rangle$ represent the configuration where all spins within each of the individual loops comprising Γ have been flipped, as discussed in §**??** and depicted in fig. **??**. Let $n^\Gamma_{x,y}$ denote the total number of x- and y-directed links in Γ, respectively. The partition function $Z(T, J_x, J_y)$ may be written as

$$Z(T, J_x, J_y) = 2 \sum_\Gamma e^{(N-2n^\Gamma_x)\beta J_y}\, e^{(N-2n^\Gamma_y)\beta J_x} \quad , \tag{6.133}$$

since the spins on the plaquettes located at $\boldsymbol{R}$ and $\boldsymbol{R} + \hat{\boldsymbol{x}}$ on opposite sides of each $\hat{\boldsymbol{y}}$-directed link in Γ are anti-aligned, according to the construction of $|\,\Gamma\,\rangle$, thereby raising the energy by $2J_x$ relative to E_0. Similarly, the anti-aligned plaquette spins at $\boldsymbol{R}$ and $\boldsymbol{R} + \hat{\boldsymbol{y}}$ on opposite sides of an $\hat{\boldsymbol{x}}$-directed link raise the energy by $2J_y$. The overall factor of 2 is because the set of states Γ is only 2^{N-1} in number. For example, the state $|\Downarrow\rangle$ cannot be constructed according to the rules. For each state $|\,\Gamma\,\rangle$, we can obtain a unique symmetry-related state $|\,\Gamma'\,\rangle$ by applying a $\mathbb{Z}_2$ global spin flip, which completes the full set of 2^N spin configurations.

Now define the *dual* couplings $K_{x,y}$ as follows[14]:

$$e^{-2\beta J_x} = \tanh(\beta K_y) \quad , \quad e^{-2\beta J_y} = \tanh(\beta K_x) \quad \Rightarrow \quad \beta K_{x,y} = \tfrac{1}{2} \log \text{ctnh}\,(\beta J_{y,x}) \quad . \tag{6.134}$$

In the isotropic case $J_x = J_y = J$ we have $\exp(-2\beta J) = \tanh(\beta K)$ and thus for $J \to 0$ we have $K \to \infty$ while for $J \to \infty$ we have $K \to 0$. Thus, in the phase diagram of the dual couplings, *the temperature is inverted*. We now have

$$Z(T, J_x, J_y) = \big[\tanh(\beta K_y)\tanh(\beta K_x)\big]^{-N/2} \cdot 2 \sum_\Gamma \big[\tanh(\beta K_y)\big]^{n^\Gamma_x} \big[\tanh(\beta K_x)\big]^{n^\Gamma_y} \quad . \tag{6.135}$$

We next invoke the identity

$$2 \sum_\Gamma \big[\tanh(\beta K_y)\big]^{n^\Gamma_x} \big[\tanh(\beta K_x)\big]^{n^\Gamma_y} = 2^{-N}\, \mathsf{Tr} \prod_{\boldsymbol{r}} \big[1 + \tanh(\beta K_x)\, \mu_{\boldsymbol{r}} \mu_{\boldsymbol{r}+\hat{\boldsymbol{x}}}\big] \big[1 + \tanh(\beta K_y)\, \mu_{\boldsymbol{r}} \mu_{\boldsymbol{r}+\hat{\boldsymbol{y}}}\big] \quad , \tag{6.136}$$

where $\mu_{\boldsymbol{r}} \in \{+1, -1\}$ is an Ising spin located at the *site* $\boldsymbol{r}$. Note that $\boldsymbol{R}$ denotes a location of a *plaquette* while $\boldsymbol{r}$ denotes the location of a *site*. Each site can be uniquely associated with a plaquette (*e.g.*, the site in the lower left corner), so there are N sites and 2^N configurations $\{\mu_{\boldsymbol{r}}\}$. But from where do we get eqn. 6.136? Observe that the product on the RHS can be expressed as giant sum over 2^{2N} terms. Each such term has a graphical interpretation as a collection of nearest neighbor links $\langle \boldsymbol{r}\boldsymbol{r}'\rangle$, and we label each such collection by Θ. Unless each site $\boldsymbol{r}$ appears an even number of times (0, 2, or 4) in Θ, when we take the trace over the spin configurations the term will vanish. The surviving Θ configurations then correspond to the set of loop configurations $\{\Gamma\}$! We then have that

$$\mathsf{Tr} \prod_{\boldsymbol{r}} \big[1{+}\tanh(\beta K_x)\, \sigma_{\boldsymbol{r}} \sigma_{\boldsymbol{r}+\hat{\boldsymbol{x}}}\big] \big[1{+}\tanh(\beta K_y)\, \sigma_{\boldsymbol{r}} \sigma_{\boldsymbol{r}+\hat{\boldsymbol{y}}}\big] = \big[\cosh(\beta K_x)\big]^{-N} \big[\cosh(\beta K_y)\big]^{-N}\, \mathsf{Tr}\, e^{-\beta \hat{H}^{\mathsf{D}}(K_x, K_y)} \quad , \tag{6.137}$$

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[13] Thus we assume the model is ferromagnetic. If $J_{x,y} < 0$ the model is antiferromagnetic, which we may rewrite as a ferromagnet defining $\sigma'_{\boldsymbol{R}} = -\sigma_{\boldsymbol{R}}$ on one sublattice (*i.e.* the white squares on a chessboard) and retaining $\sigma'_{\boldsymbol{R}} = -\sigma_{\boldsymbol{R}}$ on the other, effectively reversing the signs of $J_{x,y}$.

[14] Note that if $\exp(-2y) = \tanh x$ then $\exp(-2x) = \tanh y$.

where

$$\hat{H}^{\mathsf{D}}(X_x, X_y) = -K_x \sum_{\boldsymbol{r}} \sigma_{\boldsymbol{r}}\, \sigma_{\boldsymbol{r}+\hat{\boldsymbol{x}}} - K_y \sum_{\boldsymbol{r}} \sigma_{\boldsymbol{r}}\, \sigma_{\boldsymbol{r}+\hat{\boldsymbol{y}}} \quad . \tag{6.138}$$

is the *dual Hamiltonian* defined on the *dual lattice* of sites. The plaquette lattice is *dual* to the site lattice (and vice versa). Therefore we have

$$Z(T, J_x, J_y) = \big[\sinh(2\beta K_x)\sinh(2\beta K_y)\big]^{-N/2}\, Z(T, K_x, K_y) \quad . \tag{6.139}$$

This establishes a *duality relation* between the original and inverted temperature regions. At the critical point, the system must be *self-dual*, *i.e.* $J_{x,y} = K_{x,y}$, hence we have the relation

$$\sinh(2\beta_{\rm c} J_x)\sinh(2\beta_{\rm c} J_y) = 1 \quad . \tag{6.140}$$

This equation defines a critical surface $T_{\rm c}(J_x, J_y)$. If $J_x = J_y = J$, we have

$$k_{\rm B} T_{\rm c} = \frac{2J}{\sinh^{-1}(1)} = \frac{2J}{\log\big(1+\sqrt{2}\big)} = 2.2692\, J \quad . \tag{6.141}$$

Thus we have derived the exact critical temperature for the two-dimensional square lattice Ising model.