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Chapter 6

Classical Interacting Systems

6.1 References

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6.2 Ising Model

6.2.1 Hamiltonian

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

$$\hat{H} = -J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j - \mu_0 H \sum_i \sigma_i \quad . \tag{6.1}$$

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 $\langle \sigma_i \rangle = \mu_0 \tanh(\mu_0 H / k_{\mathrm{B}} T)$.

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 $\sigma_i \, \sigma_j$[1]. 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*,

$$\widetilde{C}_{ij}(T,H) \equiv \langle \sigma_i \, \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle \quad , \tag{6.2}$$

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

When $J \neq 0$, however, 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. *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 $E_0 = -N_{\mathrm{links}} J$, where N_{links} is the number of nearest neighbor links on $\mathcal{L}$[2]. The (ergodic) zero temperature density matrix is $\rho_0 = \frac{1}{2} |\Uparrow\rangle\langle\Uparrow| + \frac{1}{2} |\Downarrow\rangle\langle\Downarrow|$, and we compute averages by $\langle \mathcal{O} \rangle = \mathsf{Tr}(\rho_0 \, \mathcal{O})$. Thus $\langle \sigma_i \rangle = 0$ and $\widetilde{C}_{ij}(T, H = 0) = 1$.

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[1] 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.

[2] On a lattice with coordination number z and with periodic boundary conditions, $N_{\mathrm{links}} = \frac{1}{2} z N$.

6.2.2 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 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[3]. 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_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 $\mathcal{L}_\mathrm{E} = \frac{1}{2}(\boldsymbol{\nabla}\phi)^2 + V(\phi)$, for $d > 1$ and $T < T_\mathrm{c}$, 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[4], 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

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[3] 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.

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

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 $m(T, N, H) = \langle \sigma_i \rangle$ 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

  $$m(T) = \lim_{h\to 0} \lim_{N\to\infty} m(T, N, H) \quad . \tag{6.3}$$

  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 $\mathrm{sgn}\,(m) = \mathrm{sgn}\,(H)$. 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.

6.2.3 Ising model in one dimension

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

$$Z_{\mathsf{PBC}}(T, L, H) = \mathsf{Tr}\; e^{-\beta \hat{H}} = \sum_{\{\sigma_n\}} \prod_{n=1}^{L} e^{\beta J \sigma_n \sigma_{n+1}} \, e^{\beta \mu_0 H \sigma_n} \quad , \tag{6.4}$$

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

$$R_{\sigma\sigma'} = e^{\beta J \sigma\sigma'} \, e^{\beta\mu_0 H(\sigma+\sigma')/2} = \begin{pmatrix} e^{\beta J}\, e^{\beta\mu_0 H} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J}\, e^{-\beta\mu_0 H} \end{pmatrix}_{\sigma\sigma'} \quad , \tag{6.5}$$

called the *transfer matrix*. Expressed in terms of the Pauli matrices, we have[5]

$$R = e^{\beta J} \cosh(\beta\mu_0 H)\, I + e^{-\beta J}\, X + e^{\beta J} \sinh(\beta\mu_0 H)\, Z \quad , \tag{6.6}$$

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

$$Z(T, L, H) = \lambda_+^L + \lambda_-^L \quad , \tag{6.7}$$

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

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

$$\lambda_\pm(T,H) = e^{\beta J} \cosh(\beta\mu_0 H) \pm \sqrt{e^{2\beta J} \sinh^2(\beta\mu_0 H) + e^{-2\beta J}} \quad . \tag{6.8}$$

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

$$F(T,L,H) = -L k_\mathrm{B} T \ln \lambda_+(T,H) \quad . \tag{6.9}$$

From the free energy, we can compute the magnetization,

$$M = -\bigg(\frac{\partial F}{\partial H}\bigg)_{T,L} = \frac{L\mu_0 \sinh(\beta\mu_0 H)}{\sqrt{\sinh^2(\beta\mu_0 H) + e^{-4\beta J}}} \tag{6.10}$$

and the zero field isothermal susceptibility,

$$\chi(T) = \frac{1}{L} \frac{\partial M}{\partial H}\bigg|_{H=0} = \frac{\mu_0^2}{k_\mathrm{B} T}\, e^{2J/k_\mathrm{B} T} \quad . \tag{6.11}$$

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

$$\big\langle \sigma_1\, \sigma_{n+1} \big\rangle = \frac{\mathsf{Tr}\,\big(\sigma_1\, R_{\sigma_1 \sigma_2} \cdots R_{\sigma_n \sigma_{n+1}}\, \sigma_{n+1}\, R_{\sigma_{n+1}\sigma_{n+2}} \cdots R_{\sigma_L \sigma_1}\big)}{\mathsf{Tr}\,\big(R^L\big)} = \frac{\mathsf{Tr}\,\big(Z\, R^n\, Z\, R^{L-n}\big)}{\mathsf{Tr}\,\big(R^L\big)} \quad , \tag{6.12}$$

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

$$C(n) = \frac{\lambda_+^L\, Z_{++} Z_{++} + \lambda_-^L\, Z_{--} Z_{--} + \big(\lambda_+^{L-n}\, \lambda_-^n + \lambda_+^n\, \lambda_-^{L-n}\big)\, Z_{+-} Z_{-+}}{\lambda_+^L + \lambda_-^L} \quad , \tag{6.13}$$

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

$$\psi_\pm = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} \quad , \tag{6.14}$$

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

$$\begin{aligned} C(n) \equiv \big\langle \sigma_1\, \sigma_{n+1} \big\rangle &= \frac{\lambda_+^{L-|n|}\, \lambda_-^{|n|} + \lambda_+^{|n|}\, \lambda_-^{L-|n|}}{\lambda_+^L + \lambda_-^L} \\ &= \frac{\tanh^{|n|}(\beta J) + \tanh^{L-|n|}(\beta J)}{1 + \tanh^L(\beta J)} \approx \tanh^{|n|}(\beta J) \quad \text{for } L \to \infty \quad . \end{aligned} \tag{6.15}$$

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

$$\xi(T) = \frac{1}{\ln \text{ctnh}(J/k_{\rm B}T)} \quad . \tag{6.16}$$

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

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

$$Z_{\sf OBC}(T, L, H) = \sum_{\sigma,\sigma'} \big(R^{L-1}\big)_{\sigma\sigma'} = \sum_{\sigma,\sigma'} \Big\{ \lambda_+^{L-1}\, \psi_+(\sigma)\, \psi_+(\sigma') + \lambda_-^{L-1}\, \psi_-(\sigma)\, \psi_-(\sigma') \Big\} \quad , \tag{6.17}$$

where $\psi_\pm(\sigma) = \langle\, \sigma \,|\, \pm \,\rangle$. When $H = 0$, we make use of eqn. 6.14 to obtain

$$R^{L-1} = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \big(2\cosh\beta J\big)^{L-1} + \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \big(2\sinh\beta J\big)^{L-1} \quad , \tag{6.18}$$

and therefore $Z_{\sf OBC} = 2^L \cosh^{L-1}(\beta J)$. 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

$$H_{\sf OBC} = -J \sum_{n=1}^{L-1} \sigma_n\, \sigma_{n+1} = -J \sum_{n=1}^{L-1} \nu_n \quad . \tag{6.19}$$

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

$$\begin{aligned} Z_{\sf OBC}(T, L, H) = \text{Tr}\, e^{-\beta H_{\sf OBC}} &= \sum_{\sigma_1} \sum_{\nu_1} \cdots \sum_{\nu_{L-1}} e^{\beta J \nu_1} e^{\beta J \nu_2} \cdots e^{\beta J \nu_{L-1}} \\ &= \sum_{\sigma_1} \bigg(\sum_{\nu} e^{\beta J \nu} \bigg)^{L-1} = 2^L \cosh^{L-1}(\beta J) \quad . \end{aligned} \tag{6.20}$$

6.2.4 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

$$F = 2MJ - k_{\rm B}T \ln \binom{L}{M} = L \cdot \bigg\{ 2Jx + k_{\rm B}T \Big[x \ln x + (1-x) \ln(1-x) \Big] \bigg\} \quad , \tag{6.21}$$

Minimizing the free energy with respect to x, one finds $x = 1\big/\big(e^{2J/k_{\rm B}T} + 1\big)$, 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,

$$H = -J \sum_{\langle ij \rangle} \delta_{\sigma_i, \sigma_j} - h \sum_i \delta_{\sigma_i, 1} \quad . \tag{6.22}$$

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 §6.6 for a transfer matrix solution of the one-dimensional Potts model.

6.2.5 Ising model in two dimensions : Peierls' argument

What about higher dimensions? A nifty argument due to R. Peierls shows that there will be a finite temperature phase transition for the Ising model on the square lattice[6]. Consider the Ising model, in zero magnetic field, on a $N = L_x \times L_y$ square lattice, with $L_{x,y} \to \infty$ in the thermodynamic limit. Along the perimeter of the system we impose the boundary condition $\sigma_i = +1$. Any configuration of the spins may then be represented uniquely in the following manner. Start with a configuration in which all spins are up. Next, draw a set of closed loops on the lattice. By definition, the loops cannot share any links along their boundaries, *i.e.* each link on the lattice is associated with at most one such loop. Now flip all the spins inside each loop from up to down. Identify each such loop configuration with a label $\varGamma$. The

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[6] Here we modify slightly the discussion in chapter 5 of the book by L. Peliti.

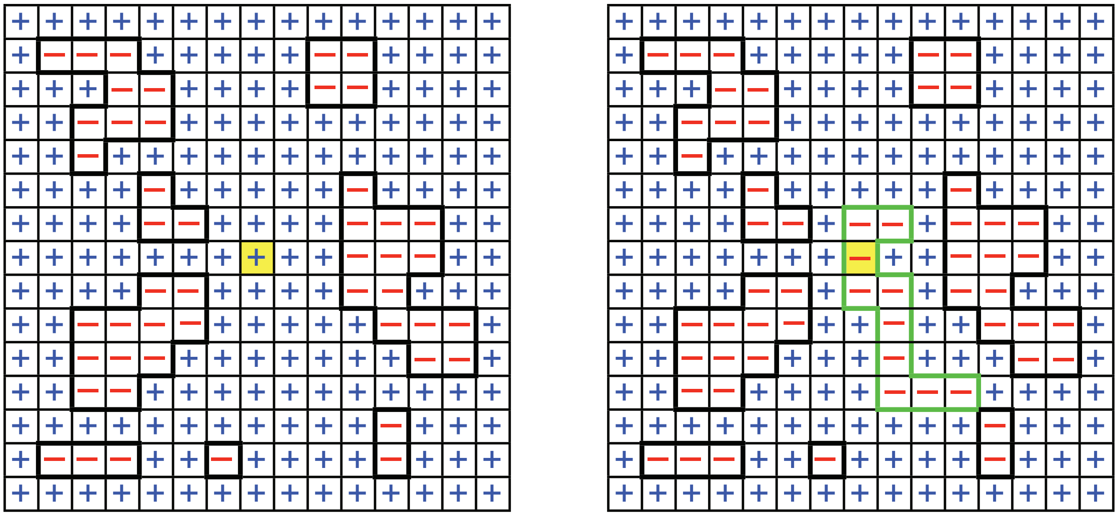

Figure 6.1: Clusters and boundaries for the square lattice Ising model. Left panel: a configuration $\varGamma$ where the central spin is up. Right panel: a configuration $C_\gamma \circ \varGamma$ where the interior spins of a new loop γ containing the central spin have been flipped.

partition function is

$$Z = \mathsf{Tr}\, e^{-\beta \hat{H}} = \sum_{\varGamma} e^{-2\beta J L_{\varGamma}} \quad , \tag{6.23}$$

where $L_\varGamma$ is the total perimeter of the loop configuration $\varGamma$. The domain walls are now loops, rather than individual links, but as in the one-dimensional case, each link of each domain wall contributes an energy $+2J$ relative to the ground state.

Now we wish to compute the average magnetization of the central site (assume $L_{x,y}$ are both odd, so there is a unique central site). This is given by the difference $P_+(0) - P_-(0)$, where $P_\mu(0) = \big\langle \delta_{\sigma_0\, ,\, \mu} \big\rangle$ is the probability that the central spin has spin polarization μ. If $P_+(0) > P_-(0)$, then the magnetization per site $m = P_+(0) - P_-(0)$ is finite in the thermodynamic limit, and the system is ordered. Clearly

$$P_+(0) = \frac{1}{Z} \sum_{\varGamma \in \Sigma_+} e^{-2\beta J L_\varGamma} \quad , \tag{6.24}$$

where the restriction on the sum indicates that only those configurations where the central spin is up ($\sigma_0 = +1$) are to be included. (see fig. 6.1a). Similarly,

$$P_-(0) = \frac{1}{Z} \sum_{\widetilde{\varGamma} \in \Sigma_-} e^{-2\beta J L_{\widetilde{\varGamma}}} \quad , \tag{6.25}$$

where only configurations in which $\sigma_0 = -1$ are included in the sum, where $\Sigma_\pm \equiv \Big\{ \varGamma \,\big|\, \sigma_0 = \pm \Big\}$. That is, $\Sigma_+ (\varSigma_-)$ is the set of configurations $\varGamma$ in which the central spin is always up (down). Consider now the construction in fig. 6.1b. Any loop configuration $\widetilde{\varGamma} \in \Sigma_-$ may be associated with a unique loop configuration $\varGamma \in \Sigma_+$ by reversing all the spins within the loop of $\widetilde{\varGamma}$ which contains the origin. Note that the map from $\widetilde{\varGamma}$ to $\varGamma$ is many-to-one. That is, we can write $\widetilde{\varGamma} = C_\gamma \circ \varGamma$, where C_γ overturns the spins within the loop γ, with the conditions that (i) γ contains the origin, and (ii) none of the links in the perimeter of γ coincide with any of the links from the constituent loops of $\varGamma$. Let us denote this set of loops as $\Upsilon_\varGamma$:

$$\Upsilon_\varGamma = \Big\{ \gamma \,:\, 0 \in \text{int}(\gamma) \text{ and } \gamma \cap \varGamma = \emptyset \Big\} \quad . \tag{6.26}$$

Then

$$m = P_+(0) - P_-(0) = \frac{1}{Z} \sum_{\varGamma \in \Sigma_+} e^{-2\beta J L_\varGamma} \bigg(1 - \sum_{\gamma \in \Upsilon_\varGamma} e^{-2\beta J L_\gamma} \bigg) \quad . \tag{6.27}$$

If we can prove that $\sum_{\gamma \in \Upsilon_\varGamma} e^{-2\beta J L_\gamma} < 1$, then we will have established that $m > 0$. Let us ask: how many loops γ are there in $\Upsilon_\varGamma$ with perimeter L? We cannot answer this question exactly, but we can derive a rigorous upper bound for this number, which, following Peliti, we call $g(L)$. We claim that

$$g(L) < \frac{2}{3L} \cdot 3^L \cdot \left(\frac{L}{4} \right)^2 = \frac{L}{24} \cdot 3^L \quad . \tag{6.28}$$

To establish this bound, consider any site on such a loop γ. Initially we have 4 possible directions to proceed to the next site, but thereafter there are only 3 possibilities for each subsequent step, since the loop cannot run into itself. This gives $4 \cdot 3^{L-1}$ possibilities. But we are clearly overcounting, since any point on the loop could have been chosen as the initial point, and moreover we could have started by proceeding either clockwise or counterclockwise. So we are justified in dividing this by $2L$. We are still overcounting, because we have not accounted for the constraint that γ is a closed loop, nor that $\gamma \cap \varGamma = \emptyset$. We won't bother trying to improve our estimate to account for these constraints. However, we are clearly undercounting due to the fact that a given loop can be translated in space so long as the origin remains within it. To account for this, we multiply by the area of a square of side length $L/4$, which is the maximum area that can be enclosed by a loop of perimeter L. We therefore arrive at eqn. 6.28. Finally, we note that the smallest possible value of L is $L = 4$, corresponding to a square enclosing the central site alone. Therefore

$$\sum_{\gamma \in \Upsilon_\varGamma} e^{-2\beta J L_\gamma} < \frac{1}{12} \sum_{k=2}^{\infty} k \cdot \big(3\, e^{-2\beta J} \big)^{2k} = \frac{x^4\,(2 - x^2)}{12\,(1 - x^2)^2} \equiv r \quad , \tag{6.29}$$

where $x = 3\, e^{-2\beta J}$. Note that we have accounted for the fact that the perimeter L of each loop γ must be an even integer. The sum is smaller than unity provided $x < x_0 = 0.869756\ldots$, hence the system is ordered provided

$$\frac{k_\text{B} T}{J} < \frac{2}{\ln(3/x_0)} = 1.61531 \quad , \tag{6.30}$$

which establishes a rigorous lower bound for the critical temperature. The exact result is $k_\text{B} T_\text{c}/J = 2/\sinh^{-1}(1) = 2.26918\ldots$ Peierls' argument has been generalized to higher dimensional lattices as well[7].

With a little more work we can derive a bound for the magnetization. We have shown that

$$P_-(0) = \frac{1}{Z} \sum_{\varGamma \in \Sigma_+} e^{-2\beta J L_\varGamma} \sum_{\gamma \in \Upsilon_\varGamma} e^{-2\beta J L_\gamma} < r \cdot \frac{1}{Z} \sum_{\varGamma \in \Sigma_+} e^{-2\beta J L_\varGamma} = r\, P_+(0) \quad . \tag{6.31}$$

---

[7] See. *e.g.* J. L. Lebowitz and A. E. Mazel, *J. Stat. Phys.* **90**, 1051 (1998).

Thus,

$$1 = P_+(0) + P_-(0) < (1+r)\, P_+(0) \tag{6.32}$$

and therefore

$$m = P_+(0) - P_-(0) > (1-r)\, P_+(0) > \frac{1-r}{1+r} \quad , \tag{6.33}$$

where $r(T)$ is given in eqn. 6.29.

6.2.6 Importance of interaction range

We showed that the one-dimensional Ising model has no finite temperature phase transition, and is disordered at any finite temperature T, but in two dimensions on the square lattice there is a finite critical temperature T_c below which there is long-ranged order. Consider now the construction depicted in fig. 6.2, where the sites of a two-dimensional square lattice are mapped onto those of a linear chain[8]. Clearly we can elicit a one-to-one mapping between the sites of a two-dimensional square lattice and those of a one-dimensional chain. That is, the two-dimensional square lattice Ising model may be written as a one-dimensional Ising model, *i.e.*

$$\hat{H} = -J \overset{\text{square lattice}}{\sum_{\langle ij \rangle}} \sigma_i\, \sigma_j = -\overset{\text{linear chain}}{\sum_{n,n'}} J_{nn'}\, \sigma_n\, \sigma_{n'} \quad . \tag{6.34}$$

How can this be consistent with the results we have just proven?

The fly in the ointment here is that the interaction along the chain $J_{n,n'}$ is long-ranged. This is apparent from inspecting the site labels in fig. 6.2. Note that site $n = 15$ is linked to sites $n' = 14$ and $n' = 16$, but also to sites $n' = -6$ and $n' = -28$. With each turn of the concentric spirals in the figure, the ranged of the interaction increases. To complicate matters further, the interactions are no longer translationally invariant, *i.e.* $J_{nn'} \neq J(n-n')$. But it is the long-ranged nature of the interactions on our contrived one-dimensional chain which spoils our previous energy-entropy argument, because now the domain walls themselves interact via a long-ranged potential. Consider for example the linear chain with $J_{n,n'} = J\,|n-n'|^{-\alpha}$, where $\alpha > 0$. Let us compute the energy of a domain wall configuration where $\sigma_n = +1$ if $n > 0$ and $\sigma_n = -1$ if $n \leq 0$. The domain wall energy is then

$$\Delta = \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} \frac{2J}{|m+n|^{\alpha}} \quad . \tag{6.35}$$

Here we have written one of the sums in terms of $m = -n'$. For asymptotically large m and n, we can write $\boldsymbol{R} = (m,n)$ and we obtain an integral over the upper right quadrant of the plane:

$$\int\limits_1^{\infty} \! dR\, R \int\limits_0^{\pi/2} \! d\phi\, \frac{2J}{R^{\alpha}\,(\cos\phi + \sin\phi)^{\alpha}} = 2^{-\alpha/2} \int\limits_{-\pi/4}^{\pi/4} \frac{d\phi}{\cos^{\alpha}\!\phi} \int\limits_1^{\infty} \frac{dR}{R^{\alpha-1}} \quad . \tag{6.36}$$

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[8] A corresponding mapping can be found between a cubic lattice and the linear chain as well.

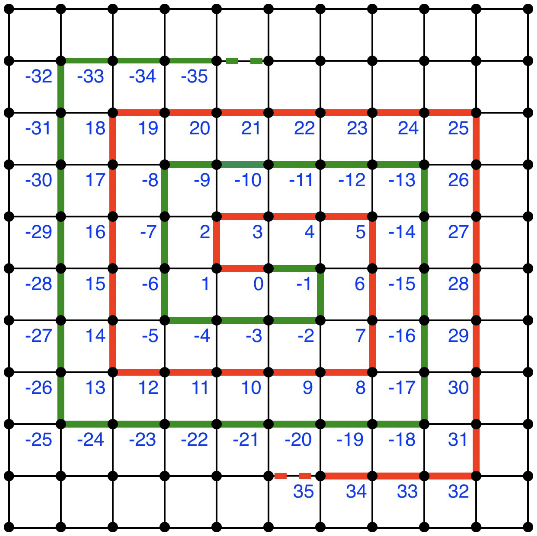


Figure 6.2: A two-dimensional square lattice mapped onto a one-dimensional chain.

The ϕ integral is convergent, but the R integral diverges for $\alpha \leq 2$. For a finite system, the upper bound on the R integral becomes the system size L. For $\alpha > 2$ the domain wall energy is finite in the thermodynamic limit $L \to \infty$. In this case, entropy again wins. *I.e.* the entropy associated with a single domain wall is $k_{\text{B}} \ln L$, and therefore $F = E - k_{\text{B}} T$ is always lowered by having a finite density of domain walls. For $\alpha < 2$, the energy of a single domain wall scales as $L^{2-\alpha}$. It was first proven by F. J. Dyson in 1969 that this model has a finite temperature phase transition provided $1 < \alpha < 2$. There is no transition for $\alpha < 1$ or $\alpha > 2$. The case $\alpha = 2$ is special, and is discussed as a special case in the beautiful renormalization group analysis by J. M. Kosterlitz in *Phys. Rev. Lett.* **37**, 1577 (1976).

6.2.7 High temperature expansion

Consider once again the ferromagnetic Ising model in zero field ($H = 0$), but on an arbitrary lattice. The partition function is

$$Z = \text{Tr}\; e^{\beta J \sum_{\langle ij \rangle} \sigma_i \sigma_j} = \big(\cosh \beta J\big)^{N_{\text{links}}}\, \text{Tr} \left\{ \prod_{\langle ij \rangle} \big(1 + x\, \sigma_i \sigma_j\big) \right\} \quad , \tag{6.37}$$

where $x = \tanh \beta J$ and N_{links} is the number of links (*i.e.* bonds). For regular lattices, $N_{\text{links}} = \frac{1}{2} z N$, where N is the number of lattice sites and z is the lattice coordination number, *i.e.* the number of nearest neighbors for each site. We have used

$$e^{\beta J \sigma \sigma'} = \cosh \beta J \cdot \Big\{ 1 + \sigma \sigma' \, \tanh \beta J \Big\} = \begin{cases} e^{+\beta J} & \text{if } \sigma\sigma' = +1 \\ e^{-\beta J} & \text{if } \sigma\sigma' = -1 \end{cases} \quad . \tag{6.38}$$

We expand eqn. 6.37 in powers of x, resulting in a sum of $2^{N_{\text{links}}}$ terms, each of which can be represented graphically in terms of so-called *lattice animals*. A lattice animal is a distinct (including reflections and

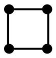
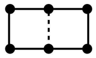
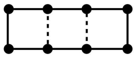
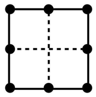
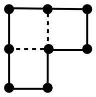
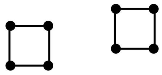
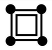
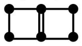
diagram Γ	L_Γ	g_Γ	remarks
	0	1	empty lattice
	4	N	N translations
	6	$2N$	2 rotations, N translations
	8	$2N$	2 rotations, N translations
	8	N	N translations
	8	$4N$	4 rotations, N translations
	8	$\frac{1}{2}(N^2-5N)$	exclude five invalid diagrams; halve for equivalent squares  (1)  (4)

Figure 6.3: HTE diagrams on the square lattice and their multiplicities.

rotations) arrangement of adjacent plaquettes on a lattice. In order that the trace not vanish, only such configurations and their compositions are permitted. This is because each σ_i for every given site i must occur an even number of times in order for a given term in the sum not to vanish. For all such terms, the trace is 2^N. Let $\{\Gamma\}$ represent a collection of lattice animals, and g_Γ the multiplicity of Γ. Then

$$Z = 2^N \big(\cosh\beta J\big)^{N_{\text{links}}} \sum_\Gamma g_\Gamma \, \big(\tanh\beta J\big)^{L_\Gamma} \quad , \tag{6.39}$$

where L_Γ is the total number of sites in the diagram Γ, and g_Γ is the multiplicity of Γ. Since x vanishes as $T \to \infty$, this procedure is known as the *high temperature expansion* (HTE).

For the square lattice, he enumeration of all lattice animals with up to order eight is given in fig. 6.3. For the diagram represented as a single elementary plaquette, there are N possible locations for the lower left vertex. For the 2×1 plaquette animal, one has $g = 2N$, because there are two inequivalent orientations as well as N translations. For two disjoint elementary squares, one has $g = \frac{1}{2}N(N-5)$, which arises from subtracting $5N$ 'illegal' configurations involving double lines (remember each link in the partition sum appears only once!), shown in the figure, and finally dividing by two because the individual squares are identical. Note that $N(N-5)$ is always even for any integer value of N. Thus, to lowest interesting order on the square lattice,

$$Z = 2^N \big(\cosh\beta J\big)^{2N} \Big\{ 1 + Nx^4 + 2Nx^6 + \big(7 - \tfrac{5}{2}\big)Nx^8 + \tfrac{1}{2}N^2x^8 + \mathcal{O}(x^{10}) \Big\} \quad . \tag{6.40}$$

The free energy is therefore

$$F = -k_{\mathrm{B}}T\ln 2 + Nk_{\mathrm{B}}T\ln(1-x^2) - Nk_{\mathrm{B}}T\Big[x^4 + 2\,x^6 + \tfrac{9}{2}\,x^8 + \mathcal{O}(x^{10})\Big] \\ = Nk_{\mathrm{B}}T\ln 2 - Nk_{\mathrm{B}}T\Big\{x^2 + \tfrac{3}{2}\,x^4 + \tfrac{7}{3}\,x^6 + \tfrac{19}{4}\,x^8 + \mathcal{O}(x^{10})\Big\}, \tag{6.41}$$

again with $x = \tanh\beta J$. Here we have substituted $\cosh^2\!\beta J = 1/(1-x^2)$ to write the final result as a power series in x. Notice that the $\mathcal{O}(N^2)$ factor in Z has cancelled upon taking the logarithm, so the free energy is properly extensive.

For the one-dimensional chain or ring, the high temperature expansion yields

$$Z_{\mathsf{OBC}}(T,N) = 2^N\cosh^{N-1}\!\beta J \quad , \quad Z_{\mathsf{PBC}}(T,N) = 2^N\big(\cosh^N\!\beta J + \sinh^N\!\beta J\big) \quad , \tag{6.42}$$

in agreement with the transfer matrix calculations. Notice how for OBC there is only one lattice animal which contributes, *i.e.* the empty lattice. For PBC there are two contributing animals, the empty lattice and the entire ring. In higher dimensions, where there is a finite temperature phase transition, one typically computes the specific heat $c(T)$ and tries to extract its singular behavior in the vicinity of T_{c}, where $c(T) \sim A\,(T-T_{\mathrm{c}})^{-\alpha}$. Since $x(T) = \tanh(J/k_{\mathrm{B}}T)$ is analytic in T, we have $c(x) \sim A'\,(x-x_{\mathrm{c}})^{-\alpha}$, where $x_{\mathrm{c}} = x(T_{\mathrm{c}})$. One assumes x_{c} is the singularity closest to the origin and corresponds to the radius of convergence of the high temperature expansion. If we write

$$c(x) = \sum_{n=0}^{\infty} a_n\, x^n \sim A''\bigg(1 - \frac{x}{x_{\mathrm{c}}}\bigg)^{-\alpha} \quad , \tag{6.43}$$

then according to the binomial theorem we should expect

$$\frac{a_n}{a_{n-1}} = \frac{1}{x_{\mathrm{c}}}\bigg[1 - \frac{1-\alpha}{n}\bigg] \quad . \tag{6.44}$$

Thus, by plotting a_n/a_{n-1} *versus* $1/n$, one extracts $1/x_{\mathrm{c}}$ as the intercept, and $(\alpha-1)/x_{\mathrm{c}}$ as the slope.

High temperature expansion for correlation functions

Can we also derive a high temperature expansion for the spin-spin correlation function $C_{kl} = \langle\sigma_k\,\sigma_l\rangle$? Yes we can. We have

$$C_{kl} = \frac{\mathsf{Tr}\Big[\sigma_k\,\sigma_l\,e^{\beta J\sum_{\langle ij\rangle}\sigma_i\,\sigma_j}\Big]}{\mathsf{Tr}\Big[e^{\beta J\sum_{\langle ij\rangle}\sigma_i\,\sigma_j}\Big]} \equiv \frac{Y_{kl}}{Z} \quad . \tag{6.45}$$

Recall our analysis of the partition function Z. We concluded that in order for the trace not to vanish, the spin variable σ_i on each site i must occur an even number of times in the expansion of the product. Similar considerations hold for Y_{kl}, except now due to the presence of σ_k and σ_l, those variables now must occur an *odd* number of times when expanding the product. It is clear that the only nonvanishing diagrams will be those in which there is a finite string connecting sites k and l, in addition to the usual closed HTE loops. See fig. 6.4 for an instructive sketch. One then expands both Y_{kl} as well as Z in powers of $x = \tanh\beta J$, taking the ratio to obtain the correlator C_{kl}. At high temperatures $(x \to 0)$,

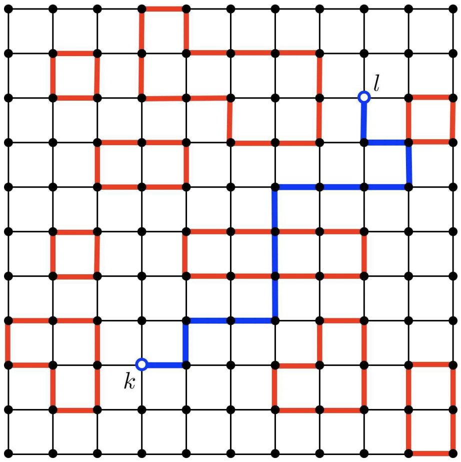


Figure 6.4: HTE diagrams for the numerator Y_{kl} of the correlation function C_{kl}. The blue path connecting sites k and l is the string. The remaining red paths are all closed loops.

both numerator and denominator are dominated by the configurations $\varGamma$ with the shortest possible total perimeter. For Z, this means the trivial path $\varGamma = \{\emptyset\}$, while for Y_{kl} this means finding the shortest length path from k to l. (If there is no straight line path from k to l, there will in general be several such minimizing paths.) Note, however, that the presence of the string between sites k and l complicates the analysis of $g_{\varGamma}$ for the closed loops, since none of the links of $\varGamma$ can intersect the string. It is worth stressing that this does not mean that the string and the closed loops cannot intersect at isolated *sites*, but only that they share no common *links*; see once again fig. 6.4.

6.3 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.

6.3.1 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

$$\begin{aligned} Z(T,V,N) &= \frac{1}{N!}\int\prod_{i=1}^{N}\frac{d^d\!p_i\, d^d\!x_i}{h^d}\, e^{-\hat{H}/k_{\rm B}T} \\ &= \frac{\lambda_T^{-Nd}}{N!}\int\prod_{i=1}^{N} d^d\!x_i\, \exp\bigg(-\frac{1}{k_{\rm B}T}\sum_{i<j} u\big(|\boldsymbol{x}_i-\boldsymbol{x}_j|\big)\bigg) \quad . \end{aligned} \tag{6.46}$$

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

$$\hat{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j} u\big(|\boldsymbol{x}_i - \boldsymbol{x}_j|\big) \quad , \tag{6.47}$$

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

$$Z(T,V,N) = \lambda_T^{-Nd}\, Q_N(T,V) \quad , \tag{6.48}$$

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

$$Q_N(T,V) = \frac{1}{N!}\int\! d^d\!x_1 \cdots \int\! d^d\!x_N \prod_{i<j} e^{-\beta u(r_{ij})} \quad . \tag{6.49}$$

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

6.3.2 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

$$u(x-x') = \begin{cases} \infty & \text{if } |x-x'| < a \\ 0 & \text{if } |x-x'| \ge a \quad . \end{cases} \tag{6.50}$$

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

$$v(x) = \begin{cases} \infty & \text{if } x < \frac{1}{2}a \\ 0 & \text{if } \frac{1}{2}a \le x \le L - \frac{1}{2}a \\ \infty & \text{if } x > L - \frac{1}{2}a \quad . \end{cases} \tag{6.51}$$

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

$$Q_N(T,L) = \frac{1}{N!}\int_0^L\! dx_1 \cdots \int_0^L\! dx_N\, \chi(x_1,\ldots,x_N) \quad , \tag{6.52}$$

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

$$\begin{aligned}
Q_N(T,L) &= \int\limits_{a/2}^{Y_1} \!dx_1 \int\limits_{x_1+a}^{Y_2} \!dx_2 \cdots \int\limits_{x_{N-1}+a}^{Y_N} \!dx_N = \int\limits_{a/2}^{Y_1} \!dx_1 \int\limits_{x_1+a}^{Y_2} \!dx_2 \cdots \int\limits_{x_{N-2}+a}^{Y_{N-1}} \!dx_{N-1} \, \big(Y_{N-1} - x_{N-1}\big) \qquad (6.53)\\
&= \frac{1}{2} \int\limits_{a/2}^{Y_1} \!dx_1 \int\limits_{x_1+a}^{Y_2} \!dx_2 \cdots \int\limits_{x_{N-3}+a}^{Y_{N-2}} \!dx_{N-2} \, \big(Y_{N-2} - x_{N-2}\big)^2 = \cdots = \frac{1}{k!} \int\limits_{a/2}^{Y_1} \!dx_1 \int\limits_{x_1+a}^{Y_2} \!dx_2 \cdots \int\limits_{x_{N-k-1}+a}^{Y_{N-k}} \!dx_{N-k} \, \big(Y_{N-k} - x_{N-k}\big)^k\\
&= \frac{1}{N!} \big(Y_1 - \tfrac{1}{2}a\big)^N = \frac{1}{N!} \, (L - Na)^N \quad .
\end{aligned}$$

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

$$F = -k_B T \ln Z = -N k_B T \Bigg\{ -\ln \lambda_T + 1 + \ln\bigg(\frac{L}{N} - a\bigg) \Bigg\} \quad , \qquad (6.54)$$

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

$$p = -\frac{\partial F}{\partial L} = \frac{k_B T}{\frac{L}{N} - a} = \frac{n k_B T}{1 - na} \quad , \qquad (6.55)$$

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, $pL = N k_B T$, is replaced by $pL_{\text{eff}} = N k_B T$, where $L_{\text{eff}} = L - Na$ 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 $v = N_A V/N$ is the molar volume. Defining $\tilde{a} \equiv a/N_A^2$ and $\tilde{b} \equiv b/N_A$, we have

$$p + \tilde{a} n^2 = \frac{n k_B T}{1 - \tilde{b} n} \quad , \qquad (6.56)$$

where $n = N_A/v$ 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.

6.3.3 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

$$f(r) = e^{-\beta u(r)} - 1 \quad , \qquad (6.57)$$

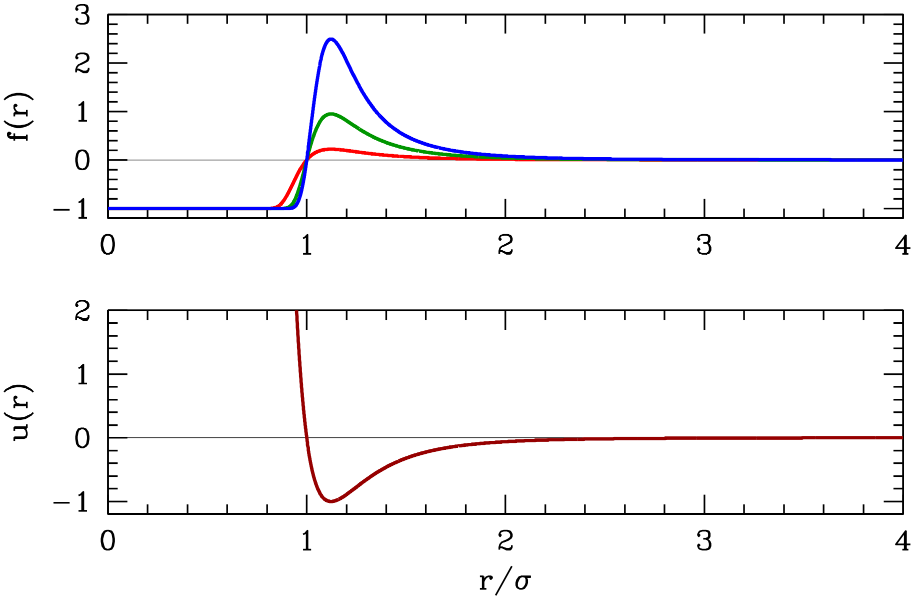


Figure 6.5: Bottom panel: Lennard-Jones potential $u(r) = 4\epsilon\left(x^{-12} - x^{-6}\right)$, with $x = r/\sigma$ and $\epsilon = 1$. Note the weak attractive tail and the strong repulsive core. Top panel: Mayer function $f(r,T) = e^{-u(r)/k_BT} - 1$ for $k_BT = 0.8\,\epsilon$ (blue), $k_BT = 1.5\,\epsilon$ (green), and $k_BT = 5\,\epsilon$ (red).

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

$$Q_N(T,V) = \frac{1}{N!}\int\!d^dx_1 \cdots \int\!d^dx_N \prod_{i<j}\left(1 + f_{ij}\right) \quad . \tag{6.58}$$

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

$$u(r) = 4\,\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} \quad . \tag{6.59}$$

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. 6.5.

The Lennard-Jones potential[9] 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

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[9] Disambiguation footnote: Take care not to confuse Philipp Lenard (Hungarian-German, cathode ray tubes, Nazi), Alfred-Marie Liénard (French, Liénard-Wiechert potentials, not a Nazi), John Lennard-Jones (British, molecular structure, also not a Nazi), and Lynyrd Skynyrd (American, "Free Bird"). I thank my colleague Oleg Shpyrko for setting me straight on this.

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

$$\Updownarrow$$

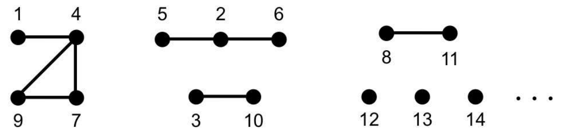

Figure 6.6: Diagrammatic interpretation of a term involving a product of eight Mayer functions.

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.

We begin by expanding the product in eqn. 6.58 as

$$\prod_{i<j}\big(1+f_{ij}\big)=1+\sum_{i<j}f_{ij}+\sum_{\substack{i<j\,,\,k<l\\(ij)\neq(kl)}}f_{ij}\,f_{kl}+\ldots\quad. \tag{6.60}$$

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. 6.6. 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. 6.6, the contribution to the configurational integral would be

$$\begin{aligned}\Delta Q=\frac{V^{N-11}}{N!}&\int\!d^d\!x_1\,d^d\!x_4\,d^d\!x_7\,d^d\!x_9\;f_{1,4}\,f_{4,7}\,f_{4,9}\,f_{7,9}\\&\times\int\!d^d\!x_2\,d^d\!x_5\,d^d\!x_6\;f_{2,5}\,f_{2,6}\times\int\!d^d\!x_3\,d^d\!x_{10}\;f_{3,10}\times\int\!d^d\!x_8\,d^d\!x_{11}\;f_{8,11}\quad.\end{aligned}\tag{6.61}$$

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

$$N=\sum_\gamma m_\gamma\,n_\gamma\quad, \tag{6.62}$$

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

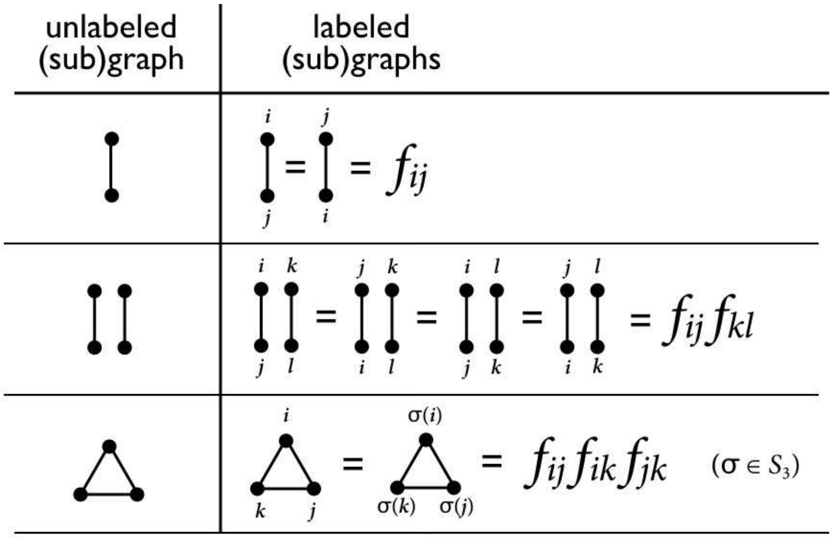

Figure 6.7: Different assignations of labels to vertices may not result in a distinct term in the expansion of the configuration integral.

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. 6.7. 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. 6.7. 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. 6.8. 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

$$\begin{aligned} Z &= \frac{\lambda_T^{-Nd}}{N!} \sum_{\{m_\gamma\}} \frac{N!}{\prod m_\gamma! \, s_\gamma^{m_\gamma}} \cdot \prod_\gamma \bigg(\int d^d\!x_1 \cdots d^d\!x_{n_\gamma} \prod_{i<j}^{\gamma} f_{ij} \bigg)^{m_\gamma} \delta_{N\,,\sum m_\gamma n_\gamma} \\ &= \sum_{\{m_\gamma\}} \prod_\gamma \frac{1}{m_\gamma!} \bigg(\frac{V b_\gamma(T)}{\lambda_T^d} \bigg)^{m_\gamma} \delta_{N\,,\sum m_\gamma n_\gamma} \end{aligned} \tag{6.63}$$

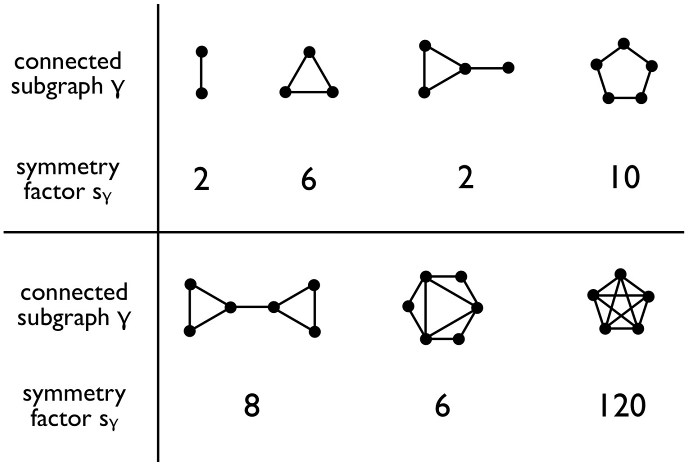

Figure 6.8: The symmetry factor s_γ for a connected subgraph γ is the number of permutations of its indices which leaves the term $\prod_{(ij)\in\gamma} f_{ij}$ invariant.

where the product $\prod_{i<j}^{\gamma} f_{ij}$ is over all links in the subgraph γ. The final Kronecker delta enforces the constraint $N = \sum_\gamma m_\gamma \, n_\gamma$. We have defined the *dimensionless cluster integrals* b_γ as

$$b_\gamma(T) \equiv \frac{1}{s_\gamma} \int \frac{d^dx_1}{\lambda_T^d} \cdots \int \frac{d^dx_{n_\gamma - 1}}{\lambda_T^d} \prod_{i<j}^{\gamma} f_{ij} \quad , \tag{6.64}$$

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. 6.63. Thus, each cluster integral is *intensive*[10], scaling as V^0.

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

$$\begin{aligned} \Xi(T,V,\mu) &= \sum_{\{m_\gamma\}} \big(e^{\beta\mu}\big)^{\sum m_\gamma n_\gamma} \prod_\gamma \frac{1}{m_\gamma!} \left(\frac{V b_\gamma(T)}{\lambda_T^d}\right)^{m_\gamma} \\ &= \prod_\gamma \sum_{m_\gamma=0}^{\infty} \frac{1}{m_\gamma!} \left(\frac{V z^{n_\gamma}\, b_\gamma(T)}{\lambda_T^d}\right)^{m_\gamma} = \exp\!\bigg(V \lambda_T^{-d} \sum_\gamma z^{n_\gamma}\, b_\gamma\bigg) \quad , \end{aligned} \tag{6.65}$$

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

$$\Omega(T,V,\mu) = -\frac{V k_\mathrm{B} T}{\lambda_T^d} \sum_\gamma z^{n_\gamma}\, b_\gamma(T) \quad , \tag{6.66}$$

---

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

and we can write

$$\begin{aligned} p &= k_{\mathrm{B}} T\, \lambda_T^{-d} \sum_\gamma z^{n_\gamma}\, b_\gamma(T) \\ n &= \lambda_T^{-d} \sum_\gamma n_\gamma\, z^{n_\gamma}\, b_\gamma(T) \quad , \end{aligned} \tag{6.67}$$

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,

$$p = nk_{\mathrm{B}}T \left\{ 1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots \right\} \quad . \tag{6.68}$$

It is useful to define the dimensionless quantities $\nu \equiv n\lambda_T^d$ and $\pi = p\lambda_T^d / k_{\mathrm{B}}T$, as well as the dimensionless cluster integral sums

$$\mathsf{b}_k \equiv \sum_\gamma b_\gamma\, \delta_{k,n_\gamma} \quad , \tag{6.69}$$

which is the sum of all cluster integrals b_γ with $n_\gamma = k$ vertices, multiplied by $\lambda_T^{-(k-1)d}$. Then

$$\nu(z) = \sum_{k=1}^\infty k\, \mathsf{b}_k\, z^k \qquad , \qquad \pi(z) = \sum_{k=1}^\infty \mathsf{b}_k\, z^k \quad . \tag{6.70}$$

The virial expansion of the dimensionless equation of state is then

$$\pi(\nu) = \sum_{k=1}^\infty \mathsf{B}_k\, \nu^k \tag{6.71}$$

We may again apply the Lagrange method introduced in §5.3.2 for the quantum virial coefficients, writing

$$\mathsf{B}_k = \oint \frac{d\nu}{2\pi i}\, \frac{\pi(\nu)}{\nu^{k+1}} = \oint \frac{dz}{2\pi i}\, \frac{\nu'(z)\, \pi(z)}{\big[\nu(z)\big]^{k+1}} = -\frac{1}{k} \oint \frac{dz}{2\pi i}\, \pi(z)\, \frac{d}{dz} \big[\nu(z)\big]^{-k} \quad , \tag{6.72}$$

where the contour encloses the origin in the complex plane. Integrating by parts, and using the relation $\pi'(z) = \nu(z)/z$, we obtain[11]

$$\begin{aligned} \mathsf{B}_k &= \frac{1}{k} \oint \frac{dz}{2\pi i}\, \pi'(z)\, \big[\nu(z)\big]^{-k} = \frac{1}{k} \oint \frac{dz}{2\pi i}\, \frac{1}{z}\, \big[\nu(z)\big]^{1-k} \\ &= \frac{1}{k} \oint \frac{dz}{2\pi i}\, \frac{1}{z^k} \Big(1 + 2\mathsf{b}_2 z + 3\mathsf{b}_3 z^2 + 4\mathsf{b}_4 z^4 + \ldots \Big)^{1-k} \quad , \end{aligned} \tag{6.73}$$

where the contour is a small circle enclosing the origin. Working out the first two virial coefficients, we find

$$\mathsf{B}_2 = -\mathsf{b}_2 \qquad , \qquad \mathsf{B}_3 = 4\mathsf{b}_2^2 - 2\mathsf{b}_3 \quad . \tag{6.74}$$

The dimensionful virial coefficients in eqn. 6.68 are then given by $B_k = \mathsf{B}_k\, \lambda_T^{(k-1)d}$.

---

[11] Since there is no term proportional to $\ln w$ in the Laurent expansion of $\pi(w)\big[n(w)\big]^{-k}$, there is no residue arising from integrating its derivative around the unit circle.

Lowest order expansion

We have

$$b_{-}(T) = \tfrac{1}{2}\int\!\frac{d^d\!x_1}{\lambda_T^d}\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_2|\big) = \tfrac{1}{2}\int\!\frac{d^d\!r}{\lambda_T^d}\, f(r) \tag{6.75}$$

and

$$\begin{aligned} b_{\wedge}(T) &= \tfrac{1}{2}\int\!\frac{d^d\!x_1}{\lambda_T^d}\int\!\frac{d^d\!x_2}{\lambda_T^d}\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_2|\big)\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_3|\big) \\ &= \tfrac{1}{2}\int\!\frac{d^d\!r}{\lambda_T^d}\int\!\frac{d^d\!r'}{\lambda_T^d}\, f(r)\, f(r') = 2\big(b_{-}\big)^2 \end{aligned} \tag{6.76}$$

and

$$\begin{aligned} b_{\triangle}(T) &= \tfrac{1}{6}\int\!\frac{d^d\!x_1}{\lambda_T^d}\int\!\frac{d^d\!x_2}{\lambda_T^d}\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_2|\big)\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_3|\big)\, f\big(|\boldsymbol{x}_2 - \boldsymbol{x}_3|\big) \\ &= \tfrac{1}{6}\int\!\frac{d^d\!r}{\lambda_T^d}\int\!\frac{d^d\!r'}{\lambda_T^d}\, f(r)\, f(r')\, f\big(|\boldsymbol{r} - \boldsymbol{r}'|\big) \quad . \end{aligned} \tag{6.77}$$

Thus we have $\mathsf{b}_2 = b_{-}$ and $\mathsf{b}_3 = b_{\wedge} + b_{\triangle} = 2b_{-}^2 + b_{\triangle}$. From eqn. 6.74 we now have

$$\begin{aligned} \mathsf{B}_2(T) &= -\mathsf{b}_2(T) = -b_{-}(T) \\ \mathsf{B}_3(T) &= \big[4\mathsf{b}_2^2(T) - 2\mathsf{b}_3(T)\big] = -2b_{\triangle}(T) \quad . \end{aligned} \tag{6.78}$$

Note that $b_{\wedge}$ does not contribute to B_3, even though the graph $\wedge$ has three vertices, and only $b_{\triangle}$ appears. This is because the virial coefficients B_j involve only cluster integrals b_γ for *one-particle irreducible* clusters, *i.e.* those clusters which remain connected and don't fall into multiple pieces if any of its vertices is removed, as depicted in fig. 6.9.

Cookbook recipe

Just follow these simple steps:

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

$$\begin{aligned} p &= k_{\rm B}T\, \lambda_T^{-d} \sum_\gamma z^{n_\gamma}\, b_\gamma(T) \\ n &= \lambda_T^{-d} \sum_\gamma n_\gamma\, z^{n_\gamma}\, b_\gamma(T) \quad , \end{aligned} \tag{6.79}$$

  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.

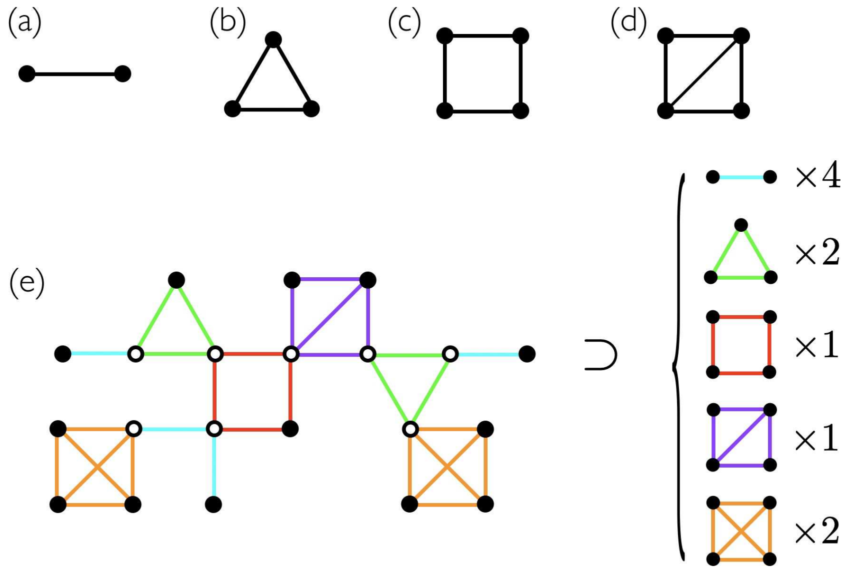

Figure 6.9: Connected *versus* irreducible clusters. Clusters (a) through (d) are *irreducible* in that they remain connected if any component site and its connecting links are removed. Cluster (e) is connected, but is *reducible*. Its integral b_γ is proportional to a product over its irreducible components, 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.

- 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

$$b_\gamma(T) \equiv \frac{1}{s_\gamma} \int \frac{d^d\!x_1}{\lambda_T^d} \cdots \int \frac{d^d\!x_{n_\gamma-1}}{\lambda_T^d} \prod_{i<j}^{\gamma} f_{ij} \quad , \tag{6.80}$$

  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,

$$p = nk_\text{B}T \, \Big\{ 1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots \Big\} \quad , \tag{6.81}$$

where

$$B_k(T) = -(k-1)\,\lambda_T^{(k-1)d} \sum_{\gamma \in \varGamma_k} b_\gamma(T) \quad , \tag{6.82}$$

with $\varGamma_k$ 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.

6.3.4 Examples

Hard sphere gas in three dimensions

The hard sphere potential is given by

$$u(r) = \begin{cases} \infty & \text{if } r \le a \\ 0 & \text{if } r > a \quad . \end{cases} \tag{6.83}$$

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

$$f(r) = \begin{cases} -1 & \text{if } r \le a \\ 0 & \text{if } r > a \quad . \end{cases} \tag{6.84}$$

We can change variables to obtain

$$\mathsf{b}_2(T) = \tfrac{1}{2}\int \frac{d^3\!r}{\lambda_T^3}\, f(r) = -\tfrac{2}{3}\pi a^3 \lambda_T^{-3} \quad . \tag{6.85}$$

The calculation of b_3 is more challenging. We have

$$\mathsf{b}_3 = \tfrac{1}{6}\int \frac{d^3\!\rho}{\lambda_T^3} \int \frac{d^3\!r}{\lambda_T^3}\, f(\rho)\, f(r)\, f\big(|\boldsymbol{r} - \boldsymbol{\rho}|\big) \quad . \tag{6.86}$$

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 $\boldsymbol{\rho}$:

$$\begin{aligned} \mathcal{V} &= \int d^3\!r\, f(r)\, f\big(|\boldsymbol{r} - \boldsymbol{\rho}|\big) \\ &= 2\int\limits_{\rho/2}^{a} dz\, \pi(a^2 - z^2) = \tfrac{4\pi}{3} a^3 - \pi a^2 \rho + \tfrac{\pi}{12}\,\rho^3 \quad . \end{aligned} \tag{6.87}$$

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

$$\mathsf{b}_3 = -\tfrac{1}{6}\cdot 4\pi \lambda_T^{-6} \int\limits_0^a d\rho\, \rho^2 \cdot \Big\{ \tfrac{4\pi}{3} a^3 - \pi a^2 \rho + \tfrac{\pi}{12}\,\rho^3 \Big\} = -\tfrac{5\pi^2}{36}\, a^6 \lambda_T^{-6} \quad . \tag{6.88}$$

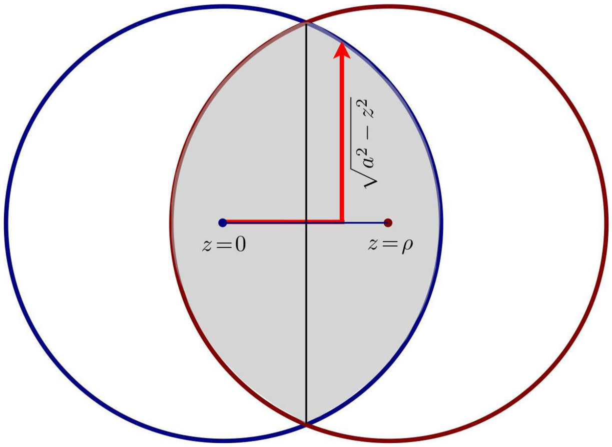

Figure 6.10: The overlap of hard sphere Mayer functions. The shaded volume is $\mathcal{V}$.

Thus, we have

$$B_2(T) = -\lambda_T^3\,\mathsf{b}_2(T) = \tfrac{2\pi}{3}a^3 \qquad , \qquad B_3(T) = -2\lambda_T^6\,\mathsf{b}_3(T) = \tfrac{5\pi^2}{18}a^6 \tag{6.89}$$

and the equation of state is then

$$p = nk_{\mathrm{B}}T\left\{1 + \tfrac{2\pi}{3}a^3 n + \tfrac{5\pi^2}{18}a^6 n^2 + \mathcal{O}(n^3)\right\} \quad . \tag{6.90}$$

Weakly attractive tail

Suppose

$$u(r) = \begin{cases} \infty & \text{if } r \le a \\ -u_0(r) & \text{if } r > a \quad . \end{cases} \tag{6.91}$$

Then the corresponding Mayer function is

$$f(r) = \begin{cases} -1 & \text{if } r \le a \\ e^{\beta u_0(r)} - 1 & \text{if } r > a \quad . \end{cases} \tag{6.92}$$

Thus,

$$\mathsf{b}_2(T) = \tfrac{1}{2}\int\!\frac{d^3\!r}{\lambda_T^3}\,f(r) = -\tfrac{2\pi}{3}a^3\lambda_T^{-3} + 2\pi\lambda_T^{-3}\int\limits_a^\infty\!dr\,r^2\left[e^{\beta u_0(r)} - 1\right] \quad . \tag{6.93}$$

Thus, the second virial coefficient is

$$B_2(T) = -\lambda_T^3\,\mathsf{b}_2(T) \approx \tfrac{2\pi}{3}a^3 - \frac{2\pi}{k_{\mathrm{B}}T}\int\limits_a^\infty\!dr\,r^2\,u_0(r) \quad , \tag{6.94}$$

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,

$$u(r)=\begin{cases}\infty & \text{if } r\le a\\ -\epsilon & \text{if } a<r<R\\ 0 & \text{if } r>R\quad.\end{cases}\tag{6.95}$$

Then the corresponding Mayer function is

$$f(r)=\begin{cases}-1 & \text{if } r\le a\\ e^{\beta\epsilon}-1 & \text{if } a<r<R\\ 0 & \text{if } r>R\quad.\end{cases}\tag{6.96}$$

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

$$\begin{aligned}B_2(T)=-\lambda_T^3\,\mathsf{b}_2(T)&=-\tfrac{1}{2}\int\! d^3\!r\, f(r)\\ &=-\frac{1}{2}\bigg\{(-1)\cdot\tfrac{4\pi}{3}a^3+\big(e^{\beta\epsilon}-1\big)\cdot\tfrac{4\pi}{3}a^3(s^3-1)\bigg\}\\ &=\tfrac{2\pi}{3}a^3\bigg\{1-(s^3-1)\big(e^{\beta\epsilon}-1\big)\bigg\}\quad.\end{aligned}\tag{6.97}$$

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

$$k_{\rm B}T_0=\epsilon\Big/\ln\!\left(\frac{s^3}{s^3-1}\right)\quad.\tag{6.98}$$

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

$$\Delta T=\int\limits_{p_1}^{p_2}\!dp\,\left(\frac{\partial T}{\partial p}\right)_{\!H}\quad,\tag{6.99}$$

where

$$\left(\frac{\partial T}{\partial p}\right)_{\!H}=\frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_{\!p}-V\right]\quad.\tag{6.100}$$

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

$$p=\frac{N}{V}\,k_{\rm B}T+\frac{N^2}{V^2}\,k_{\rm B}T\,B_2(T)+\ldots\tag{6.101}$$

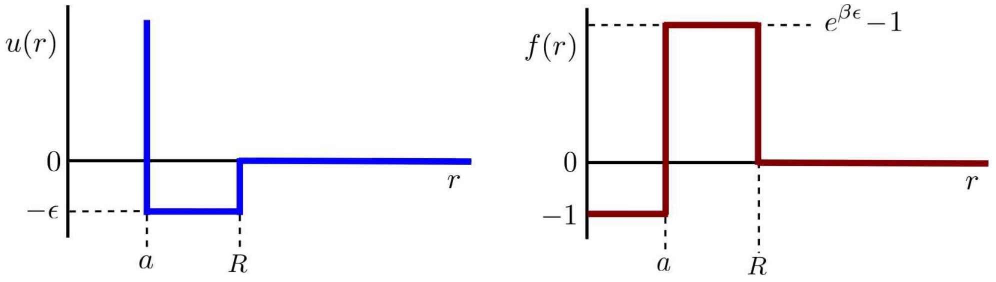

Figure 6.11: An attractive spherical well with a repulsive core $u(r)$ and its associated Mayer function $f(r)$.

and we compute $\left(\frac{\partial V}{\partial T}\right)_p$ by seting

$$0 = dp = -\frac{Nk_{\rm B}T}{V^2}\,dV + \frac{Nk_{\rm B}}{V}\,dT - \frac{2N^2}{V^3}\,k_{\rm B}T\,B_2(T)\,dV + \frac{N^2}{V^2}\,d\big(k_{\rm B}T\,B_2(T)\big) + \ldots \quad . \tag{6.102}$$

Dividing by dT, we find

$$T\left(\frac{\partial V}{\partial T}\right)_p - V = N\left[T\,\frac{\partial B_2}{\partial T} - B_2\right] \quad . \tag{6.103}$$

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

$$\frac{d\ln B_2}{d\ln T}\bigg|_{T^*} = 1 \quad . \tag{6.104}$$

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

$$\frac{B}{T^*} = A - \frac{B}{T^*} \qquad \Longrightarrow \qquad T^* = \frac{2B}{A} \quad . \tag{6.105}$$

Hard spheres with a hard wall

Consider a hard sphere gas in three dimensions in the presence of a hard wall at $z = 0$. The gas is confined to the region $z > 0$. The total potential energy is now

$$W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N) = \sum_i v(\boldsymbol{x}_i) + \sum_{i<j} u(\boldsymbol{x}_i - \boldsymbol{x}_j) \quad , \tag{6.106}$$

where

$$v(\boldsymbol{r}) = v(z) = \begin{cases} \infty & \text{if} \quad z \le \frac{1}{2}a \\ 0 & \text{if} \quad z > \frac{1}{2}a \quad , \end{cases} \tag{6.107}$$

and $u(\boldsymbol{r})$ is given in eqn. 6.83. The grand potential is written as a series in the total particle number N, and is given by

$$\Xi = e^{-\beta\Omega} = 1 + \xi\int\! d^3\!r\; e^{-\beta v(z)} + \tfrac{1}{2}\xi^2\int\! d^3\!r\int\! d^3\!r'\; e^{-\beta v(z)}\, e^{-\beta v(z')}\, e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} + \ldots \quad , \tag{6.108}$$

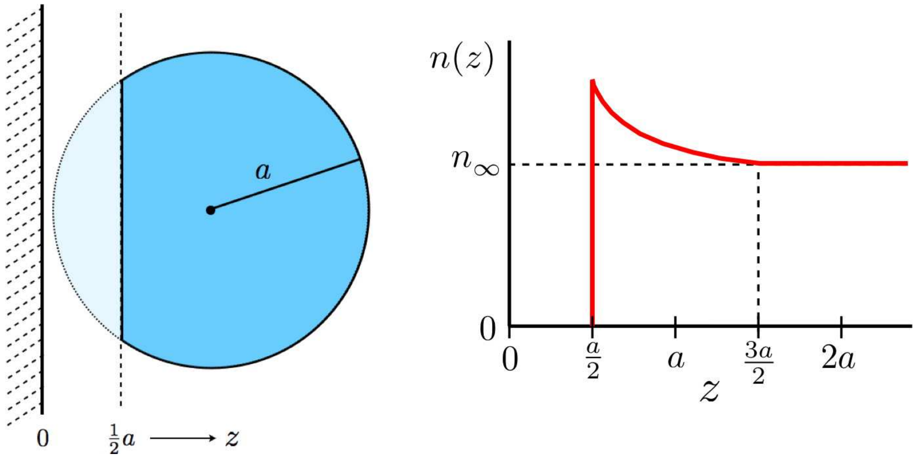

Figure 6.12: In the presence of a hard wall, the Mayer sphere is cut off on the side closest to the wall. The resulting density $n(z)$ vanishes for $z < \frac{1}{2}a$ since the center of each sphere must be at least one radius $(\frac{1}{2}a)$ away from the wall. Between $z = \frac{1}{2}a$ and $z = \frac{3}{2}a$ there is a density *enhancement*. If the calculation were carried out to higher order, $n(z)$ would exhibit damped spatial oscillations with wavelength $\lambda \sim a$.

where $\xi = z\,\lambda_T^{-3}$, with $z = e^{\mu/k_\mathrm{B}T}$ the fugacity. Taking the logarithm, and invoking the Taylor series $\ln(1+\delta) = \delta - \frac{1}{2}\delta^2 + \frac{1}{3}\delta^3 - \ldots$, we obtain

$$-\beta\Omega = \xi \int\limits_{z>\frac{a}{2}} \! d^3\!r + \tfrac{1}{2}\xi^2 \int\limits_{z>\frac{a}{2}} \! d^3\!r \int\limits_{z'>\frac{a}{2}} \! d^3\!r' \left[e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} - 1 \right] + \ldots \tag{6.109}$$

The volume is $V = \int\limits_{z>0} d^3\!r$. Dividing by V, we have, in the thermodynamic limit,

$$\begin{aligned} -\frac{\beta\Omega}{V} = \beta p &= \xi + \tfrac{1}{2}\xi^2 \frac{1}{V} \int\limits_{z>\frac{a}{2}} \! d^3\!r \int\limits_{z'>\frac{a}{2}} \! d^3\!r' \left[e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} - 1 \right] + \ldots \\ &= \xi - \tfrac{2}{3}\pi a^3\, \xi^2 + \mathcal{O}(\xi^3) \quad . \end{aligned} \tag{6.110}$$

The number density is

$$n = \xi \, \frac{\partial}{\partial \xi}\,(\beta p) = \xi - \tfrac{4}{3}\pi a^3\, \xi^2 + \mathcal{O}(\xi^3) \quad , \tag{6.111}$$

and inverting to obtain $\xi(n)$ and then substituting into the pressure equation, we obtain the lowest order virial expansion for the equation of state,

$$p = k_\mathrm{B}T \left\{ n + \tfrac{2}{3}\pi a^3\, n^2 + \ldots \right\} \quad . \tag{6.112}$$

As expected, the presence of the wall does not affect a bulk property such as the equation of state.

Next, let us compute the number density $n(z)$, given by

$$n(z) = \Big\langle \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \Big\rangle \quad . \tag{6.113}$$

Due to translational invariance in the (x, y) plane, we know that the density must be a function of z alone. The presence of the wall at $z = 0$ breaks translational symmetry in the z direction. The number density is

$$\begin{aligned} n(z) &= \mathrm{Tr}\Big[e^{\beta(\mu\hat{N}-\hat{H})}\sum_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{r}_i)\Big]\Big/\mathrm{Tr}\,e^{\beta(\mu\hat{N}-\hat{H})} \\ &= \Xi^{-1}\bigg\{\xi\,e^{-\beta v(z)} + \xi^2\,e^{-\beta v(z)}\!\int\! d^3\!r'\,e^{-\beta v(z')}\,e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} + \ldots\bigg\} \\ &= \xi\,e^{-\beta v(z)} + \xi^2\,e^{-\beta v(z)}\!\int\! d^3\!r'\,e^{-\beta v(z')}\Big[e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')}-1\Big] + \ldots \quad . \end{aligned} \tag{6.114}$$

Note that the term in square brackets in the last line is the Mayer function $f(\boldsymbol{r}-\boldsymbol{r}') = e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} - 1$. Consider the function

$$e^{-\beta v(z)}\,e^{-\beta v(z')}\,f(\boldsymbol{r}-\boldsymbol{r}') = \begin{cases} 0 & \text{if } z < \frac{1}{2}a \text{ or } z' < \frac{1}{2}a \\ 0 & \text{if } |\boldsymbol{r}-\boldsymbol{r}'| > a \\ -1 & \text{if } z > \frac{1}{2}a \text{ and } z' > \frac{1}{2}a \text{ and } |\boldsymbol{r}-\boldsymbol{r}'| < a \quad . \end{cases} \tag{6.115}$$

Now consider the integral of the above function with respect to $\boldsymbol{r}'$. Clearly the result depends on the value of z. If $z > \frac{3}{2}a$, then there is no excluded region in $\boldsymbol{r}'$ and the integral is (-1) times the full Mayer sphere volume, *i.e.* $-\frac{4}{3}\pi a^3$. If $z < \frac{1}{2}a$ the integral vanishes due to the $e^{-\beta v(z)}$ factor. For z infinitesimally larger than $\frac{1}{2}a$, the integral is (-1) times half the Mayer sphere volume, *i.e.* $-\frac{2}{3}\pi a^3$. For $z \in \big[\frac{a}{2}\,,\,\frac{3a}{2}\big]$ the integral interpolates between $-\frac{2}{3}\pi a^3$ and $-\frac{4}{3}\pi a^3$. Explicitly, one finds by elementary integration,

$$\int\! d^3\!r'\,e^{-\beta v(z)}\,e^{-\beta v(z')}\,f(\boldsymbol{r}-\boldsymbol{r}') = \begin{cases} 0 & \text{if } z < \frac{1}{2}a \\ \Big[-1-\frac{3}{2}\big(\frac{z}{a}-\frac{1}{2}\big)+\frac{1}{2}\big(\frac{z}{a}-\frac{1}{2}\big)^3\Big]\cdot\frac{2}{3}\pi a^3 & \text{if } \frac{1}{2}a < z < \frac{3}{2}a \\ -\frac{4}{3}\pi a^3 & \text{if } z > \frac{3}{2}a \quad . \end{cases} \tag{6.116}$$

After substituting $\xi = n + \frac{4}{3}\pi a^3 n^2 + \mathcal{O}(n^3)$ to relate ξ to the bulk density $n = n_\infty$, we obtain the desired result:

$$n(z) = \begin{cases} 0 & \text{if } z < \frac{1}{2}a \\ n + \Big[1-\frac{3}{2}\big(\frac{z}{a}-\frac{1}{2}\big)+\frac{1}{2}\big(\frac{z}{a}-\frac{1}{2}\big)^3\Big]\cdot\frac{2}{3}\pi a^3\,n^2 & \text{if } \frac{1}{2}a < z < \frac{3}{2}a \\ n & \text{if } z > \frac{3}{2}a \quad . \end{cases} \tag{6.117}$$

A sketch is provided in the right hand panel of fig. 6.12. Note that the density $n(z)$ vanishes identically for $z < \frac{1}{2}$ due to the exclusion of the hard spheres by the wall. For z between $\frac{1}{2}a$ and $\frac{3}{2}a$, there is a density *enhancement*, the origin of which has a simple physical interpretation. Since the wall excludes particles from the region $z < \frac{1}{2}$, there is an empty slab of thickness $\frac{1}{2}z$ coating the interior of the wall. There are then no particles in this region to exclude neighbors to their right, hence the density builds up just on the other side of this slab. The effect vanishes to the order of the calculation past $z = \frac{3}{2}a$, where $n(z) = n$ returns to its bulk value. Had we calculated to higher order, we'd have found damped oscillations with spatial period $\lambda \sim a$.

6.4 Liquid State Physics

6.4.1 The many-particle distribution function

The virial expansion is typically applied to low-density systems. When the density is high, *i.e.* when $na^3 \sim 1$, where a is a typical molecular or atomic length scale, the virial expansion is impractical. There are to many terms to compute, and to make progress one must use sophisticated resummation techniques to investigate the high density regime.

To elucidate the physics of liquids, it is useful to consider the properties of various *correlation functions*. These objects are derived from the general N-body Boltzmann distribution for identical particles,

$$\varrho_N(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N,\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N) = \frac{1}{N!}\times\begin{cases} Z_N^{-1}\, e^{-\beta\hat{H}_N(\{\boldsymbol{p}_i\},\{\boldsymbol{x}_i\})} & \text{OCE} \\ \Xi^{-1}\, e^{\beta\mu N}\, e^{-\beta\hat{H}_N(\{\boldsymbol{p}_i\},\{\boldsymbol{x}_i\})} & \text{GCE}\end{cases} \quad , \tag{6.118}$$

where

$$\begin{aligned} Z_N &= \mathsf{Tr}\; e^{-\beta\hat{H}_N} = \frac{1}{N!}\int\prod_{j=1}^N \frac{d^dx_j\, d^dp_j}{h^d}\; e^{-\beta\hat{H}_N(\{\boldsymbol{p}_i\},\{\boldsymbol{x}_i\})} \\ \Xi &= \mathsf{Tr}\; e^{\beta\mu\hat{N}}\, e^{-\beta\hat{H}} = \sum_{N=0}^\infty \frac{e^{\beta\mu N}}{N!}\int\prod_{j=1}^N \frac{d^dx_j\, d^dp_j}{h^d}\; e^{-\beta\hat{H}_N(\{\boldsymbol{p}_i\},\{\boldsymbol{x}_i\})} \end{aligned} \tag{6.119}$$

are the respective canonical and grand canonical partition functions. Note that the definition of the trace (Tr) includes a factor $1/N!$ in order to account for particle indistinguishability, and that ϱ_N is normalized according to

$$\int\prod_{j=1}^N \frac{d^dx_j\, d^dp_j}{h^d}\; \varrho(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N,\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N) = 1 \quad . \tag{6.120}$$

We assume a Hamiltonian of the form

$$\hat{H}_N = \sum_{i=1}^N \frac{\boldsymbol{p}_i^2}{2m} + W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N). \tag{6.121}$$

The quantity

$$\varrho_N(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N,\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N)\,\frac{d^dx_1\, d^dp_1}{h^d}\cdots\frac{d^dx_N\, d^dp_N}{h^d} \tag{6.122}$$

is the propability of finding N particles in the system, with particle #1 lying within d^3x_1 of $\boldsymbol{x}_1$ and having momentum within d^dp_1 of $\boldsymbol{p}_1$, *etc.* Note $\mathsf{Tr}\;\varrho_N = 1$. If we compute averages of quantities which only depend on the positions $\{\boldsymbol{x}_j\}$ and not on the momenta $\{\boldsymbol{p}_j\}$, then we may integrate out the momenta to obtain, in the OCE,

$$\begin{aligned} P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) &= \int\prod_{j=1}^N \frac{d^dp_j}{h^d}\;\varrho_N(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N,\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N) \\ &\equiv Q_N^{-1}\cdot\frac{1}{N!}\, e^{-\beta W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)} \quad , \end{aligned} \tag{6.123}$$

where W is the total potential energy,

$$W(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)=\sum_i v(\boldsymbol{x}_i)+\sum_{i<j} u(\boldsymbol{x}_i-\boldsymbol{x}_j)+\sum_{i<j<k} w(\boldsymbol{x}_i-\boldsymbol{x}_j\,,\,\boldsymbol{x}_j-\boldsymbol{x}_k)+\ldots \quad , \tag{6.124}$$

and Q_N is the configuration integral,

$$Q_N(T,V)=\frac{1}{N!}\int\! d^d\!x_1\cdots\!\int\! d^d\!x_N\; e^{-\beta W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)} \quad . \tag{6.125}$$

We will, for the most part, consider only two-body central potentials as contributing to W, which is to say we will only retain the middle term on the RHS. Note that $P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)$ is invariant under any permutation of the particle labels, and is normalized according to $\int\prod_{j=1}^N d^d\!x_j\; P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)=1$.

6.4.2 Averages over the distribution

To compute an average, one integrates over the distribution:

$$\big\langle F(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)\big\rangle=\int\! d^d\!x_1\cdots\!\int\! d^d\!x_N\; P(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)\,F(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N) \quad . \tag{6.126}$$

The overall N-particle probability density is normalized according to $\int\! d^d\!x_N\; P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)=1$.

The average local density is

$$n_1(\boldsymbol{r})=\big\langle\sum_i\delta(\boldsymbol{r}-\boldsymbol{x}_i)\big\rangle=N\!\int\! d^d\!x_2\cdots\!\int\! d^d\!x_N\; P(\boldsymbol{r},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N) \quad . \tag{6.127}$$

Note that the local density obeys the sum rule $\int\! d^d\!r\; n_1(\boldsymbol{r})=N$. In a translationally invariant system, $n_1=n=\frac{N}{V}$ is a constant independent of position. The boundaries of a system will in general break translational invariance, so in order to maintain the notion of a translationally invariant system of finite total volume, one must impose periodic boundary conditions.

The two-particle density matrix $n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is defined by

$$\begin{aligned} n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)&=\big\langle\sum_{i\neq j}\delta(\boldsymbol{r}_1-\boldsymbol{x}_i)\,\delta(\boldsymbol{r}_2-\boldsymbol{x}_j)\big\rangle\\ &=N(N-1)\!\int\! d^d\!x_3\cdots\!\int\! d^d\!x_N\; P(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{x}_3,\ldots,\boldsymbol{x}_N) \quad . \end{aligned} \tag{6.128}$$

As in the case of the one-particle density matrix, *i.e.* the local density $n_1(\boldsymbol{r})$, the two-particle density matrix also satisfies a sum rule:

$$\int\! d^d\!r_1\!\int\! d^d\!r_2\; n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)=N(N-1) \quad . \tag{6.129}$$

Generalizing further, one defines the *k-particle density matrix* as

$$\begin{aligned} n_k(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k)&=\big\langle\sum_{i_1\cdots i_k}{}^{\!\prime}\,\delta(\boldsymbol{r}_1-\boldsymbol{x}_{i_1})\cdots\delta(\boldsymbol{r}_k-\boldsymbol{x}_{i_k})\,\big\rangle\\ &=\frac{N!}{(N-k)!}\!\int\! d^d\!x_{k+1}\cdots\!\int\! d^d\!x_N\; P(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k,\boldsymbol{x}_{k+1},\ldots,\boldsymbol{x}_N) \quad , \end{aligned} \tag{6.130}$$

where the prime on the sum indicates that all the indices $i_1, \ldots, i_k$ are distinct. The corresponding sum rule is then

$$\int d^d\!r_1 \cdots \int d^d\!r_k \, n_k(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_k) = \frac{N!}{(N-k)!} \quad . \tag{6.131}$$

The average potential energy can be expressed in terms of the distribution functions. Assuming only two-body interactions, we have

$$\begin{aligned} \langle W \rangle &= \Big\langle \sum_{i<j} u(\boldsymbol{x}_i - \boldsymbol{x}_j) \Big\rangle \\ &= \tfrac{1}{2} \int d^d\!r_1 \int d^d\!r_2 \, u(\boldsymbol{r}_1 - \boldsymbol{r}_2) \, \Big\langle \sum_{i \neq j} \delta(\boldsymbol{r}_1 - \boldsymbol{x}_i) \, \delta(\boldsymbol{r}_2 - \boldsymbol{x}_j) \Big\rangle \\ &= \tfrac{1}{2} \int d^d\!r_1 \int d^d\!r_2 \, u(\boldsymbol{r}_1 - \boldsymbol{r}_2) \, n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) \quad . \end{aligned} \tag{6.132}$$

As the separations $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ get large, we expect the correlations to vanish, in which case

$$\begin{aligned} n_k(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_k) &= \Big\langle {\sum_{i_1 \cdots i_k}}' \delta(\boldsymbol{r}_1 - \boldsymbol{x}_{i_1}) \cdots \delta(\boldsymbol{r}_k - \boldsymbol{x}_{i_k}) \Big\rangle \xrightarrow[r_{ij} \to \infty]{} {\sum_{i_1 \cdots i_k}}' \big\langle \delta(\boldsymbol{r}_1 - \boldsymbol{x}_{i_1}) \big\rangle \cdots \big\langle \delta(\boldsymbol{r}_k - \boldsymbol{x}_{i_k}) \big\rangle \\ &= \frac{N!}{(N-k)!} \cdot \frac{1}{N^k} \, n_1(\boldsymbol{r}_1) \cdots n_1(\boldsymbol{r}_k) \\ &= \left(1 - \frac{1}{N}\right)\left(1 - \frac{2}{N}\right) \cdots \left(1 - \frac{k-1}{N}\right) n_1(\boldsymbol{r}_1) \cdots n_1(\boldsymbol{r}_k) \quad . \end{aligned} \tag{6.133}$$

The *k-particle distribution function* is defined as the ratio

$$g_k(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_k) \equiv \frac{n_k(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_k)}{n_1(\boldsymbol{r}_1) \cdots n_1(\boldsymbol{r}_k)} \quad . \tag{6.134}$$

For large separations, then,

$$g_k(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_k) \xrightarrow[r_{ij} \to \infty]{} \prod_{j=1}^{k-1} \left(1 - \frac{j}{N}\right) \quad . \tag{6.135}$$

For isotropic systems, the two-particle distribution function $g_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ depends only on the magnitude $|\boldsymbol{r}_1 - \boldsymbol{r}_2|$. As a function of this scalar separation, the function is known as the *radial distribution function*:

$$g(r) \equiv g_2(\boldsymbol{r}) = \frac{1}{n^2} \Big\langle \sum_{i \neq j} \delta(\boldsymbol{r} - \boldsymbol{x}_i) \, \delta(\boldsymbol{x}_j) \Big\rangle = \frac{1}{V n^2} \Big\langle \sum_{i \neq j} \delta(\boldsymbol{r} - \boldsymbol{x}_i + \boldsymbol{x}_j) \Big\rangle \quad . \tag{6.136}$$

The radial distribution function is of great importance in the physics of liquids because

- thermodynamic properties of the system can be related to $g(r)$
- $g(r)$ is directly measurable by scattering experiments

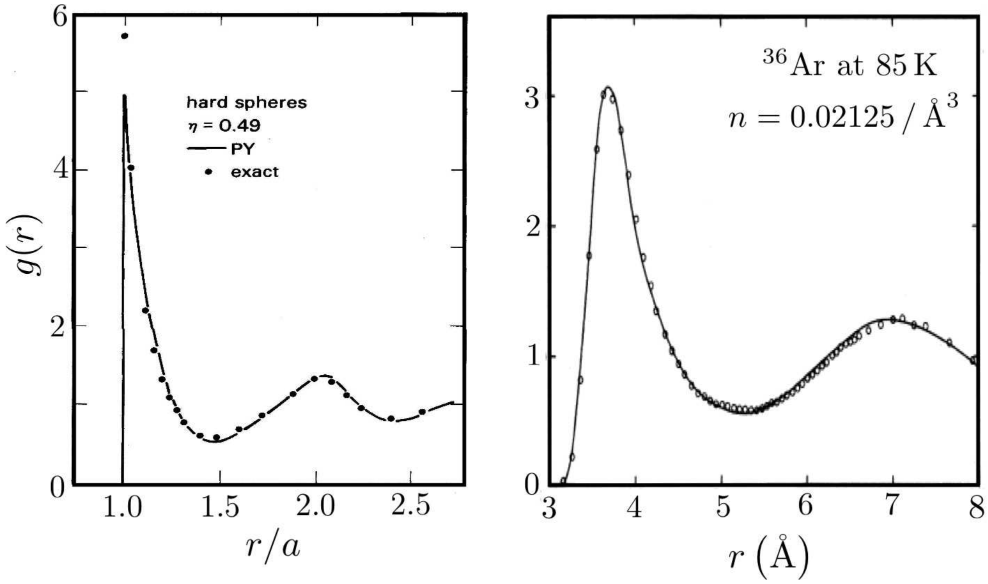

Figure 6.13: Pair distribution functions for hard spheres of diameter a at filling fraction $\eta = \frac{\pi}{6} a^3 n = 0.49$ (left) and for liquid Argon at $T = 85\,\text{K}$ (right). Molecular dynamics data for hard spheres (points) is compared with the result of the Percus-Yevick approximation. Reproduced (without permission) from J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, fig 5.5. Experimental data on liquid argon are from the neutron scattering work of J. L. Yarnell *et al.*, *Phys. Rev. A* **7**, 2130 (1973). The data (points) are compared with molecular dynamics calculations by Verlet (1967) for a Lennard-Jones fluid.

For example, in an isotropic system the average potential energy is given by

$$\begin{aligned}\langle W\rangle &= \tfrac{1}{2}\int\! d^d\!r_1 \int\! d^d\!r_2 \; u(\boldsymbol{r}_1 - \boldsymbol{r}_2)\, n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) \\ &= \tfrac{1}{2} n^2 \int\! d^d\!r_1 \int\! d^d\!r_2 \; u(\boldsymbol{r}_1 - \boldsymbol{r}_2)\, g\big(|\boldsymbol{r}_1 - \boldsymbol{r}_2|\big) = \frac{N^2}{2V} \int\! d^d\!r \; u(r)\, g(r) \quad .\end{aligned} \tag{6.137}$$

For a three-dimensional system, the average internal (*i.e.* potential) energy per particle is

$$\frac{\langle W\rangle}{N} = 2\pi n \int\limits_0^\infty \! dr\, r^2\, g(r)\, u(r) \quad . \tag{6.138}$$

Intuitively, $f(r)\,dr \equiv 4\pi r^2\, n\, g(r)\, dr$ is the average number of particles lying at a radial distance between r and $r + dr$ from a given reference particle. The total potential energy of interaction with the reference particle is then $f(r)\,u(r)\,dr$. Now integrate over all r and divide by two to avoid double-counting. This recovers eqn. 6.138.

In the OCE, $g(r)$ obeys the sum rule

$$\int\! d^d\!r\; g(r) = \frac{V}{N^2} \cdot N(N-1) = V - \frac{V}{N} \quad , \tag{6.139}$$

hence

$$n \int\! d^d\!r\; \big[g(r) - 1\big] = -1 \qquad \text{(OCE)} \quad . \tag{6.140}$$

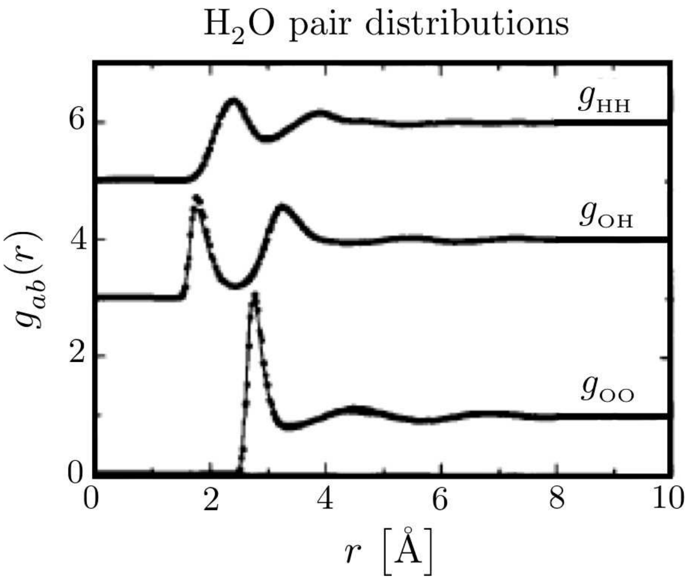

Figure 6.14: Monte Carlo pair distribution functions for liquid water. From A. K. Soper, *Chem Phys.* **202**, 295 (1996).

The function $h(r) \equiv g(r) - 1$ is called the *pair correlation function*.

In the grand canonical formulation, we have

$$\begin{aligned} n\!\int\! d^3\!r\, h(r) &= \frac{\langle N \rangle}{V} \cdot \left[\frac{\langle N(N-1) \rangle}{\langle N \rangle^2}\, V - V \right] \\ &= \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} - 1 = n k_{\mathrm{B}} T \kappa_T - 1 \qquad \text{(GCE)} \quad , \end{aligned} \tag{6.141}$$

where κ_T is the isothermal compressibility. Note that in an ideal gas we have $h(r) = 0$ and $\kappa_T = \kappa_T^0 \equiv 1/n k_{\mathrm{B}} T$. Self-condensed systems, such as liquids and solids far from criticality, are nearly incompressible, hence $0 < n k_{\mathrm{B}} T\, \kappa_T \ll 1$, and therefore $n\!\int\! d^3\!r\, h(r) \approx -1$. For incompressible systems, where $\kappa_T = 0$, this becomes an equality.

As we shall see below in §6.4.4, the function $h(r)$, or rather its Fourier transform $\hat{h}(\boldsymbol{k})$, is directly measured in a scattering experiment. The question then arises as to which result applies: the OCE result from eqn. 6.140 or the GCE result from eqn. 6.141. The answer is that under almost all experimental conditions it is the GCE result which applies. The reason for this is that the scattering experiment typically illuminates only a subset of the entire system. This subsystem is in particle equilibrium with the remainder of the system, hence it is appropriate to use the grand canonical ensemble. The OCE results would only apply if the scattering experiment were to measure the entire system.

6.4.3 Virial equation of state

The *virial* of a mechanical system is defined to be

$$G = \sum_i \boldsymbol{x}_i \cdot \boldsymbol{F}_i \quad , \tag{6.142}$$

where $\boldsymbol{F}_i$ is the total force acting on particle i. If we average G over time, we obtain

$$\begin{aligned} \langle G \rangle &= \lim_{T\to\infty} \frac{1}{T} \int\limits_0^T \! dt \, \sum_i \boldsymbol{x}_i \cdot \boldsymbol{F}_i \\ &= - \lim_{T\to\infty} \frac{1}{T} \int\limits_0^T \! dt \, \sum_i m \, \dot{\boldsymbol{x}}_i^2 = -3Nk_{\rm B}T \quad . \end{aligned} \tag{6.143}$$

Here, we have made use of

$$\boldsymbol{x}_i \cdot \boldsymbol{F}_i = m \, \boldsymbol{x}_i \cdot \ddot{\boldsymbol{x}}_i = - \, m \, \dot{\boldsymbol{x}}_i^2 + \frac{d}{dt}\Big(m \, \boldsymbol{x}_i \cdot \dot{\boldsymbol{x}}_i \Big) \quad , \tag{6.144}$$

as well as ergodicity and equipartition of kinetic energy. We have also assumed three space dimensions. In a bounded system, there are two contributions to the force $\boldsymbol{F}_i$. One contribution is from the surfaces which enclose the system. This is given by[12]

$$\langle G \rangle_{\rm surfaces} = \Big\langle \sum_i \boldsymbol{x}_i \cdot \boldsymbol{F}_i^{\rm (surf)} \Big\rangle = -3pV \quad . \tag{6.145}$$

The remaining contribution is due to the interparticle forces. Thus,

$$\frac{p}{k_{\rm B}T} = \frac{N}{V} - \frac{1}{3Vk_{\rm B}T} \Big\langle \sum_i \boldsymbol{x}_i \cdot \boldsymbol{\nabla}_{\!i} W \Big\rangle \quad . \tag{6.146}$$

Invoking the definition of $g(r)$, we have

$$p = nk_{\rm B}T \left\{ 1 - \frac{2\pi n}{3k_{\rm B}T} \int\limits_0^\infty \! dr \, r^3 \, g(r) \, u'(r) \right\} \quad . \tag{6.147}$$

As an alternate derivation, consider the First Law of Thermodynamics,

$$d\Omega = -S \, dT - p \, dV - N \, d\mu \quad , \tag{6.148}$$

---

[12] To derive this expression, note that $\boldsymbol{F}^{\rm (surf)}$ is directed inward and vanishes away from the surface. Each Cartesian direction $\alpha = (x, y, z)$ then contributes $-F_\alpha^{\rm (surf)} L_\alpha$, where L_α is the corresponding linear dimension. But $F_\alpha^{\rm (surf)} = pA_\alpha$, where A_α is the area of the corresponding face and p. is the pressure. Summing over the three possibilities for α, one obtains eqn. 6.145.

from which we derive

$$p = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad . \tag{6.149}$$

Now let $V \to \ell^3 V$, where ℓ is a scale parameter. Then

$$p = -\frac{\partial \Omega}{\partial V} = -\frac{1}{3V}\,\frac{\partial}{\partial \ell}\bigg|_{\ell=1} \Omega(T, \ell^3 V, \mu) \quad . \tag{6.150}$$

Now

$$\begin{aligned} \Xi(T, \ell^3 V, \mu) &= \sum_{N=0}^{\infty} \frac{1}{N!}\, e^{\beta\mu N}\, \lambda_T^{-3N} \int\limits_{\ell^3 V} \! d^3\!x_1 \cdots \int\limits_{\ell^3 V} \! d^3\!x_N \; e^{-\beta W(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)} \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \left(e^{\beta\mu}\, \lambda_T^{-3}\right)^N \ell^{3N} \int\limits_{V} \! d^3\!x_1 \cdots \int\limits_{V} \! d^3\!x_N \; e^{-\beta W(\ell \boldsymbol{x}_1, \ldots, \ell \boldsymbol{x}_N)} \end{aligned} \tag{6.151}$$

Thus,

$$\begin{aligned} p &= -\frac{1}{3V}\,\frac{\partial \Omega(\ell^3 V)}{\partial \ell}\bigg|_{\ell=1} = \frac{k_{\rm B}T}{3V}\,\frac{1}{\Xi}\,\frac{\partial \Xi(\ell^3 V)}{\partial \ell}\bigg|_{\ell=1} \\ &= \frac{k_{\rm B}T}{3V}\,\frac{1}{\Xi} \sum_{N=0}^{\infty} \frac{1}{N!} \big(z\lambda_T^{-3}\big)^N \left\{ \int\limits_{V} \! d^3\!x_1 \cdots \int\limits_{V} \! d^3\!x_N \; e^{-\beta W(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)} \left[3N - \beta \sum_i \boldsymbol{x}_i \cdot \frac{\partial W}{\partial \boldsymbol{x}_i} \right] \right\} \\ &= n k_{\rm B}T - \frac{1}{3V} \left\langle \frac{\partial W}{\partial \ell} \right\rangle_{\ell=1} \quad . \end{aligned} \tag{6.152}$$

Finally, from $W = \sum_{i<j} u(\ell \boldsymbol{x}_{ij})$ we have

$$\left\langle \frac{\partial W}{\partial \ell} \right\rangle_{\ell=1} = \left\langle \sum_{i<j} \boldsymbol{x}_{ij} \cdot \boldsymbol{\nabla} u(\boldsymbol{x}_{ij}) \right\rangle = \frac{2\pi N^2}{V} \int\limits_0^\infty \! dr\, r^3 g(r)\, u'(r) \quad , \tag{6.153}$$

and hence

$$p = n k_{\rm B}T - \tfrac{2}{3}\pi n^2 \int\limits_0^\infty \! dr\, r^3\, g(r)\, u'(r) \quad . \tag{6.154}$$

Note that the density n enters the equation of state explicitly on the RHS of the above equation, but also implicitly through the pair distribution function $g(r)$, which has implicit dependence on both n and T.

6.4.4 Correlations and scattering

Consider the scattering of a light or particle beam (*i.e.* photons or neutrons) from a liquid. We label the states of the beam particles by their wavevector $\boldsymbol{k}$ and we assume a general dispersion $\varepsilon_{\boldsymbol{k}}$. For photons,

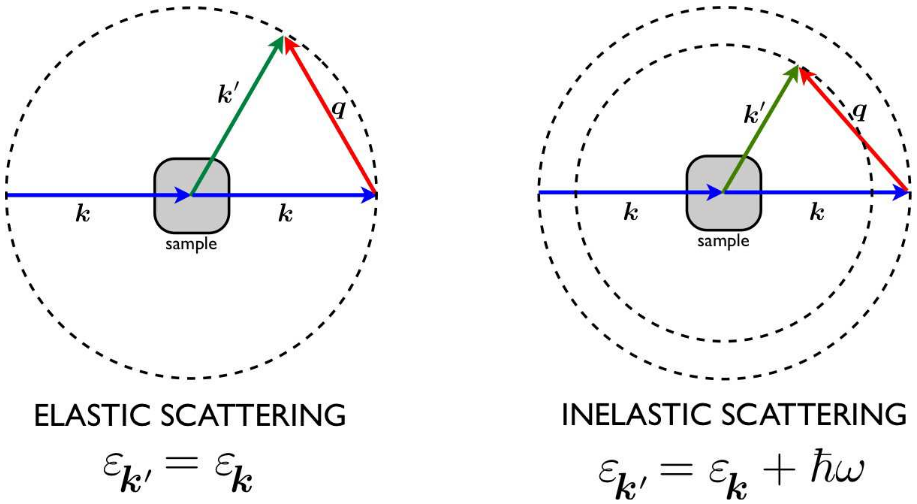

Figure 6.15: In a scattering experiment, a beam of particles interacts with a sample and the beam particles scatter off the sample particles. A momentum $\hbar\boldsymbol{q}$ and energy $\hbar\omega$ are transferred to the beam particle during such a collision. If $\omega = 0$, the scattering is said to be *elastic*. For $\omega \neq 0$, the scattering is *inelastic*.

$\varepsilon_{\boldsymbol{k}} = \hbar c|\boldsymbol{k}|$, while for neutrons $\varepsilon_{\boldsymbol{k}} = \hbar^2\boldsymbol{k}^2/2m_{\rm n}$. We assume a single scattering process with the liquid, during which the total momentum and energy of the liquid plus beam are conserved. We write

$$\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{q} \qquad , \qquad \varepsilon_{\boldsymbol{k}'} = \varepsilon_{\boldsymbol{k}} + \hbar\omega \quad , \tag{6.155}$$

where $\boldsymbol{k}'$ is the final state of the scattered beam particle. Thus, the fluid transfers momentum $\Delta\boldsymbol{p} = \hbar\boldsymbol{q}$ and energy $\hbar\omega$ to the beam.

Now consider the scattering process between an initial state $|\, i, \boldsymbol{k}\,\rangle$ and a final state $|\, j, \boldsymbol{k}'\,\rangle$, where these states describe both the beam and the liquid. According to Fermi's Golden Rule, the scattering rate is

$$\Gamma_{i\boldsymbol{k}\to j\boldsymbol{k}'} = \frac{2\pi}{\hbar}\,\big|\langle\, j, \boldsymbol{k}' \,|\, \mathcal{V} \,|\, i, \boldsymbol{k}\,\rangle\big|^2\, \delta(E_j - E_i + \hbar\omega) \quad , \tag{6.156}$$

where $\mathcal{V}$ is the scattering potential and E_i is the initial internal energy of the liquid. Note that overall energy conservation requires $E_j + \varepsilon_{\boldsymbol{k}'} = E_i + \varepsilon_{\boldsymbol{k}}$ and therefore $E_j = E_i - \hbar\omega$. If $\boldsymbol{r}$ is the position of the beam particle and $\{\boldsymbol{x}_l\}$ are the positions of the liquid particles, then

$$\mathcal{V}(\boldsymbol{r}) = \sum_{l=1}^{N} v(\boldsymbol{r} - \boldsymbol{x}_l) \quad . \tag{6.157}$$

For elastic scattering, the *differential scattering cross section* $d\sigma$ is defined to be

$$d\sigma(\hat{\Omega}) = \frac{\text{rate at which particles scattered into solid angle } d\Omega}{\text{incident flux}} \quad . \tag{6.158}$$

For inelastic scattering,

$$d^2\sigma(\hat{\Omega},\omega) = \frac{\text{rate at which particles scattered into solid angle } d\Omega \text{ and energy change within } \hbar\, d\omega}{\text{incident flux}} \quad . \tag{6.159}$$

The inelastic differential scattering cross section (per unit frequency per unit solid angle) is

$$\frac{\partial^2\sigma}{\partial\Omega\,\partial\omega}=\frac{\hbar}{4\pi}\,\frac{g(\varepsilon_{\boldsymbol{k}'})}{|\boldsymbol{v}_{\boldsymbol{k}}|}\sum_{i,j}P_i\,\Gamma_{i\boldsymbol{k}\to j\boldsymbol{k}'}\quad, \tag{6.160}$$

where $g(\varepsilon)=\int\!\frac{d^dk}{(2\pi)^d}\,\delta(\varepsilon-\varepsilon_{\boldsymbol{k}})$ is the density of states for the beam particles, and $P_i=Z^{-1}\,e^{-\beta E_i}$ is the Boltzmann weight.

Consider now the matrix element

$$\begin{aligned}\langle\, j,\boldsymbol{k}'\,|\,\mathcal{V}\,|\,i,\boldsymbol{k}\,\rangle&=\langle\, j\,|\,\frac{1}{V}\sum_{l=1}^{N}\int\! d^d\!r e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}}\,v(\boldsymbol{r}-\boldsymbol{x}_l)\,|\,i\,\rangle\\&=\frac{1}{V}\,\hat{v}(\boldsymbol{q})\,\langle\, j\,|\,\sum_{l=1}^{N}e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_l}\,|\,i\,\rangle\quad,\end{aligned}\tag{6.161}$$

where we have assumed that the incident and scattered beams are plane waves. We then have

$$\begin{aligned}\frac{\partial^2\sigma}{\partial\Omega\,\partial\omega}&=\frac{\hbar}{2}\,\frac{g(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{|\boldsymbol{\nabla}_{\boldsymbol{k}}\varepsilon_{\boldsymbol{k}}|}\,\frac{|\hat{v}(\boldsymbol{q})|^2}{V^2}\sum_i P_i\sum_j\big|\langle\, j\,|\sum_{l=1}^{N}e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_l}\,|\,i\,\rangle\big|^2\,\delta(E_j-E_i+\hbar\omega)\\&=\frac{g(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{4\pi\,|\boldsymbol{\nabla}_{\boldsymbol{k}}\varepsilon_{\boldsymbol{k}}|}\,\frac{N}{V^2}\,|\hat{v}(\boldsymbol{q})|^2\,S(\boldsymbol{q},\omega)\quad,\end{aligned}\tag{6.162}$$

where $S(\boldsymbol{q},\omega)$ is the *dynamic structure factor*,

$$S(\boldsymbol{q},\omega)=\frac{2\pi\hbar}{N}\sum_i P_i\sum_j\big|\langle\, j\,|\sum_{l=1}^{N}e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_l}\,|\,i\,\rangle\big|^2\,\delta(E_j-E_i+\hbar\omega)\tag{6.163}$$

Note that for an arbitrary operator A,

$$\begin{aligned}\sum_j\big|\langle\, j\,|\,A\,|\,i\,\rangle\big|^2\,\delta(E_j-E_i+\hbar\omega)&=\frac{1}{2\pi\hbar}\sum_j\int\limits_{-\infty}^{\infty}\!dt\;e^{i(E_j-E_i+\hbar\omega)\,t/\hbar}\,\langle\, i\,|\,A^\dagger\,|\,j\,\rangle\,\langle\, j\,|\,A\,|\,i\,\rangle\\&=\frac{1}{2\pi\hbar}\sum_j\int\limits_{-\infty}^{\infty}\!dt\;e^{i\omega t}\,\langle\, i\,|\,A^\dagger\,|\,j\,\rangle\,\langle\, j\,|\,e^{i\hat{H}t/\hbar}\,A\,e^{-i\hat{H}t/\hbar}\,|\,i\,\rangle\\&=\frac{1}{2\pi\hbar}\int\limits_{-\infty}^{\infty}\!dt\;e^{i\omega t}\,\langle\, i\,|\,A^\dagger(0)\,A(t)\,|\,i\,\rangle\quad.\end{aligned}\tag{6.164}$$

Thus,

$$\begin{aligned}S(\boldsymbol{q},\omega)&=\frac{1}{N}\int\limits_{-\infty}^{\infty}\!dt\;e^{i\omega t}\,\sum_i P_i\,\langle\, i\,|\sum_{l,l'}e^{i\boldsymbol{q}\cdot\boldsymbol{x}_l(0)}\,e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_{l'}(t)}\,|\,i\,\rangle\\&=\frac{1}{N}\int\limits_{-\infty}^{\infty}\!dt\;e^{i\omega t}\,\big\langle\sum_{l,l'}e^{i\boldsymbol{q}\cdot\boldsymbol{x}_l(0)}\,e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_{l'}(t)}\big\rangle\quad,\end{aligned}\tag{6.165}$$

where the angular brackets in the last line denote a thermal expectation value of a quantum mechanical operator. If we integrate over all frequencies, we obtain the equal time correlator,

$$\begin{aligned} S(\boldsymbol{q}) &= \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, S(\boldsymbol{q},\omega) = \frac{1}{N} \sum_{l,l'} \big\langle e^{i\boldsymbol{q}\cdot(\boldsymbol{x}_l - \boldsymbol{x}_{l'})} \big\rangle \\ &= N\,\delta_{\boldsymbol{q},0} + 1 + n \int\! d^d\!r\, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}} \big[g(r)-1\big] \quad . \end{aligned} \tag{6.166}$$

known as the *static structure factor*[13]. Note that $S(\boldsymbol{q}=0)=N$, since all the phases $e^{i\boldsymbol{q}\cdot(\boldsymbol{x}_i-\boldsymbol{x}_j)}$ are then unity. As $q\to\infty$, the phases oscillate rapidly with changes in the distances $|\boldsymbol{x}_i-\boldsymbol{x}_j|$, and average out to zero. However, the 'diagonal' terms in the sum, *i.e.* those with $i=j$, always contribute a total of 1 to $S(\boldsymbol{q})$. Therefore in the $q\to\infty$ limit we have $S(q\to\infty)=1$.

In general, the detectors used in a scattering experiment are sensitive to the energy of the scattered beam particles, although there is always a finite experimental resolution, both in $\boldsymbol{q}$ and ω. This means that what is measured is actually something like

$$S_{\text{meas}}(\boldsymbol{q},\omega) = \int\! d^d\!q' \int\! d\omega'\, F(\boldsymbol{q}-\boldsymbol{q}')\, G(\omega-\omega')\, S(\boldsymbol{q}',\omega') \quad , \tag{6.167}$$

where F and G are essentially Gaussian functions of their argument, with width given by the experimental resolution. If one integrates over all frequencies ω, *i.e.* if one simply counts scattered particles as a function of $\boldsymbol{q}$ but without any discrimination of their energies, then one measures the static structure factor $S(\boldsymbol{q})$. Elastic scattering is determined by $S(\boldsymbol{q},\omega=0)$, *i.e.* at no energy transfer.

6.4.5 Correlation and response

Suppose an external potential $v(\boldsymbol{x})$ is also present. Then

$$P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) = \frac{1}{Q_N[v]}\cdot\frac{1}{N!}\, e^{-\beta W(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)}\, e^{-\beta\sum_i v(\boldsymbol{x}_i)} \quad , \tag{6.168}$$

where

$$Q_N[v] = \frac{1}{N!}\int\! d^d\!x_1 \cdots \int\! d^d\!x_N\, e^{-\beta W(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)}\, e^{-\beta\sum_i v(\boldsymbol{x}_i)} \quad . \tag{6.169}$$

The Helmholtz free energy is then

$$F = -\frac{1}{\beta}\,\ln\Big(\lambda_T^{-dN}\, Q_N[v]\Big) \quad . \tag{6.170}$$

Now consider the functional derivative

$$\frac{\delta F}{\delta v(\boldsymbol{r})} = -\frac{1}{\beta}\cdot\frac{1}{Q_N}\cdot\frac{\delta Q_N}{\delta v(\boldsymbol{r})} \quad . \tag{6.171}$$

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[13] We may write $\delta_{\boldsymbol{q},0} = \frac{1}{V}\,(2\pi)^d\,\delta(\boldsymbol{q})$.

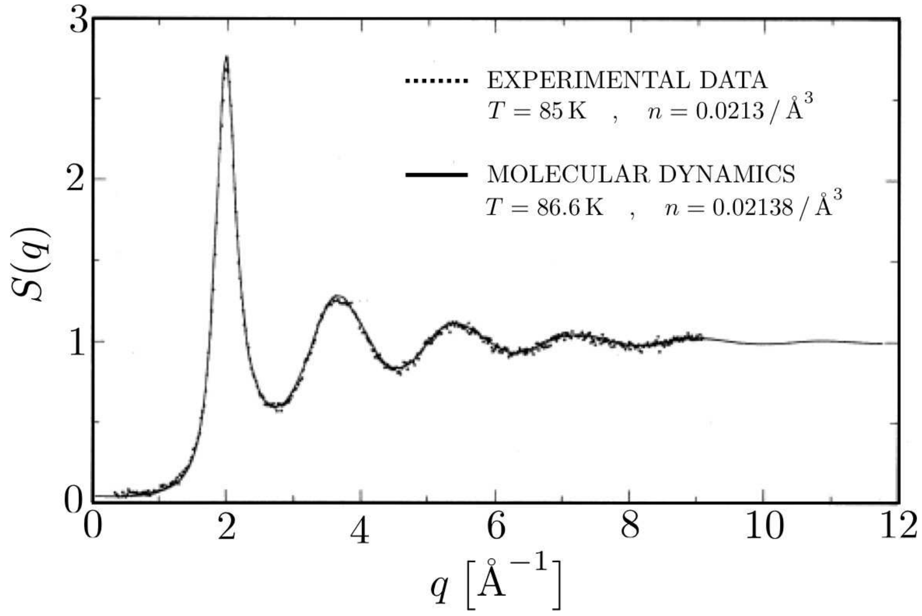

Figure 6.16: Comparison of the static structure factor for liquid Argon as determined by neutron scattering work of J. L. Yarnell *et al.*, *Phys. Rev. A* **7**, 2130 (1973) with molecular dynamics calculations by Verlet (1967) for a Lennard-Jones fluid.

Using

$$\sum_i v(\boldsymbol{x}_i) = \int \! d^d\!r \, v(\boldsymbol{r}) \sum_i \delta(\boldsymbol{r} - \boldsymbol{x}_i) \quad , \tag{6.172}$$

hence

$$\frac{\delta F}{\delta v(\boldsymbol{r})} = \int \! d^d\!x_1 \cdots \! \int \! d^d\!x_N \, P(\boldsymbol{x}_1 \, , \, \ldots \, , \, \boldsymbol{x}_N) \sum_i \delta(\boldsymbol{r} - \boldsymbol{x}_i) = n_1(\boldsymbol{r}) \quad , \tag{6.173}$$

which is the local density at $\boldsymbol{r}$.

Next, consider the *response function*,

$$\begin{aligned} \chi(\boldsymbol{r}, \boldsymbol{r}') \equiv \frac{\delta n_1(\boldsymbol{r})}{\delta v(\boldsymbol{r}')} &= \frac{\delta^2 F[v]}{\delta v(\boldsymbol{r}) \, \delta v(\boldsymbol{r}')} \\ &= \frac{1}{\beta} \cdot \frac{1}{Q_N^2} \, \frac{\delta Q_N}{\delta v(\boldsymbol{r})} \, \frac{\delta Q_N}{\delta v(\boldsymbol{r}')} - \frac{1}{\beta} \cdot \frac{1}{Q_N} \, \frac{\delta^2 Q_N}{\delta v(\boldsymbol{r}) \, \delta v(\boldsymbol{r}')} \\ &= \beta \, n_1(\boldsymbol{r}) \, n_1(\boldsymbol{r}') - \beta \, n_1(\boldsymbol{r}) \, \delta(\boldsymbol{r} - \boldsymbol{r}') - \beta \, n_2(\boldsymbol{r}, \boldsymbol{r}') \quad . \end{aligned} \tag{6.174}$$

In an isotropic system, $\chi(\boldsymbol{r}, \boldsymbol{r}') = \chi(\boldsymbol{r} - \boldsymbol{r}')$ is a function of the coordinate separation, and

$$\begin{aligned} -k_{\mathrm{B}} T \, \chi(\boldsymbol{r} - \boldsymbol{r}') &= -n^2 + n \, \delta(\boldsymbol{r} - \boldsymbol{r}') + n^2 g\big(|\boldsymbol{r} - \boldsymbol{r}'|\big) \\ &= n^2 \, h\big(|\boldsymbol{r} - \boldsymbol{r}'|\big) + n \, \delta(\boldsymbol{r} - \boldsymbol{r}') \quad . \end{aligned} \tag{6.175}$$

Taking the Fourier transform,

$$- k_{\rm B}T\,\hat{\chi}(\boldsymbol{q}) = n + n^2\,\hat{h}(\boldsymbol{q}) = n\,S(\boldsymbol{q}) \quad . \tag{6.176}$$

We may also write

$$\frac{\kappa_T}{\kappa_T^0} = 1 + n\,\hat{h}(0) = -nk_{\rm B}T\,\hat{\chi}(0) \quad , \tag{6.177}$$

i.e. $\kappa_T = -\hat{\chi}(0)$.

What does this all mean? Suppose we have an isotropic system which is subjected to a weak, spatially inhomogeneous potential $v(\boldsymbol{r})$. We expect that the density $n(\boldsymbol{r})$ in the presence of the inhomogeneous potential to itself be inhomogeneous. The first corrections to the $v = 0$ value $n = n_0$ are linear in v, and given by

$$\begin{aligned} \delta n(\boldsymbol{r}) &= \int\! d^d\!r'\, \chi(\boldsymbol{r},\boldsymbol{r}')\, v(\boldsymbol{r}') \\ &= -\beta n_0\, v(\boldsymbol{r}) - \beta n_0^2 \!\int\! d^d\!r'\, h(\boldsymbol{r}-\boldsymbol{r})\, v(\boldsymbol{r}') \quad . \end{aligned} \tag{6.178}$$

Note that if $v(\boldsymbol{r}) > 0$ it becomes energetically more costly for a particle to be at $\boldsymbol{r}$. Accordingly, the density response is negative, and proportional to the ratio $v(\boldsymbol{r})/k_{\rm B}T$ – this is the first term in the above equation. If there were no correlations between the particles, then $h = 0$ and this would be the entire story. However, the particles in general *are* correlated. Consider, for example, the case of hard spheres of diameter a, and let there be a repulsive potential at $\boldsymbol{r} = 0$. This means that it is less likely for a particle to be centered anywhere within a distance a of the origin. But then it will be *more* likely to find a particle in the next 'shell' of radial thickness a.

6.4.6 Ornstein-Zernike theory

The *direct correlation function* $c(\boldsymbol{r})$ is defined by the equation

$$h(\boldsymbol{r}) = c(\boldsymbol{r}) + n\!\int\! d^3\!r'\, h(\boldsymbol{r}-\boldsymbol{r}')\, c(\boldsymbol{r}') \quad , \tag{6.179}$$

where $h(r) = g(r) - 1$ and we assume an isotropic system. This is called the *Ornstein-Zernike equation*. The first term, $c(\boldsymbol{r})$, accounts for local correlations, which are then propagated in the second term to account for long-ranged correlations.

The OZ equation is an integral equation, but it becomes a simple algebraic one upon Fourier transforming:

$$\hat{h}(\boldsymbol{q}) = \hat{c}(\boldsymbol{q}) + n\,\hat{h}(\boldsymbol{q})\,\hat{c}(\boldsymbol{q}) \quad , \tag{6.180}$$

the solution of which is

$$\hat{h}(\boldsymbol{q}) = \frac{\hat{c}(\boldsymbol{q})}{1 - n\,\hat{c}(\boldsymbol{q})} \quad . \tag{6.181}$$

The static structure factor is then

$$S(\boldsymbol{q}) = 1 + n\,\hat{h}(\boldsymbol{q}) = \frac{1}{1 - n\,\hat{c}(\boldsymbol{q})} \quad . \tag{6.182}$$

In the grand canonical ensemble, we can write

$$\kappa_T = \frac{1 + n\,\hat{h}(0)}{nk_{\mathrm{B}}T} = \frac{1}{nk_{\mathrm{B}}T} \cdot \frac{1}{1 - n\,\hat{c}(0)} \qquad \Longrightarrow \qquad n\,\hat{c}(0) = 1 - \frac{\kappa_T^0}{\kappa_T} \quad , \tag{6.183}$$

where $\kappa_T^0 = 1/nk_{\mathrm{B}}T$ is the ideal gas isothermal compressibility.

At this point, we have merely substituted one unknown function, $h(\boldsymbol{r})$, for another, namely $c(\boldsymbol{r})$. To close the system, we need to relate $c(\boldsymbol{r})$ to $h(\boldsymbol{r})$ again in some way. There are various approximation schemes which do just this.

Ornstein-Zernike approximation at long wavelengths

Let's expand the direct correlation function $\hat{c}(\boldsymbol{q})$ in powers of the wavevector $\boldsymbol{q}$, *viz.*

$$\hat{c}(\boldsymbol{q}) = \hat{c}(0) + c_2\,q^2 + c_4\,q^4 + \ldots \quad . \tag{6.184}$$

Here we have assumed spatial isotropy. Then

$$\begin{aligned} 1 - n\,\hat{c}(\boldsymbol{q}) = \frac{1}{S(\boldsymbol{q})} &= 1 - n\,\hat{c}(0) - n\,c_2\,q^2 + \ldots \\ &\equiv \xi^{-2}R^2 + q^2R^2 + \mathcal{O}(q^4) \quad , \end{aligned} \tag{6.185}$$

where

$$R^2 = -n\,c_2 = 2\pi n \int\limits_0^\infty dr\; r^4\,c(r) \tag{6.186}$$

and

$$\xi^{-2} = \frac{1 - n\,\hat{c}(0)}{R^2} = \frac{1 - 4\pi n\int_0^\infty dr\,r^2\,c(r)}{2\pi n\int_0^\infty dr\,r^4\,c(r)} \quad . \tag{6.187}$$

The quantity $R(T)$ tells us something about the effective range of the interactions, while $\xi(T)$ is the *correlation length*. As we approach a critical point, the correlation length diverges as a power law:

$$\xi(T) \sim A|T - T_{\mathrm{c}}|^{-\nu} \quad . \tag{6.188}$$

The susceptibility is given by

$$\hat{\chi}(\boldsymbol{q}) = -n\beta\,S(\boldsymbol{q}) = -\frac{n\beta R^{-2}}{\xi^{-2} + q^2 + \mathcal{O}(q^4)} \tag{6.189}$$

In the *Ornstein-Zernike approximation*, one drops the $\mathcal{O}(q^4)$ terms in the denominator and retains only the long wavelength behavior. in the direct correlation function. Thus,

$$\hat{\chi}^{\mathrm{OZ}}(\boldsymbol{q}) = -\frac{n\beta R^{-2}}{\xi^{-2} + q^2} \quad . \tag{6.190}$$

We now apply the inverse Fourier transform back to real space to obtain $\chi^{\rm OZ}(\boldsymbol{r})$. In $d=1$ dimension the result can be obtained exactly:

$$\chi^{\rm OZ}_{d=1}(x) = -\frac{n}{k_{\rm B}TR^2}\int\limits_{-\infty}^{\infty}\frac{dq}{2\pi}\,\frac{e^{iqx}}{\xi^{-2}+q^2} = -\frac{n\xi}{2k_{\rm B}TR^2}\,e^{-|x|/\xi} \quad . \tag{6.191}$$

In higher dimensions $d>1$ we can obtain the result asymptotically in two limits:

- Take $r\to\infty$ with ξ fixed. Then

  $$\chi^{\rm OZ}_d(\boldsymbol{r}) \simeq -C_d\,n\cdot\frac{\xi^{(3-d)/2}}{k_{\rm B}T\,R^2}\cdot\frac{e^{-r/\xi}}{r^{(d-1)/2}}\cdot\left\{1+\mathcal{O}\bigg(\frac{d-3}{r/\xi}\bigg)\right\} \quad , \tag{6.192}$$

  where the C_d are dimensionless constants.

- Take $\xi\to\infty$ with r fixed; this is the limit $T\to T_{\rm c}$ at fixed r. In dimensions $d>2$ we obtain

  $$\chi^{\rm OZ}_d(\boldsymbol{r}) \simeq -\frac{C'_d\,n}{k_{\rm B}TR^2}\cdot\frac{e^{-r/\xi}}{r^{d-2}}\cdot\left\{1+\mathcal{O}\bigg(\frac{d-3}{r/\xi}\bigg)\right\} \quad . \tag{6.193}$$

  In $d=2$ dimensions we obtain

  $$\chi^{\rm OZ}_{d=2}(\boldsymbol{r}) \simeq -\frac{C'_2\,n}{k_{\rm B}TR^2}\cdot\ln\bigg(\frac{r}{\xi}\bigg)\,e^{-r/\xi}\cdot\left\{1+\mathcal{O}\bigg(\frac{1}{\ln(r/\xi)}\bigg)\right\} \quad , \tag{6.194}$$

  where the C'_d are dimensionless constants.

At criticality, $\xi\to\infty$, and clearly our results in $d=1$ and $d=2$ dimensions are nonsensical, as they are divergent. To correct this behavior, M. E. Fisher in 1963 suggested that the OZ correlation functions in the $r\ll\xi$ limit be replaced by

$$\chi(\boldsymbol{r}) \simeq -C''_d\,n\cdot\frac{\xi^{\eta}}{k_{\rm B}TR^2}\cdot\frac{e^{-r/\xi}}{r^{d-2+\eta}} \quad , \tag{6.195}$$

a result known as *anomalous scaling*. Here, η is the *anomalous scaling exponent*.

Recall that the isothermal compressibility is given by $\kappa_T=-\hat\chi(0)$. Near criticality, the integral in $\hat\chi(0)$ is dominated by the $r\ll\xi$ part, since $\xi\to\infty$. Thus, using Fisher's anomalous scaling,

$$\begin{aligned}\kappa_T = -\hat\chi(0) &= -\int\! d^d\!r\,\chi(\boldsymbol{r}) \\ &\sim A\!\int\! d^d\!r\,\frac{e^{-r/\xi}}{r^{d-2+\eta}} \sim B\,\xi^{2-\eta} \sim C\,\big|T-T_{\rm c}\big|^{-(2-\eta)\nu} \quad ,\end{aligned} \tag{6.196}$$

where A, B, and C are temperature-dependent constants which are nonsingular at $T=T_{\rm c}$. Thus, since $\kappa_T\propto|T-T_{\rm c}|^{-\gamma}$, we conclude

$$\gamma = (2-\eta)\,\nu \quad , \tag{6.197}$$

a result known as *hyperscaling*.

6.5 Coulomb Systems : Plasmas and the Electron Gas

6.5.1 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

$$U=\tfrac{1}{2}\int\! d^d\!r\int\! d^d\!r'\,\rho(\boldsymbol{r})\,u(\boldsymbol{r}-\boldsymbol{r}')\,\rho(\boldsymbol{r}') \quad , \tag{6.198}$$

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

$$\nabla^2 u(\boldsymbol{r}-\boldsymbol{r}')=-4\pi\,\delta(\boldsymbol{r}-\boldsymbol{r}') \quad . \tag{6.199}$$

Thus,

$$u(\boldsymbol{r})=\begin{cases}-2\pi\,|x-x'| & ,\ d=1\\ -2\,\ln|\boldsymbol{r}-\boldsymbol{r}'| & ,\ d=2\\ |\boldsymbol{r}-\boldsymbol{r}'|^{-1} & ,\ d=3 \quad .\end{cases} \tag{6.200}$$

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

$$\rho(\boldsymbol{r})=\sum_i q_i\,\delta(\boldsymbol{r}-\boldsymbol{x}_i) \quad , \tag{6.201}$$

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

$$\phi(\boldsymbol{r})=\int\! d^d\!r'\,u(\boldsymbol{r}-\boldsymbol{r}')\,\rho(\boldsymbol{r}')=\sum_i q_i\,u(\boldsymbol{r}-\boldsymbol{x}_i) \quad . \tag{6.202}$$

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

$$U=\tfrac{1}{2}\int\! d^d\!r\,\phi(\boldsymbol{r})\,\rho(\boldsymbol{r})=\tfrac{1}{2}\sum_i q_i\,\phi(\boldsymbol{x}_i) \quad , \tag{6.203}$$

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

6.5.2 Debye-Hückel theory

We now write the grand partition function:

$$\begin{aligned}\varXi(T,V,\mu_+,\mu_-)=\sum_{N_+=0}^\infty\sum_{N_-=0}^\infty \frac{1}{N_+!}\,e^{\beta\mu_+N_+}\,\lambda_+^{-N_+d}\cdot\frac{1}{N_-!}\,e^{\beta\mu_-N_-}\,\lambda_-^{-N_-d}&\\ \cdot\int\! d^d\!r_1\cdots\int\! d^d\!r_{N_{\rm tot}}\,e^{-\beta U(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_{N_{\rm tot}})} \quad ,&\end{aligned} \tag{6.204}$$

where $N_{\text{tot}} = N_+ + N_-$. We adopt a *mean field* approach, known as *Debye-Hückel theory*, writing

$$\rho(\boldsymbol{r}) = \bar{\rho}(\boldsymbol{r}) + \delta\rho(\boldsymbol{r}) \qquad , \qquad \phi(\boldsymbol{r}) = \bar{\phi}(\boldsymbol{r}) + \delta\phi(\boldsymbol{r}) \quad . \tag{6.205}$$

We then have

$$\begin{aligned} U &= \tfrac{1}{2}\!\int\! d^d\!r\, \big[\bar{\rho}(\boldsymbol{r}) + \delta\rho(\boldsymbol{r})\big]\cdot\big[\bar{\phi}(\boldsymbol{r}) + \delta\phi(\boldsymbol{r})\big] \\ &= \tfrac{1}{2}\!\int\! d^d\!r\, \bar{\phi}(\boldsymbol{r})\,\bar{\rho}(\boldsymbol{r}) + \overbrace{\tfrac{1}{2}\!\int\! d^d\!r\, \bar{\phi}(\boldsymbol{r})\,\delta\rho(\boldsymbol{r}) + \tfrac{1}{2}\!\int\! d^d\!r\, \bar{\rho}(\boldsymbol{r})\,\delta\phi(\boldsymbol{r})}^{\text{these two terms are the same}} + \tfrac{1}{2}\!\int\! d^d\!r\, \delta\rho(\boldsymbol{r})\,\delta\phi(\boldsymbol{r}) \\ &= -\int\! d^d\!r\, \bar{\phi}(\boldsymbol{r})\,\bar{\rho}(\boldsymbol{r}) + \int\! d^d\!r\, \bar{\phi}(\boldsymbol{r})\,\rho(\boldsymbol{r}) + \overbrace{\tfrac{1}{2}\!\int\! d^d\!r\, \delta\rho(\boldsymbol{r})\,\delta\phi(\boldsymbol{r})}^{\text{ignore fluctuation term}} \\ &= -U_0 + \int\! d^d\!r\, \bar{\phi}(\boldsymbol{r})\,\rho(\boldsymbol{r}) + (\text{flucts})^2 \quad , \end{aligned} \tag{6.206}$$

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

$$\varXi = e^{U_0/k_{\text{B}}T} \exp\!\left(z_+ \lambda_+^{-d} \int\! d^d\!r_+\, e^{-e\,\bar{\phi}(\boldsymbol{r}_+)/k_{\text{B}}T} \right) \exp\!\left(z_- \lambda_-^{-d} \int\! d^d\!r_-\, e^{e\,\bar{\phi}(\boldsymbol{r}_-)/k_{\text{B}}T} \right) \tag{6.207}$$

whence

$$\varOmega(T,V,\mu_+,\mu_-) = -U_0 - k_{\text{B}}T z_+ \lambda_+^{-d}\!\int\! d^d\!r\, \exp\!\bigg(-\frac{e\,\bar{\phi}(\boldsymbol{r})}{k_{\text{B}}T}\bigg) - k_{\text{B}}T z_- \lambda_-^{-d}\!\int\! d^d\!r\, \exp\!\bigg(+\frac{e\,\bar{\phi}(\boldsymbol{r})}{k_{\text{B}}T}\bigg) \quad , \tag{6.208}$$

where

$$\lambda_\pm = \bigg(\frac{2\pi\hbar^2}{m_\pm k_{\text{B}}T}\bigg) \qquad , \qquad z_\pm = \exp\!\bigg(\frac{\mu_\pm}{k_{\text{B}}T}\bigg) \quad . \tag{6.209}$$

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

$$\frac{\delta U_0}{\delta\bar{\phi}(\boldsymbol{r})} = \bar{\rho}(\boldsymbol{r}) \quad . \tag{6.210}$$

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

$$0 = \frac{\delta\varOmega}{\delta\bar{\phi}(\boldsymbol{r})} = -\bar{\rho}(\boldsymbol{r}) + e\,\lambda_+^{-d}\, z_+\, \exp\!\bigg(-\frac{e\,\bar{\phi}(\boldsymbol{r})}{k_{\text{B}}T}\bigg) - e\,\lambda_-^{-d}\, z_-\, \exp\!\bigg(+\frac{e\,\bar{\phi}(\boldsymbol{r})}{k_{\text{B}}T}\bigg) \quad . \tag{6.211}$$

At $r \to \infty$, we assume charge neutrality and $\phi(\infty) = 0$. Thus

$$\lambda_+^{-d}\, z_+ = n_+(\infty) = \lambda_-^{-d}\, z_- = n_-(\infty) \equiv n_\infty \quad , \tag{6.212}$$

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

$$\rho(\boldsymbol{r}) = -2e\, n_\infty \sinh\!\bigg(\frac{e\,\phi(\boldsymbol{r})}{k_{\text{B}}T}\bigg) \quad , \tag{6.213}$$

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

$$\nabla^2\phi = 8\pi e n_\infty \sinh(\beta e\phi) - 4\pi\rho_{\rm ext} \quad , \tag{6.214}$$

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

$$\nabla^2\phi = \kappa_{\rm D}^2\,\phi - 4\pi\rho_{\rm ext} \quad , \tag{6.215}$$

where

$$\kappa_{\rm D} = \bigg(\frac{8\pi n_\infty e^2}{k_{\rm B}T}\bigg)^{1/2} \qquad , \qquad \lambda_{\rm D} = \bigg(\frac{k_{\rm B}T}{8\pi n_\infty e^2}\bigg)^{1/2} \quad . \tag{6.216}$$

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,

$$\nabla^2\phi = \kappa_{\rm D}^2\,\phi - 4\pi Q\,\delta(\boldsymbol{r}) \quad . \tag{6.217}$$

Fourier transforming, we obtain

$$-\,\boldsymbol{q}^2\,\hat{\phi}(\boldsymbol{q}) = \kappa_{\rm D}^2\,\hat{\phi}(\boldsymbol{q}) - 4\pi Q \qquad \Longrightarrow \qquad \hat{\phi}(\boldsymbol{q}) = \frac{4\pi Q}{\boldsymbol{q}^2 + \kappa_{\rm D}^2} \quad . \tag{6.218}$$

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

$$\phi(\boldsymbol{r}) = \int\!\frac{d^3\!q}{(2\pi)^3}\,\frac{4\pi Q\,e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{\boldsymbol{q}^2 + \kappa_{\rm D}^2} = \frac{Q}{r}\cdot e^{-\kappa_{\rm D} r} \quad . \tag{6.219}$$

This solution must break down sufficiently close to $r = 0$, since the assumption $e\phi(r) \ll k_{\rm B}T$ is no longer valid there. However, for larger r, the Yukawa form is increasingly accurate.

For another example, consider an electrolyte held between two conducting plates, one at potential $\phi(x = 0) = 0$ 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

$$\phi(x) = A\,e^{\kappa_{\rm D} x} + B\,e^{-\kappa_{\rm D}\, x} \quad . \tag{6.220}$$

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

$$\phi(x) = V\cdot\frac{\sinh(\kappa_{\rm D} x)}{\sinh(\kappa_{\rm D} L)} \quad . \tag{6.221}$$

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.

6.5.3 The electron gas : Thomas-Fermi screening

Assuming $k_\mathrm{B}T \ll \varepsilon_\mathrm{F}$, 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

$$\varepsilon_\mathrm{F} = \frac{\hbar^2 k_\mathrm{F}^2}{2m} - e\phi(\boldsymbol{r}) \quad . \tag{6.222}$$

Thus, the Fermi wavevector k_F is spatially varying, according to the relation

$$k_\mathrm{F}(\boldsymbol{r}) = \left[\frac{2m}{\hbar^2}\Big(\varepsilon_\mathrm{F} + e\phi(\boldsymbol{r})\Big)\right]^{1/2} \quad . \tag{6.223}$$

The local electron number density is

$$n(\boldsymbol{r}) = \frac{k_\mathrm{F}^3(\boldsymbol{r})}{3\pi^2} = n_\infty \left(1 + \frac{e\phi(\boldsymbol{r})}{\varepsilon_\mathrm{F}}\right)^{3/2} \quad . \tag{6.224}$$

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

$$\nabla^2\phi = 4\pi e\, n_\infty \cdot \left[\left(1 + \frac{e\phi(\boldsymbol{r})}{\varepsilon_\mathrm{F}}\right)^{3/2} - 1\right] - 4\pi\rho_\mathrm{ext}(\boldsymbol{r}) \quad . \tag{6.225}$$

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

$$\nabla^2\phi = \frac{6\pi n_\infty e^2}{\varepsilon_\mathrm{F}}\,\phi \equiv \kappa_\mathrm{TF}^2\,\phi - 4\pi\rho_\mathrm{ext}(\boldsymbol{r}) \quad . \tag{6.226}$$

Here, κ_TF is the *Thomas-Fermi wavevector*,

$$\kappa_\mathrm{TF} = \left(\frac{6\pi n_\infty e^2}{\varepsilon_\mathrm{F}}\right)^{1/2} \quad . \tag{6.227}$$

Thomas-Fermi theory is valid provided $n_\infty\,\lambda_\mathrm{TF}^3 \gg 1$, where $\lambda_\mathrm{TF} = \kappa_\mathrm{TF}^{-1}$, 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 $[\mathrm{Ar}]\,3d^{10}\,4s^1$. The $4s$ electron forms an energy band which contains the Fermi surface. Zinc has a configuration of

[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,

$$\phi(\boldsymbol{r}) = \frac{Q}{r} \cdot e^{-\kappa_{\rm TF} r} \quad . \tag{6.228}$$

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

$$\delta n(\boldsymbol{r}) = e\phi(\boldsymbol{r})\, g(\varepsilon_{\rm F}) \quad , \tag{6.229}$$

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

$$\nabla^2\phi = (-4\pi)(-e\,\delta n) = 4\pi e^2 g(\varepsilon_{\rm F})\,\phi = \kappa^2_{\rm TF}\,\phi \quad , \tag{6.230}$$

where

$$\kappa_{\rm TF} = \sqrt{4\pi e^2\, g(\varepsilon_{\rm F})} \quad . \tag{6.231}$$

The value of $g(\varepsilon_{\rm F})$ will depend on the form of the dispersion. For ballistic bands with an effective mass m^*, the formula in eqn. 6.226 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

$$\nabla^2\phi(\boldsymbol{r}) = 4\pi e \cdot \frac{(2m)^{3/2}}{3\pi^2\hbar^3}\Big(\varepsilon_{\rm F} + e\phi(\boldsymbol{r})\Big)^{3/2} - 4\pi Ze\,\delta(\boldsymbol{r}) \quad . \tag{6.232}$$

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

$$\varepsilon_{\rm F} + e\phi(\boldsymbol{r}) = \frac{Ze^2}{r} \cdot \chi(r/r_0) \quad , \tag{6.233}$$

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

$$\nabla^2\left\{\frac{Ze^2}{r} \cdot \chi(r/r_0)\right\} = \frac{1}{r_0^2}\,\frac{Ze^2}{r}\,\chi''(r/r_0) \quad , \tag{6.234}$$

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

$$\chi''(t) = \frac{1}{\sqrt{t}}\,\chi^{3/2}(t) \quad , \tag{6.235}$$

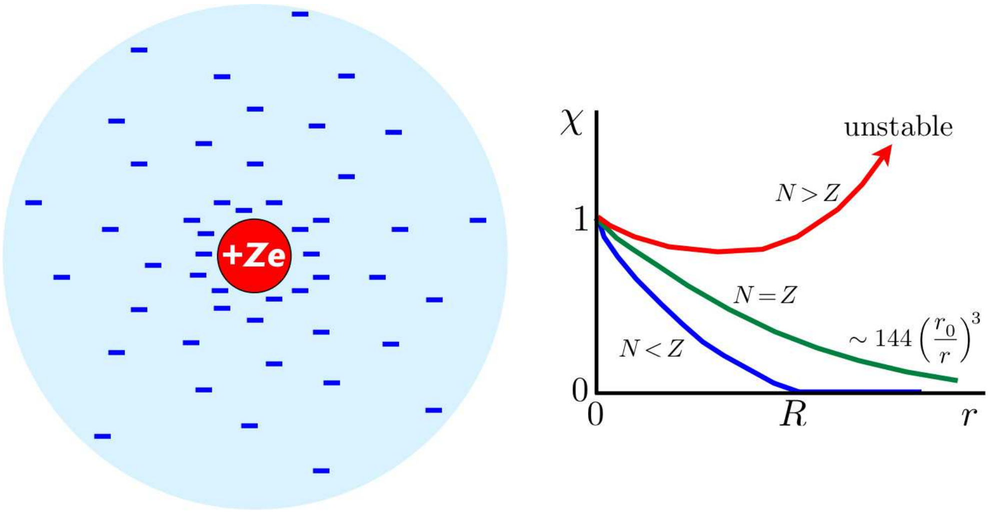

Figure 6.17: The Thomas-Fermi atom consists of a nuclear charge $+Ze$ surrounded by N electrons distributed in a cloud. The electric potential $\phi(\boldsymbol{r})$ felt by any electron at position $\boldsymbol{r}$ is screened by the electrons within this radius, resulting in a self-consistent potential $\phi(\boldsymbol{r}) = \phi_0 + (Ze^2/r)\,\chi(r/r_0)$.

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

$$r_0 = \frac{\hbar^2}{2me^2}\left(\frac{3\pi}{4\sqrt{Z}}\right)^{2/3} = 0.885\,Z^{-1/3}\,a_{\rm B} \quad , \tag{6.236}$$

where $a_{\rm B} = \frac{\hbar^2}{me^2} = 0.529\,\text{Å}$ 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

$$\boldsymbol{E} = -\boldsymbol{\nabla}\phi = \left[-\frac{Ze^2}{R^2}\,\chi(R/r_0) + \frac{Ze^2}{R\,r_0}\,\chi'(R/r_0)\right]\hat{\boldsymbol{r}} = \frac{(Z-N)\,e}{R^2}\,\hat{\boldsymbol{r}} \quad . \tag{6.237}$$

This requires

$$-\,t^*\,\chi'(t^*) = 1 - \frac{N}{Z} \quad . \tag{6.238}$$

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.

6.6 Appendix : Potts Model in One Dimension

6.6.1 Hamiltonian

The Potts model is defined by the Hamiltonian

$$H = -J \sum_{\langle ij \rangle} \delta_{\sigma_i,\sigma_j} - h \sum_i \delta_{\sigma_i,1} \quad . \tag{6.239}$$

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). Once again, it is not possible to compute the partition function on general lattices, however in one dimension we may once again find Z using the transfer matrix method.

6.6.2 Transfer matrix

On a ring of N sites, we have

$$Z = \mathrm{Tr}\, e^{-\beta H} = \sum_{\{\sigma_n\}} e^{\beta h \delta_{\sigma_1,1}} \, e^{\beta J \delta_{\sigma_1,\sigma_2}} \cdots e^{\beta h \delta_{\sigma_N,1}} \, e^{\beta J \delta_{\sigma_N,\sigma_1}} = \mathrm{Tr}\,\big(R^N\big) \quad , \tag{6.240}$$

where the $q \times q$ transfer matrix R is given by

$$R_{\sigma\sigma'} = e^{\beta J \delta_{\sigma\sigma'}} \, e^{\frac{1}{2}\beta h \delta_{\sigma,1}} \, e^{\frac{1}{2}\beta h \delta_{\sigma',1}} = \begin{cases} e^{\beta(J+h)} & \text{if } \sigma = \sigma' = 1 \\ e^{\beta J} & \text{if } \sigma = \sigma' \neq 1 \\ e^{\beta h/2} & \text{if } \sigma = 1 \text{ and } \sigma' \neq 1 \\ e^{\beta h/2} & \text{if } \sigma \neq 1 \text{ and } \sigma' = 1 \\ 1 & \text{if } \sigma \neq 1 \text{ and } \sigma' \neq 1 \text{ and } \sigma \neq \sigma' \quad . \end{cases} \tag{6.241}$$

In matrix form,

$$R = \begin{pmatrix} e^{\beta(J+h)} & e^{\beta h/2} & e^{\beta h/2} & \cdots & & e^{\beta h/2} \\ e^{\beta h/2} & e^{\beta J} & 1 & \cdots & & 1 \\ e^{\beta h/2} & 1 & e^{\beta J} & \cdots & & 1 \\ \vdots & \vdots & \vdots & \ddots & & \vdots \\ e^{\beta h/2} & 1 & 1 & \cdots & e^{\beta J} & 1 \\ e^{\beta h/2} & 1 & 1 & \cdots & 1 & e^{\beta J} \end{pmatrix} \tag{6.242}$$

The matrix R has q eigenvalues λ_j, with $j = 1, \ldots, q$. The partition function for the Potts chain is then

$$Z = \sum_{j=1}^{q} \lambda_j^N \quad . \tag{6.243}$$

We can actually find the eigenvalues of R analytically. To this end, consider the vectors

$$\phi = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \qquad , \qquad \psi = \big(q - 1 + e^{\beta h}\big)^{-1/2} \begin{pmatrix} e^{\beta h/2} \\ 1 \\ \vdots \\ 1 \end{pmatrix} \quad . \tag{6.244}$$

Then R may be written as

$$R = \big(e^{\beta J} - 1\big)\,\mathbb{I} + \big(q - 1 + e^{\beta h}\big)\,|\,\psi\,\rangle\langle\,\psi\,| + \big(e^{\beta J} - 1\big)\big(e^{\beta h} - 1\big)\,|\,\phi\,\rangle\langle\,\phi\,| \quad , \tag{6.245}$$

where $\mathbb{I}$ is the $q \times q$ identity matrix. When $h = 0$, we have a simpler form,

$$R = \big(e^{\beta J} - 1\big)\,\mathbb{I} + q\,|\,\psi\,\rangle\langle\,\psi\,| \quad . \tag{6.246}$$

From this we can read off the eigenvalues:

$$\begin{aligned} \lambda_1 &= e^{\beta J} + q - 1 \\ \lambda_j &= e^{\beta J} - 1 \quad , \quad j \in \{2, \ldots, q\} \quad , \end{aligned} \tag{6.247}$$

since $|\,\psi\,\rangle$ is an eigenvector with eigenvalue $\lambda = e^{\beta J} + q - 1$, and any vector orthogonal to $|\,\psi\,\rangle$ has eigenvalue $\lambda = e^{\beta J} - 1$. The partition function is then

$$Z = \big(e^{\beta J} + q - 1\big)^N + (q - 1)\big(e^{\beta J} - 1\big)^N \quad . \tag{6.248}$$

In the thermodynamic limit $N \to \infty$, only the λ_1 eigenvalue contributes, and we have

$$F(T, N, h = 0) = -N k_{\rm B} T \ln\big(e^{J/k_{\rm B}T} + q - 1\big) \qquad \text{for } N \to \infty \quad . \tag{6.249}$$

When h is nonzero, the calculation becomes somewhat more tedious, but still relatively easy. The problem is that $|\,\psi\,\rangle$ and $|\,\phi\,\rangle$ are not orthogonal, so we define

$$|\,\chi\,\rangle = \frac{|\,\phi\,\rangle - |\,\psi\,\rangle\langle\,\psi\,|\,\phi\,\rangle}{\sqrt{1 - \langle\,\phi\,|\,\psi\,\rangle^2}} \quad , \tag{6.250}$$

where

$$x \equiv \langle\,\phi\,|\,\psi\,\rangle = \left(\frac{e^{\beta h}}{q - 1 + e^{\beta h}}\right)^{1/2} \quad . \tag{6.251}$$

Now we have $\langle\,\chi\,|\,\psi\,\rangle = 0$, with $\langle\,\chi\,|\,\chi\,\rangle = 1$ and $\langle\,\psi\,|\,\psi\,\rangle = 1$, with

$$|\,\phi\,\rangle = \sqrt{1 - x^2}\,|\,\chi\,\rangle + x\,|\,\psi\,\rangle \quad . \tag{6.252}$$

and the transfer matrix is then

$$\begin{aligned}
R &= \big(e^{\beta J}-1\big)\,\mathbb{I} + \big(q-1+e^{\beta h}\big)\,|\,\psi\,\rangle\langle\,\psi\,| \\
&\qquad + \big(e^{\beta J}-1\big)\big(e^{\beta h}-1\big)\,\Big[(1-x^2)\,|\,\chi\,\rangle\langle\,\chi\,| + x^2\,|\,\psi\,\rangle\langle\,\psi\,| + x\,\sqrt{1-x^2}\,\Big(|\,\chi\,\rangle\langle\,\psi\,| + |\,\psi\,\rangle\langle\,\chi\,|\Big)\Big] \\
&= \big(e^{\beta J}-1\big)\,\mathbb{I} + \Bigg[\big(q-1+e^{\beta h}\big) + \big(e^{\beta J}-1\big)\big(e^{\beta h}-1\big)\bigg(\frac{e^{\beta h}}{q-1+e^{\beta h}}\bigg)\Bigg]\,|\,\psi\,\rangle\langle\,\psi\,| \\
&\qquad + \big(e^{\beta J}-1\big)\big(e^{\beta h}-1\big)\bigg(\frac{q-1}{q-1+e^{\beta h}}\bigg)\,|\,\chi\,\rangle\langle\,\chi\,| \\
&\qquad\qquad + \big(e^{\beta J}-1\big)\big(e^{\beta h}-1\big)\bigg(\frac{(q-1)\,e^{\beta h}}{q-1+e^{\beta h}}\bigg)^{1/2}\Big(|\,\chi\,\rangle\langle\,\psi\,| + |\,\psi\,\rangle\langle\,\chi\,|\Big) \quad ,
\end{aligned} \tag{6.253}$$

which in the two-dimensional subspace spanned by $|\,\chi\,\rangle$ and $|\,\psi\,\rangle$ is of the form

$$R = \begin{pmatrix} a & c \\ c & b \end{pmatrix} \quad . \tag{6.254}$$

Recall that for any 2×2 Hermitian matrix,

$$M = a_0\,\mathbb{I} + \boldsymbol{a}\cdot\boldsymbol{\tau} = \begin{pmatrix} a_0+a_3 & a_1-ia_2 \\ a_1+ia_2 & a_0-a_3 \end{pmatrix} \quad , \tag{6.255}$$

the characteristic polynomial is

$$P(\lambda) = \det\big(\lambda\,\mathbb{I}-M\big) = (\lambda-a_0)^2 - a_1^2 - a_2^2 - a_3^2 \quad , \tag{6.256}$$

and hence the eigenvalues are

$$\lambda_\pm = a_0 \pm \sqrt{a_1^2+a_2^2+a_3^2} \quad . \tag{6.257}$$

For the transfer matrix of eqn. 6.253, we obtain, after a little work,

$$\begin{aligned}
\lambda_{1,2} &= e^{\beta J} - 1 + \tfrac{1}{2}\Big[q-1+e^{\beta h} + \big(e^{\beta J}-1\big)\big(e^{\beta h}-1\big)\Big] \\
&\qquad \pm \tfrac{1}{2}\sqrt{\Big[q-1+e^{\beta h} + \big(e^{\beta J}-1\big)\big(e^{\beta h}-1\big)\Big]^2 - 4(q-1)\big(e^{\beta J}-1\big)\big(e^{\beta h}-1\big)} \quad .
\end{aligned} \tag{6.258}$$

There are $q-2$ other eigenvalues, however, associated with the $(q-2)$-dimensional subspace orthogonal to $|\,\chi\,\rangle$ and $|\,\psi\,\rangle$. Clearly all these eigenvalues are given by

$$\lambda_j = e^{\beta J} - 1 \qquad , \quad j \in \{3\,,\,\ldots\,,\,q\} \quad . \tag{6.259}$$

The partition function is then

$$Z = \lambda_1^N + \lambda_2^N + (q-2)\,\lambda_3^N \quad , \tag{6.260}$$

and in the thermodynamic limit $N\to\infty$ the maximum eigenvalue λ_1 dominates. Note that we recover the correct limit as $h\to 0$.