6 Interacting Classical Systems : Summary

• *Lattice-based models*: Amongst the many lattice-based models of physical interest are

$$\hat{H}_{\text{Ising}} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i \qquad ; \qquad \sigma_i \in \{-1, +1\}$$

$$\hat{H}_{\text{Potts}} = -J \sum_{\langle ij \rangle} \delta_{\sigma_i, \sigma_j} - H \sum_i \delta_{\sigma, 1} \qquad ; \qquad \sigma_i \in \{1, \ldots, q\}$$

$$\hat{H}_{\text{O}(n)} = -J \sum_{\langle ij \rangle} \hat{\boldsymbol{n}}_i \cdot \hat{\boldsymbol{n}}_j - \boldsymbol{H} \cdot \sum_i \hat{\boldsymbol{n}}_i \qquad ; \qquad \hat{\boldsymbol{n}}_i \in S^{n-1} \quad .$$

Here J is the coupling between neighboring sites and H (or $\boldsymbol{H}$) is a polarizing field which breaks a global symmetry (groups $\mathbb{Z}_2$, S_q, and $\text{O}(n)$, respectively). $J > 0$ describes a ferromagnet and $J < 0$ an antiferromagnet. One can generalize to include further neighbor interactions, described by a matrix of couplings J_{ij}. When $J = 0$, the degrees of freedom at each site are independent, and $Z(T, N, J = 0, H) = \zeta^N$, where $\zeta(T, H)$ is the single site partition function. When $J \neq 0$ it is in general impossible to compute the partition function analytically, except in certain special cases.

• *Transfer matrix solution in $d = 1$*: One such special case is that of one-dimensional systems. In that case, one can write $Z = \text{Tr}(R^N)$, where R is the *transfer matrix*. Consider a general one-dimensional model with nearest-neighbor interactions and Hamiltonian

$$\hat{H} = -\sum_n U(\alpha_n, \alpha_{n+1}) - \sum_n W(\alpha_n) \quad ,$$

where α_n describes the local degree of freedom, which could be discrete or continuous, single component or multi-component. Then

$$R_{\alpha\alpha'} = e^{U(\alpha, \alpha')/k_{\text{B}}T} \, e^{W(\alpha')/k_{\text{B}}T} \quad .$$

The form of the transfer matrix is not unique, although its eigenvalues are. We could have taken $R_{\alpha\alpha'} = e^{W(\alpha)/2k_{\text{B}}T} \, e^{U(\alpha, \alpha')/k_{\text{B}}T} \, e^{W(\alpha')/2k_{\text{B}}T}$, for example. The interaction matrix $U(\alpha, \alpha')$ may or may not be symmetric itself. On a ring of N sites, one has $Z = \sum_{i=1}^{K} \lambda_i^N$, where $\{\lambda_i\}$ are the eigenvalues and K the rank of R. In the thermodynamic limit, the partition function is dominated by the eigenvalue with the largest magnitude.

• *Higher dimensions*: For one-dimensional classical systems with finite range interactions, the thermodynamic properties vary smoothly with temperature for all $T > 0$. The *lower critical dimension* d_ℓ of a model is the dimension at or below which there is no finite temperature phase transition. For models with discrete global symmetry groups, $d_\ell = 1$, while for continuous global symmetries $d_\ell = 2$. In zero external field the ($d = 2$) square lattice Ising model has a critical temperature $T_{\text{c}} = 2.269 \, J$. On the honeycomb lattice, $T_{\text{c}} = 1.519 \, J$. For the $\text{O}(3)$ model on the cubic lattice, $T_{\text{c}} = 4.515 \, J$. In general, for unfrustrated systems, one expects for $d > d_\ell$ that $T_{\text{c}} \propto z$, where z is the *lattice coordination number* (*i.e.* number of nearest neighbors).

- *Nonideal classical gases*: For $\hat{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} u(|\boldsymbol{x}_i - \boldsymbol{x}_j|)$, one has $Z(T, V, N) = \lambda_T^{-Nd} Q_N(T, V)$, where

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

is the *configuration integral*. For the one-dimensional *Tonks gas* of N hard rods of length a confined to the region $x \in [0, L]$, one finds $Q_N(T, L) = (L - Na)^N$, whence the equation of state $p = nk_B T/(1 - na)$. For more complicated interactions, or in higher dimensions, the configuration integral is analytically intractable.

- *Mayer cluster expansion*: Writing the *Mayer function* $f_{ij} \equiv e^{-u_{ij}/k_B T} - 1$, and assuming $\int d^d r \, f(r)$ is finite, one can expand the pressure $p(T, z)$ and $n(T, z)$ as power series in the fugacity $z = \exp(\mu/k_B T)$, *viz.*

$$p/k_B T = \lambda_T^{-d} \sum_{\gamma} z^{n_\gamma} b_\gamma$$

$$n = \lambda_T^{-d} \sum_{\gamma} n_\gamma z^{n_\gamma} b_\gamma \quad .$$

The sum is over *unlabeled connected clusters* γ, and n_γ is the number of vertices in γ. The *dimensionless cluster integral* $b_\gamma(T)$ is obtained by assigning labels $\{1, \ldots n_\gamma\}$ to all the vertices, and computing

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

where f_{ij} appears in the product if there is a link between vertices i and j. s_γ is the *symmetry factor* of the cluster, defined to be the number of elements from the symmetric group $\mathcal{S}_{n_\gamma}$ which, acting on the labels, would leave the product $\prod_{i<j}^{\gamma} f_{ij}$ invariant. By definition, a cluster consisting of a single site has $b_\bullet = 1$. Translational invariance implies $b_\gamma(T) \propto V^0$. One then inverts $n(T, z)$ to obtain $z(T, n)$, and inserting the result into the equation for $p(T, z)$ one obtains the *virial expansion* of the equation of state,

$$p = nk_B T \left\{ 1 + B_2(T) \, n + B_3(T) \, n^2 + \ldots \right\} \quad .$$

where

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

is the kth *virial coefficient* and the sum over γ is limited to the set Γ_k of all *one-particle irreducible k-site clusters*. A one-particle irreducible cluster is a connected cluster which does not break apart into more than one piece if any of its sites and all of that site's connecting links are removed from the graph. Any site whose removal, along with all its connecting links, would result in a disconnected graph is called an *articulation point*. Irreducible clusters have no articulation points.

• *Liquids*: In the ordinary canonical ensemble,

$$P(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = Q_N^{-1} \cdot \frac{1}{N!} \, e^{-\beta W(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)} \quad,$$

where W is the total potential energy, and Q_N is the configuration integral,

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

We can use P, or its grand canonical generalization, to compute thermal averages, such as the average local density

$$n_1(\boldsymbol{r}) = \Big\langle \sum_i \delta(\boldsymbol{r} - \boldsymbol{x}_i) \Big\rangle$$

$$= N \int d^d x_2 \cdots \int d^d x_N \, P(\boldsymbol{r}, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$$

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

$$n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \Big\langle \sum_{i \neq j} \delta(\boldsymbol{r}_1 - \boldsymbol{x}_i) \, \delta(\boldsymbol{r}_2 - \boldsymbol{x}_j) \Big\rangle$$

$$= N(N-1) \int d^d x_3 \cdots \int d^d x_N \, P(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{x}_3, \ldots, \boldsymbol{x}_N) \quad.$$

• *Pair distribution function*: For translationally invariant simple fluids consisting of identical point particles interacting by a two-body central potential $u(r)$, the thermodynamic properties follow from the behavior of the *pair distribution function* (pdf),

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

where V is the total volume and $n = N/V$ the average density. The average energy per particle is then

$$\varepsilon(n, T) = \frac{\langle E \rangle}{N} = \tfrac{3}{2} \, k_\mathrm{B} T + 2\pi n \int_0^\infty dr \, r^2 \, g(r) \, u(r) \quad.$$

Here $g(r)$ is implicitly dependent on n and T as well In the grand canonical ensemble, the pdf satisfies the *compressibility sum rule*, $\int d^3 r \, [g(r) - 1] = k_\mathrm{B} T \, \kappa_T - n^{-1}$, where κ_T is the isothermal compressibility. Note $g(\infty) = 1$. The pdf also implies the *virial equation of state*,

$$p = n k_\mathrm{B} T - \tfrac{2}{3} \pi n^2 \int_0^\infty dr \, r^3 \, g(r) \, u'(r) \quad.$$

- *Scattering*: Scattering experiments are sensitive to momentum transfer $\hbar\boldsymbol{q}$ and energy transfer $\hbar\omega$, and allow determination of the *dynamic structure factor*

$$
\begin{aligned}
S(\boldsymbol{q},\omega) &= \frac{1}{N}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\,\Big\langle \sum_{l,l'} e^{i\boldsymbol{q}\cdot\boldsymbol{x}_l(0)}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_{l'}(t)}\Big\rangle_T \\
&= \frac{2\pi\hbar}{N}\sum_i P_i\,\sum_j \Big|\langle\, j\,|\, \sum_{l=1}^{N} e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_l}\,|\,i\,\rangle\Big|^2\,\delta(E_j - E_i + \hbar\omega) \quad,
\end{aligned}
$$

where $|\,i\,\rangle$ and $|\,j\,\rangle$ are (quantum) states of the system being studied, and P_i is the equilibrium probability for state i.[1] Integrating over all frequency, one obtains the *static structure factor*,

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

- *Theories of fluid structure* – The BBGKY hierarchy is set of coupled integrodifferential equations relating k- and $(k+1)$-particle distribution functions. In order to make progress, a truncation must be performed, expressing higher order distributions in terms of lower order ones. This results in various theories of fluids, known by their defining equations for the pdf $g(r)$. Examples include the Born-Green-Yvon equation, the Percus-Yevick equation, the hypernetted chains equation, the Ornstein-Zernike approximation, *etc.* Except in the simplest cases (such as the OZ approximation), these equations must be solved numerically. OZ approximation deserves special mention. There we write $S(\boldsymbol{q}) \approx \frac{1}{(R/\xi)^2 + R^2\boldsymbol{q}^2}$ for small q, where $\xi(T)$ is the *correlation length* and $R(T)$ is related to the range of interactions.
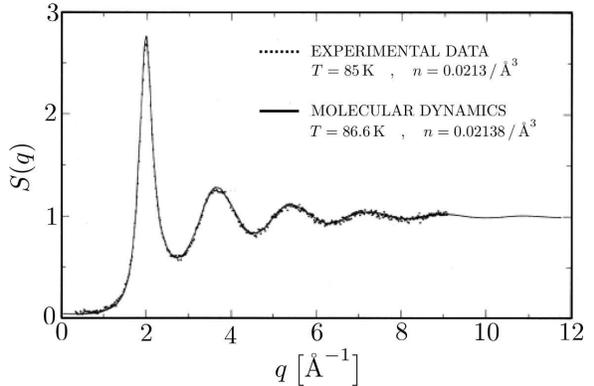

Figure 1: Comparison of the static structure factor as determined by neutron scattering work of J. L. Yarnell *et al.*, *Phys. Rev. A* **7**, 2130 (1973) with molecular dynamics calculations by Verlet (1967) for a Lennard-Jones fluid.

- *Debye-Hückel theory* – Due to the long-ranged nature of the Coulomb interaction, the Mayer function decays so slowly as $r \to \infty$ that it is not integrable, so the virial expansion is problematic. Progress can be made by a self-consistent mean field approach. For a system consisting of charges $\pm e$, one assumes a local electrostatic potential $\phi(\boldsymbol{r})$. Boltzmann

---

[1]In practice, what is measured is $S(q,\omega)$ convolved with spatial and energy resolution filters appropriate to the measuring apparatus.

statistics then gives a charge density

$$\rho(\boldsymbol{r}) = e\lambda_+^{-d} z_+ \, e^{-e\,\phi(\boldsymbol{r})/k_{\mathrm{B}}T} - e\lambda_-^{-d} z_- \, e^{e\,\phi(\boldsymbol{r})/k_{\mathrm{B}}T} \quad ,$$

where $\lambda_\pm$ and $z_\pm$ are the thermal de Broglie wavelengths and fugacities for the $+$ and $-$ species. Assuming overall charge neutrality at infinity, one has $\lambda_+^{-d} z_+ = \lambda_-^{-d} z_- = n_\infty$, and we have $\rho(\boldsymbol{r}) = -2en_\infty \, \sinh\!\big(e\,\phi(\boldsymbol{r})/k_{\mathrm{B}}T\big)$. The local potential is then determined self-consistently, using Poisson's equation:

$$\nabla^2 \phi = 8\pi en_\infty \, \sinh(e\phi/k_{\mathrm{B}}T) - 4\pi\rho_{\mathrm{ext}} \quad .$$

If $e\phi \ll k_{\mathrm{B}}T$, we can expand the sinh function to obtain $\nabla^2\phi = \kappa_{\mathrm{D}}^2 \, \phi - 4\pi\rho_{\mathrm{ext}}$, where the *Debye screening wavevector* is $\kappa_{\mathrm{D}} = (8\pi n_\infty e^2/k_{\mathrm{B}}T)^{1/2}$. The self-consistent potential arising from a point charge $\rho_{\mathrm{ext}}(\boldsymbol{r}) = Q\,\delta(\boldsymbol{r})$ is then of the Yukawa form $\phi(\boldsymbol{r}) = Q\exp(-\kappa_{\mathrm{D}}r)/r$ in three space dimensions.

• *Thomas-Fermi screening* – In an electron gas with $k_{\mathrm{B}}T \ll \varepsilon_{\mathrm{F}}$, we may take $T = 0$. If the Fermi energy is constant, we write $\varepsilon_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2(\boldsymbol{r})}{2m} - e\,\phi(\boldsymbol{r})$, and local electron number density is $n(\boldsymbol{r}) = k_{\mathrm{F}}^3(\boldsymbol{r})/3\pi^2$. Assuming a compensating smeared positive charge background $\rho_+ = e\,n_\infty$, Poisson's equation takes the form

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

If $e\phi \ll \varepsilon_{\mathrm{F}}$, we expand in the presence of external sources to obtain $\nabla^2\phi = \kappa_{\mathrm{TF}}^2 \, \phi - 4\pi\rho_{\mathrm{ext}}$, where $\kappa_{\mathrm{TF}} = (6\pi n_\infty e^2/\varepsilon_{\mathrm{F}})^{1/2}$ is the *Thomas-Fermi screening wavevector*. In metals, where the electron dispersion is a more general function of crystal momentum, the density response to a local potential $\phi(\boldsymbol{r})$ is $\delta n(\boldsymbol{r}) = e\,\phi(\boldsymbol{r})\,g(\varepsilon_{\mathrm{F}})$ to lowest order, where $g(\varepsilon_{\mathrm{F}})$ is the density of states at the Fermi energy. One then finds $\kappa_{\mathrm{TF}} = \sqrt{4\pi e^2 g(\varepsilon_{\mathrm{F}})}$.