Characteristics of Liquids

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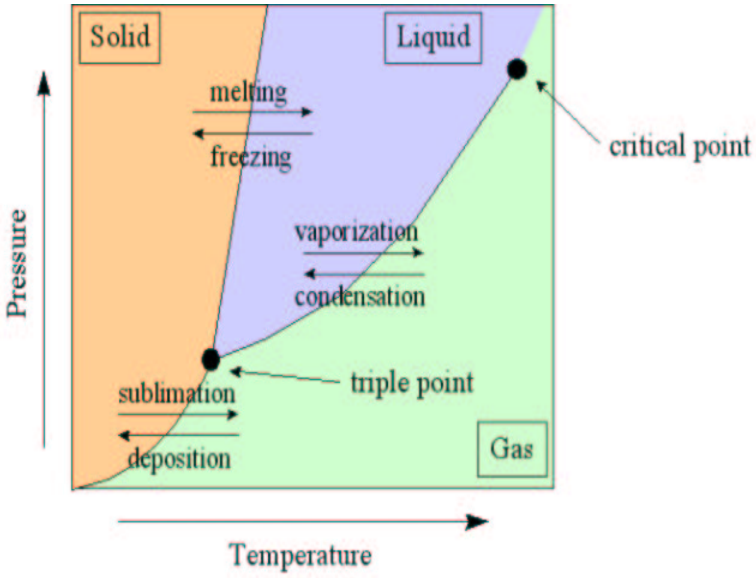
1 Physical Characteristics

- We have seen that at very high temperatures, we cannot distinguish between a gas and a liquid.
- Below some critical temperature (pressure), if we increase the pressure we get a discontinuity in density near the liquid-gas coexistence line.



- Similar discontinuity is observed from the "liquid" phase to a "solid" low-temperature or high pressure phase.
  - Typical change in density at the freezing transition is about 10%, i.e. $(\rho_s - \rho_l)/\rho_s \approx 0.1$.
- Coexistence curve for liquid-vapour is determined by equal-area Maxwell construction in unphysical regions of $P - V$ curve.
- It is possible to change "phase" from gas to liquid or vice-versa *without* observing a discontinuity in density.
  - Not clear how to define distinction between gas and liquid.

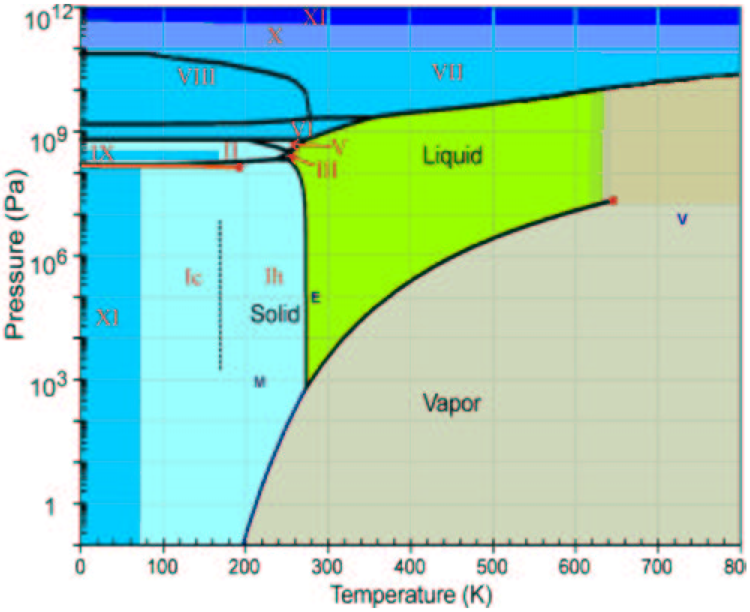
- The location of the phase boundaries can be crudely determined from thermodynamic measurements at one phase transition point (T^*, P^*) and using the Clapeyron equation:
  - Since the chemical potentials of the two phases must be equal,

$$\begin{aligned} d\mu_\alpha = -\tilde{S}_\alpha dT + \tilde{V}_\alpha dP &= -\tilde{S}_\beta dT + \tilde{V}_\beta dP = d\mu_\beta \\ \frac{dP}{dT} &= \frac{\tilde{S}_\beta - \tilde{S}_\alpha}{\tilde{V}_\beta - \tilde{V}_\alpha} = \frac{\Delta H}{T\Delta V}. \end{aligned}$$

  - For a melting transition for which $\Delta_{fus}H$ and $\Delta_{fus}V$ is relatively insensitive to temperature and pressure, integrating the equation gives the coexistence pressure for the solid-liquid coexistence line as

$$P = P^* + \frac{\Delta H}{\Delta V} \log\left(\frac{T}{T^*}\right).$$

- We will examine microscopic models that predict the coexistence curve for this transition shortly.
- Many different phase transitions exist and can, in principle, be calculated from microscopic models.



- There are some phenomenologically observed approximate scaling relationships between triple point and critical point parameters:

$$T_t \approx T_c/2 \qquad \rho_t \approx 3\rho_c.$$

- A "dense" fluid is a fluid with $\rho \geq \rho_c$.
  - Compressibility $\chi = kT(\partial\rho/\partial P)_T$ typically small (≤ 0.02). Recall that for an ideal gas $\chi = 1$. Roughly 1000 atm of pressure must be applied to produce density changes of 10%.

  - For dense fluids, the density is typically in the range $0.6 \leq \rho\sigma^3 \leq 0.9$, where σ is the typical distance between nearest neighbors in a solid (so $\rho\sigma^3 \approx 1$.)

- Obviously, there are significant differences on a macroscopic level between the way in which solids and liquids respond to a perturbation, but what about on a microscopic level? How can we understand microscopic order that is observed in X-ray diffraction of solids?

- To characterize microscopic order, we must develop a way of looking at correlations and structure at the atomic level and then rigorously define the features that differentiate solids and liquids.

2 Structural Characteristics

- For pairwise-additive potentials, all N-body interactions are represented in terms of interactions of two particles: Averages therefore involve averages over positions (and momenta) of two particles at most.

- We introduce the probability density for the positions as:

$$n(\mathbf{r}^{(N)}) = \int d\mathbf{p}^{(N)}\ f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = \frac{e^{-\beta U(\mathbf{r}^{(N)})}}{\int d\mathbf{r}^{(N)}\ e^{-\beta U(\mathbf{r}^{(N)})}} = \frac{e^{-\beta U(\mathbf{r}^{(N)})}}{Z_N}$$

  - $n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is the *joint* probability density of finding particle 1 in the vicinity of $\mathbf{r}_1$, particle 2 in the vicinity of of $\mathbf{r}_2$ and so on.

- Integrating over the coordinate positions of particles 2 to N gives:

$$\begin{aligned} n^{(1/N)}(\mathbf{r}_1) &\equiv \int d\mathbf{r}_2 \cdots d\mathbf{r}_N\ n(\mathbf{r}^{(N)}) \\ &= \text{Probability that particle 1 is in vicinity of } \mathbf{r}_1. \end{aligned}$$

- What is this (singlet) probability density for a system without an external potential? Assume

$$\begin{aligned} U(\mathbf{r}^{(N)}) &= \sum_{i<j} U(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{i=2}^{N} \sum_{j=i+1} U(|\mathbf{r}_i - \mathbf{r}_1 + \mathbf{r}_1 - \mathbf{r}_j|) \\ &= \sum_{i=2}^{N} \sum_{j=i+1} U(|\rho_i - \rho_j|) = \sum_{i=2}^{N} \sum_{j=i+1} U(|\rho_{ij}|) \end{aligned}$$

- Introducing a change of variables from $\{\mathbf{r}_2, \ldots, \mathbf{r}_N\}$ to $\{\rho_2, \ldots, \rho_N\}$, we get

$$\begin{aligned} \int_V d\mathbf{r}_2 \cdots d\mathbf{r}_N\, e^{-\beta U(\mathbf{r}^{(N)})} &= \int_V d\rho_2 \cdots d\rho_N\, e^{-\beta U(\rho_2, \ldots, \rho_N)} = C \quad \text{(a constant)} \\ Z_N &= \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N\, e^{-\beta U(\mathbf{r}^{(N)})} = \int_V d\mathbf{r}_1 C = CV \\ n^{(1/N)}(\mathbf{r}_1) &= \frac{C}{CV} = \frac{1}{V} \end{aligned}$$

  - The probability of finding particle 1 at position $\mathbf{r}_1$ is $1/V$. Thus all points in the volume are equally likely.

  - In the absence of an external potential, we are equally likely to find a given particle anywhere in the volume: on average, the system is uniform in particle (or mass) density.

- What is probability $\rho^{(1/N)}(\mathbf{r}_1)$ of finding *any* particle at a position $\mathbf{r}_1$? Note that the choice of reference particle was arbitrary, so

$$\rho^{(1/N)}(\mathbf{r}_1) = \sum_{i=1} n^{(1/N)}(\mathbf{r}_1) = N n^{(1/N)}(\mathbf{r}_1) = \frac{N}{V} = \text{bulk particle density.}$$

- Can we define a *dynamical variable* corresponding to the particle density? In other words, can we define a function $N(\mathbf{x}^{(N)}, \mathbf{r})$ such that $\langle N(\mathbf{x}^{(N)}, \mathbf{r})\rangle = \rho^{(1/N)}(\mathbf{r})$?

  - Need a function that tells us when there is a particle located in the interval $[\mathbf{r}, \mathbf{r} + d\mathbf{r}]$.

- Try the function

$$N(\mathbf{x}^{(N)}, \mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j)$$

  - Note that since all particles are contained in volume, $\int_V d\mathbf{r}\, N(\mathbf{x}^{(N)}, \mathbf{r}) = N$.

- Now

$$\begin{aligned}
\langle N(\mathbf{r})\rangle &= \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = \frac{\int d\mathbf{r}^{(N)} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) e^{-\beta U(\mathbf{r}^{(N)})}}{\int d\mathbf{r}^{(N)} e^{-\beta U(\mathbf{r}^{(N)})}} \\
&= \int d\mathbf{r}^{(N)} \frac{N \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\mathbf{r}^{(N)})}}{\int d\mathbf{r}^{(N)} e^{-\beta U(\mathbf{r}^{(N)})}} = N\langle \delta(\mathbf{r} - \mathbf{r}_1)\rangle \\
&= \frac{N \int d\mathbf{r}_1 d\rho_2 \cdots d\rho_N\, \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\rho_2, \ldots, \rho_N)}}{\int d\mathbf{r}_1 d\rho_2 \cdots d\rho_N\, \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\rho_2, \ldots, \rho_N)}} = \frac{N \int d\rho_2 \cdots d\rho_N\, \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\rho_2, \ldots, \rho_N)}}{\int d\mathbf{r}_1 d\rho_2 \cdots d\rho_N\, \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\rho_2, \ldots, \rho_N)}} \\
&= \frac{NC}{CV} = \frac{N}{V} = \rho^{(1/N)}(\mathbf{r}).
\end{aligned}$$

- These concepts are generalized in a straightforward fashion:

$$\begin{aligned}
\rho^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) &= N(N-1)\cdots(N-q+1) n^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) = \frac{N!}{(N-q)!} n^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) \\
n^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) &= \frac{\int d\mathbf{r}_{q+1} \cdots d\mathbf{r}_N\, e^{-\beta U(\mathbf{r}^{(N)})}}{Z_N}
\end{aligned}$$

- By definition, the *reduced density* can be interpreted to mean:

$$\rho^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) = \text{joint prob. that any particle is near } \mathbf{r}_1\text{, another near } \mathbf{r}_2 \text{ ....}$$

- **Properties of reduced probability density**

  1. From the definition of $\rho^{(q)}$ and the fact that $\int d\mathbf{r}_1 \cdots d\mathbf{r}_q\, n^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) = 1$,

$$\int d\mathbf{r}_1 \cdots d\mathbf{r}_q\, \rho^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) = \frac{N!}{(N-q)!}.$$

2. Since by definition $\int d\mathbf{r}_q\, n^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) = n^{(q-1/N)}(\mathbf{r}_q,\ldots,\mathbf{r}_{q-1})$, we have

$$\int d\mathbf{r}_q\, \rho^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) = \frac{1}{N-q}\rho^{(q-1/N)}(\mathbf{r}_q,\ldots,\mathbf{r}_{q-1})$$

- Example: $\rho^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) = \langle N(\mathbf{x}^{(N)},\mathbf{r}_1)N(\mathbf{x}^{(N)},\mathbf{r}_2)\rangle = N(N-1)n^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2)$.
- We define yet another reduced density (loosely called a distribution function) via the relation

$$\rho^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) = \rho^{(1/N)}(\mathbf{r}_1)\rho^{(1/N)}(\mathbf{r}_2)\cdots\rho^{(q/N)}(\mathbf{r}_q)g^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q)$$

  - In the absence of an external potential $\rho^{(1/N)}(\mathbf{r}_1) = N/V = \rho$, and $\rho^{(q/N)} = \rho^q g^{(q/N)}$.
- From this definition, we see that

$$\begin{aligned} g^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) &= \left(\frac{V}{N}\right)^q \frac{N!}{(N-q)!}\frac{\int d\mathbf{r}_{q+1}\cdots d\mathbf{r}_N\, e^{-\beta U}}{Z_N} \\ &= V^q\left(1+O\left(\frac{1}{N}\right)\right)\frac{\int d\mathbf{r}_{q+1}\cdots d\mathbf{r}_N\, e^{-\beta U}}{Z_N} \end{aligned}$$

- Consider $g^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2)$. Since

$$\begin{aligned} U(\mathbf{r}^{(N)}) &= U(|\mathbf{r}_1-\mathbf{r}_2|) + \sum_{i=3}^{N}\left[U(|\mathbf{r}_i-\mathbf{r}_1|) + U(\mathbf{r}_i-\mathbf{r}_2) + \sum j = i+1^N U(|\mathbf{r}_j-\mathbf{r}_i|)\right] \\ &= U(\rho_2) + \sum_{i=3}^{N} U(|\rho_i-\rho_2|) + \sum_{i=3}\left[U(\rho_i) + \sum_{j=i+1}^{N} U(|\rho_j-\rho_i|)\right], \end{aligned}$$

we see that U is independent of $\mathbf{r}_1$ but depends on $\rho_2 = \mathbf{r}_2 - \mathbf{r}_1$. Thus integration of $\exp\{-\beta U\}$ over $\rho_3,\ldots,\rho_N$ yields a function of ρ_2:

$$g^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{V^2\int d\rho_3\cdots d\rho_N\, e^{-\beta U}}{\int d\mathbf{r}_1 d\rho_2\cdots d\rho_N e^{-\beta U}} = g^{(2)}(r_{12}),$$

with $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ for a spherically-symmetric potential $U(\mathbf{r}_{12}) = U(r_{12})$.

- For a system with a spherically-symmetric potential,

$$\rho^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) = \rho^2 g^{(2/N)}(r_{12}).$$

  - Can be interpreted as probability of observing a second particle a distance r_{12} away from first particle in the volume.
- Note that since $\int d\mathbf{r}_1 d\mathbf{r}_2\, \rho^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) = N(N-1)$,

$$N(N-1) = \rho^2\int d\mathbf{r}_1 d\mathbf{r}_2\, g^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) = \rho^2\int d\mathbf{r}_1 d\mathbf{r}_{12} g^{(2/N)}(r_{12}) = N\rho\int d\mathbf{r}_{12} g^{(2/N)}(r_{12}),$$

so $\rho\int d\mathbf{r}_{12} g^{(2/N)}(r_{12}) = N-1 = \int_0^\infty dr 4\pi r^2 \rho g^{(2/N)}(r)$.

- Often, superscript on *radial distribution function* $g^{(2/N)}(r) = g(r)$ is dropped.
- $\rho g(r) d\mathbf{r}$ is the probability of observing a particle in volume $d\mathbf{r}$ around a particle located at origin.
- $g(r)$ can be measured directly through light or x-ray scattering experiments.

2.1 Relationship of radial distribution function to thermodynamic parameters

- Averages of dynamical variables that depend on pairwise interactions can be expressed as averages over reduced distribution functions.

- The average energy in the canonical ensemble is given by:

$$E \;=\; \langle H(\mathbf{x}^{(N)})\rangle = \int d\mathbf{x}^{(N)}\, H(\mathbf{x}^{(N)}) f(\mathbf{x}^{(N)}) = \int d\mathbf{x}^{(N)} \left[\frac{\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}}{2m} + \sum_{i<j} U(r_ij)\right].$$

- For this Hamiltonian, the coordinates and momenta are separable, and hence the canonical probability density can be written:

$$f(\mathbf{r}^{(N)},\mathbf{p}^{(N)}) \;=\; \Pi(\mathbf{p}^{(N)})n(\mathbf{r}^{(N)}) \qquad \Pi(\mathbf{p}^{(N)}) = \frac{e^{-\beta\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}/2m}}{\int d\mathbf{p}^{(N)} e^{-\beta\mathbf{p}^{(N)}\cdot\mathbf{p}^{(N)}/2m}}$$

  - The density $\Pi(\mathbf{p}^{(N)})$ is known as the *Maxwell distribution.*

- The average of the kinetic energy part gives the ideal gas contribution $3/2NkT$, so

$$\begin{aligned}
E &= \frac{3}{2}NkT + \sum_{i<j}\int d\mathbf{r}^{(N)}\, U(r_{ij})n(\mathbf{r}^{(N)}) = \frac{3}{2}NkT + \frac{N(N-1)}{2}\int d\mathbf{r}^{(N)}\, U(r_{12})n(\mathbf{r}^{(N)}) \\
&= \frac{3}{2}NkT + \frac{N(N-1)}{2}\int d\mathbf{r}_1 d\mathbf{r}_2\, U(r_{12})n^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) \\
&= \frac{3}{2}NkT + \frac{N(N-1)}{2}\int d\mathbf{r}_1 d\mathbf{r}_2\, U(r_{12})n^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) \\
&= \frac{3}{2}NkT + \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2\, U(r_{12})\rho^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) \qquad \text{since } N(N-1)n^{(2/N)} = \rho^{(2/N)} \\
&= \frac{3}{2}NkT + \frac{V}{2}\int d\mathbf{r}_{12}\, U(r_{12})\rho^{(2/N)}(r_{12}) \\
&= N\left(\frac{3}{2}kT + \frac{1}{2\rho}\int d\mathbf{r}_{12}\, U(r_{12})\rho^{(2/N)}(r_{12})\right) \\
&= N\left(\frac{3}{2}kT + \frac{1}{2}\rho\int d\mathbf{r}_{12}\, U(r_{12})g(r_{12})\right) \qquad \text{since } \rho^{(2/N)} = \rho^2 g
\end{aligned}$$

so

$$\boxed{E = N\left(\tfrac{3}{2}kT + 2\pi\rho\int_0^\infty dr_{12}\; r_{12}^2 U(r_{12})g(r_{12})\right)}$$

- Recall that the pressure is given by:

$$\begin{aligned}
P &= kT\left(\frac{\partial \ln Q_N}{\partial V}\right)_T \qquad \text{but since } Q_N = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\frac{1}{N!}Z_N(V,\beta) \\
&= kT\left(\frac{\partial \ln Z_N}{\partial V}\right)_T = \frac{kT}{Z_N}\frac{\partial}{\partial V}\left[\int_V d\mathbf{r}^{(N)}\, e^{-\beta U(\mathbf{r}^{(N)})}\right]
\end{aligned}$$

  - The partial derivative of $Z_N(V,\beta)$ with respect to V is tricky to evaluate since the volume dependence is in the limits of the integral.

- Trick: define a coordinate transform $x_i = V^{-1/3} r_i$ for each component of $\mathbf{r}_i$, then $d\mathbf{r}_i = V d\mathbf{x}$, so $d\mathbf{r}^{(N)} = V^N d\mathbf{x}^{(N)}$ with $\mathbf{r}^{(N)} = V^{1/3}\mathbf{x}^{(N)}$. With this transform,

$$Z_N(V,\beta) = V^N \int_{\text{unit sphere}} d\mathbf{x}^{(N)}\, e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})}$$

- Note that

$$\frac{\partial U(V^{1/3}\mathbf{x}^{(N)})}{\partial V} = \frac{\partial U}{\partial (V^{1/3}\mathbf{x}^{(N)})}\frac{\partial (V^{1/3}\mathbf{x}^{(N)})}{\partial V} = \frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}} \cdot \frac{1}{3V} V^{1/3}\mathbf{x}^{(N)} = \frac{1}{3V}\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}} \cdot \mathbf{r}^{(N)}$$

so

$$\begin{aligned}
\frac{\partial Z_N}{\partial V} &= NV^{N-1}\int_{\text{u.s}} d\mathbf{x}^{(N)}\, e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})} + V^N \int d\mathbf{x}^{(N)}\, \frac{\partial}{\partial V} e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})} \\
&= \frac{N}{V} V^N \int_{\text{u.s}} d\mathbf{x}^{(N)}\, e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})} - V^N \frac{\beta}{3V}\int d\mathbf{x}^{(N)} \left(\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}} \cdot \mathbf{r}^{(N)}\right) e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})} \\
&= \rho \int_V d\mathbf{r}^{(N)}\, e^{-\beta U(\mathbf{r}^{(N)})} - \frac{\beta}{3V}\int d\mathbf{r}^{(N)} \left(\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}} \cdot \mathbf{r}^{(N)}\right) e^{-\beta U(\mathbf{r}^{(N)})} \\
&= \rho Z_N - \beta \int d\mathbf{r}^{(N)}\, \frac{1}{3V}\left(\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}} \cdot \mathbf{r}^{(N)}\right) e^{-\beta U(\mathbf{r}^{(N)})}
\end{aligned}$$

- Using this expression in the equation for the pressure gives:

$$\begin{aligned}
P &= \frac{kT}{Z_N}\frac{\partial}{\partial V}\left[\int_V d\mathbf{r}^{(N)}\, e^{-\beta U(\mathbf{r}^{(N)})}\right] \\
&= \rho kT - \frac{1}{Z_N}\frac{1}{3V}\int_V d\mathbf{r}^{(N)} \left(\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}} \cdot \mathbf{r}^{(N)}\right) e^{-\beta U(\mathbf{r}^{(N)})}
\end{aligned}$$

- Now for a pairwise additive potential,

$$\begin{aligned}
\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}} \equiv \sum_{k=1}^{N} \frac{\partial U}{\partial \mathbf{r}_k} \cdot \mathbf{r}_k &= \sum_{i<j}\left(\mathbf{r}_i \cdot \frac{\partial U(r_{ij})}{\partial \mathbf{r}\_i} + \mathbf{r}_j \cdot \frac{\partial U(r_{ij})}{\partial \mathbf{r}_j}\right) \\
&= \sum_{i<j} \frac{dU(r_{ij})}{d\mathbf{r}_{ij}} \cdot \mathbf{r}_{ij}
\end{aligned}$$

- Thus the pressure equation is:

$$\begin{aligned}
\frac{P}{kT} &= \rho - \frac{\beta}{3V}\frac{\int_V d\mathbf{r}^{(N)} \sum_{i<j}\left(\nabla_{\mathbf{r}_{ij}} U(r_{ij}) \cdot \mathbf{r}_{ij}\right) e^{-\beta U}}{Z_N} \\
&= \rho - \frac{\beta}{3V}\frac{N(N-1)}{2}\frac{\int d\mathbf{r}_1 d\mathbf{r}_2 \left(\nabla_{\mathbf{r}_{12}} U(r_{12}) \cdot \mathbf{r}_{12}\right) \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U}}{Z_N} \\
&= \rho - \frac{\beta}{3V}\frac{N(N-1)}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \left(\nabla_{\mathbf{r}_{12}} U(r_{12}) \cdot \mathbf{r}_{12}\right) \frac{1}{V^2} g^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) \\
&\qquad \text{since } g^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) \approx \frac{V^2 \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U}}{Z_N} \\
&\approx \rho - \rho^2 \frac{\beta}{6V}\int d\mathbf{r}_1 d\mathbf{r}_2 \left(\nabla_{\mathbf{r}_{12}} U(r_{12}) \cdot \mathbf{r}_{12}\right) g(r_{12})
\end{aligned}$$

so we conclude that

$$\boxed{\frac{P}{kT} = \rho - \frac{\beta}{6}\rho^2 \int_V d\mathbf{r}_{12}\ (\nabla_{\mathbf{r}_{12}} U(r_{12}) \cdot \mathbf{r}_{12})\, g(r_{12})}$$

- Note that these equations are *exact* in the thermodynamic limit. All that is required is knowledge of $g(r)$.
- As is evident from this result, an estimator for the pressure is:

$$\begin{aligned}\Pi(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) &= \frac{1}{3V}\sum_{i=1}^{N}\left(\frac{p_i^2}{m} - \sum_{j<i}\left(\nabla_{\mathbf{r}_{ij}} U(r_{ij}) \cdot \mathbf{r}_{ij}\right)\right) \\ \langle \Pi(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})\rangle &= P \qquad \text{since } \left\langle \frac{\mathbf{p}^{(N)} \cdot \mathbf{p}^{(N)}}{m}\right\rangle = 3NkT.\end{aligned}$$

- Density expansion of $g(r)$ in pressure equation should give same results as virial expansion.

3 Measurement of the radial distribution function

- Local changes in polarizability due to density fluctuations lead to non-uniform scattering of light.
  - Electrons and nuclei displaced in an electric field induces an oscillating dipole that emits radiation:

    $$\mu_i(t) = \mu(\mathbf{r}_i, t) = \alpha_i E_0 e^{i(\mathbf{k}\cdot\mathbf{r}_i - \omega t)},$$

    where μ_i is the induced dipole for particle i located at $\mathbf{r}_i$.
  - Can define a total induced dipole density for the system as:

    $$\begin{aligned}\mu(\mathbf{r}, t) &= \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)\mu(\mathbf{r}_i, t) \approx \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)\alpha E_0 e^{i(\mathbf{k}\cdot\mathbf{r}_i - \omega_0 t)} \\ &= \alpha E_0 e^{i(\mathbf{k}_0\cdot\mathbf{r} - \omega_0 t)} \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t)) = \alpha E_0(\mathbf{r}, t) N(\mathbf{x}^{(N)}, \mathbf{r}, t)\end{aligned}$$

  - Solving Maxwell's equation for the total scattered electric field $E_s(\mathbf{r}, t)$ at position $\mathbf{r}$ far from the sample due to the dipole moment density is complicated, but the solution looks like:

    $$E_s(\mathbf{r}, t) \sim \int d\mathbf{r}' \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} d\omega'\, \omega'^2 e^{i(\mathbf{k}\cdot\mathbf{r}' - \omega_0 t)} \exp\left\{ i\omega' \left(t' - t + \frac{r}{c} - \frac{1}{c}\hat{\mathbf{r}}\cdot\mathbf{r}'\right)\right\} N(\mathbf{x}^{(N)}, \mathbf{r}', t')$$

- The measurement process correlates the intensity of the scattered light at different times and time averages:

$$\begin{aligned}I(\mathbf{r}, \omega) &\sim \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \lim_{T\to\infty}\frac{1}{T}\int_{-T}^{T} dt' E_s(\mathbf{r}, t' + \tau)E_s^*(\mathbf{r}, t') \\ &= \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau}\, \langle E_s(\mathbf{r}, \tau)E_s^*(\mathbf{r}, 0)\rangle\end{aligned}$$

by the ergodic theorem. Doing lots of math, we get finally

$$I(\mathbf{r},\omega) \quad \sim \quad \left(\frac{\alpha}{2\pi c^2 r}\right)^2 S(\mathbf{k},\Omega)$$

where $\mathbf{k} = \mathbf{k}_0 - (\omega_0/c)\hat{\mathbf{r}}$ and $\Omega = \omega_0 - \omega$ is the frequency shift between the incident and scattered light.

- The *scattering function* $S(\mathbf{k},\omega)$ is called the *dynamic structure factor* and is given by:

$$\begin{aligned} S(\mathbf{k},\omega) &\equiv \int_{-\infty}^{-\infty} dt\, e^{i\omega t} \left\langle N(\mathbf{x}^{(N)},\mathbf{k},t) N(\mathbf{x}^{(N)},-\mathbf{k})\right\rangle \qquad \text{where} \\ N(\mathbf{x}^{(N)},\mathbf{k},t) &= \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} N(\mathbf{x},\mathbf{r},t) = \sum_{i=1}^{N} e^{i\mathbf{k}\cdot r_i(t)} \end{aligned}$$

- This is a *time dependent correlation function.*
- $S(\mathbf{k},\omega)$ is the Fourier transform in the time domain of $S(\mathbf{k},t)$, which measures the correlation between the spatial Fourier component of the density at different times.
  - Need an effective theory for evaluating dynamics of system: either computer simulation or a model (will discuss later).
- Measurement process can also focuss on *static* correlations:

$$\begin{aligned} I(\mathbf{r}) &\sim \lim_{T\to\infty} \frac{1}{T}\int_{-T}^{T} dt' E_s(\mathbf{r},t') E_s^*(\mathbf{r},t') \\ &\sim \langle E_s(\mathbf{r},0) E_s^*(\mathbf{r},0)\rangle \sim S(\mathbf{k})\delta(\omega-\omega_0) \end{aligned}$$

  - $S(\mathbf{k})$ is called the *static structure factor* and is given by

$$S(\mathbf{k}) \quad \equiv \quad \left\langle N(\mathbf{x}^{(N)},\mathbf{k}) N(\mathbf{x}^{(N)},-\mathbf{k})\right\rangle .$$

  - Note that in this measurement $\omega = \omega_0$ meaning that the scattered light has the same frequency as the incident light (i.e no shift). This is called *Rayleigh scattering.*
- What is the relation between $S(\mathbf{k})$ and $g(r)$?
  - Note that from the definition of $S(\mathbf{k})$,

$$\begin{aligned} S(\mathbf{k}) &= \left\langle \sum_{j=1}^{N}\sum_{l=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_j} e^{-i\mathbf{k}\cdot\mathbf{r}_l}\right\rangle = \left\langle N + N(N-1) e^{i\mathbf{k}\cdot(\mathbf{r}_2-\mathbf{r}_1)}\right\rangle \\ &= \langle N\rangle + \int d\mathbf{r}_1 d\mathbf{r}_2\, e^{i\mathbf{k}\cdot\mathbf{r}_{12}} \rho^{(2/N)}(r_{12}) \\ &= \langle N\rangle + V\rho^2 \int d\mathbf{r}_{12} e^{i\mathbf{k}\cdot r_{12}} g(r_{12}) \end{aligned}$$

  - There are two contributions to $S(\mathbf{k})$, that due to scattering off the uniform density and that due to fluctuations. That is, we write:

$$N(\mathbf{x}^{(N)},\mathbf{r}) = \rho + \left(N(\mathbf{x}^{(N)},\mathbf{r}) - \langle N(\mathbf{x}^{(N)},\mathbf{r})\rangle\right) \equiv \rho + \hat{N}(\mathbf{x}^{(N)},\mathbf{r}).$$

Thus

$$
\begin{aligned}
N(\mathbf{k}) &= \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \left(\rho + \hat{N}(\mathbf{r})\right) \\
&= \frac{\langle N\rangle}{V} V \delta_{k,0} + \hat{N}(\mathbf{k}) = \langle N\rangle \delta_{k,0} + \hat{N}(\mathbf{k})
\end{aligned}
$$

and

$$
S(\mathbf{k}) = \langle N\rangle^2 \delta_{k,0} + \langle \hat{N}(\mathbf{k})\hat{N}(-\mathbf{k})\rangle.
$$

- The $\mathbf{k} \neq 0$ (non-forward scattering) is related to the radial distribution function by

$$
\begin{aligned}
\langle \hat{N}(\mathbf{k})\hat{N}(-\mathbf{k})\rangle &= \int d\mathbf{r} d\mathbf{r}'\, e^{i\mathbf{k}\cdot\mathbf{r}} e^{i\mathbf{k}'\cdot\mathbf{r}'} \left(\langle N(\mathbf{r})N(\mathbf{r}')\rangle - \langle N(\mathbf{r})\rangle\langle N(\mathbf{r}')\rangle\right) \\
&= \int d\mathbf{r} d\mathbf{r}'\, e^{i\mathbf{k}\cdot\mathbf{r}} e^{i\mathbf{k}'\cdot\mathbf{r}'} \left(\rho\delta(\mathbf{r}-\mathbf{r}') + \rho^2 (g(|\mathbf{r}-\mathbf{r}'|) - 1)\right) \\
&= \langle N\rangle + \langle N\rangle \rho \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \left(g(r) - 1\right) \\
&= \langle N\rangle \left[1 + \rho \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \left(g(r) - 1\right)\right]
\end{aligned}
$$

- From experimental light-scattering measurements of $S(\mathbf{k})$ over a range of values of $\mathbf{k}$, one can invert the Fourier transform and obtain a functional form for $g(r)$!
- Note that when $k = 0$, $\langle \hat{N}(\mathbf{k})\hat{N}(-\mathbf{k})\rangle = \sigma_N^2$ and is related to the compressibility:

$$
kT \left(\frac{\partial \rho}{\partial p}\right)_{T,V} = 1 + \rho \int d\mathbf{r} \left(g(r) - 1\right)
$$

- Since the compressibility diverges as a critical point is approached, the integral

$$
\int d\mathbf{r} \left(g(r) - 1\right) \to \infty
$$

  and the function $g(r) - 1$ becomes *long-ranged.* Thus $S(\mathbf{k})$ becomes very large and there is a lot of light scattering. This is called *critical opalescence.*

- We introduce a new function $h(r_{12}) = g(r_{12}) - 1$ to measure the total influence of molecule 1 on molecule 2 at distance r_{12}.
  - Note from the compressibility equation above:

$$
\left(\frac{\partial p}{\partial \rho}\right)_{T,V} = \frac{kT}{1 + \rho \int d\mathbf{r}\, h(r)}.
$$

  - In 1914, Ornstein and Zernike proposed a division of $h(r_{12})$ into a direct part $c(r_{12})$ and indirect part via:

$$
h(r_{12}) = c(r_{12}) + \rho \int d\mathbf{r}_3\, c(r_{13}) h(r_{23})
$$

  - The indirect part is the direct influence of of particle 1 on a third particle 3, which in turn exerts a density-weighted influence on particle 2.

  - Generally expect $c(r)$ to be a shorter-ranged function than $h(r)$. Can show this using expansions in terms of Mayer $f(r)$ functions.
  - Like $h(r)$, $c(r)$ is a function of the scaler distance r.
  - Fourier-transforming the above relation gives:

$$\begin{aligned} \hat{h}(k) &= \int d\mathbf{r}_1 d\mathbf{r}_2 \; e^{i\mathbf{k}\cdot\mathbf{r}_{12}} h(r_{12}) = \hat{c}(k) + \rho\hat{h}(k)\hat{c}(k) \\ &= \frac{\hat{c}(k)}{1-\rho\hat{c}(k)} \end{aligned}$$

- A diverging compressibility near the critical point implies that $\hat{h}(0)$ diverges, and hence $\hat{c}(0) \sim \rho^{-1}$ is well-behaved.
  - Consider expanding the Fourier transform $\hat{c}(k)$:

$$\begin{aligned} \hat{c}(k) &= \int d\mathbf{r}\; e^{i\mathbf{k}\cdot\mathbf{r}} c(r) = \int d\mathbf{r}\; \left(1 + i\mathbf{k}\cdot\mathbf{r} + \frac{1}{2} i\mathbf{k}\cdot\mathbf{r}\mathbf{r}\cdot i\mathbf{k} + \cdots\right) c(r) \\ &= \int d\mathbf{r}\; \left(1 - \frac{k^2}{6} r^2 + \cdots\right) c(r) \\ &= \hat{c}(0) - k^2 d + \ldots \qquad \text{where } d = 2\pi/3 \int_0^\infty dr\; r^4 c(r) \end{aligned}$$

    for an isotropic system in which $c(r)$ depends only on $|\mathbf{r}|$.

- Inserting this relation in the expression for $\hat{h}(k)$, for small k for which $kd << 1$,

$$\hat{h}(k) \approx \frac{\hat{c}(0)}{1-\rho\left(\hat{c}(0)-k^2 d\right)} = \frac{\hat{c}(0)/\rho d}{(1-\rho\hat{c}(0))/\rho d + k^2}.$$

  - Inverting this Fourier transform gives:

$$\begin{aligned} h(r) &= \frac{\hat{c}(0)}{4\pi\rho d}\frac{e^{-\lambda r}}{r} \qquad \lambda = \left(\frac{1-\rho\hat{c}(0)}{\rho d}\right)^{1/2} \\ g(r) &= 1 + \frac{\hat{c}(0)}{4\pi\rho d}\frac{e^{-\lambda r}}{r}. \end{aligned}$$

  - Note that as the critical point is approached, $\lambda \to 0$ and hence $h(r) \sim 1/r$.

- Away from the critical point, spatial correlations are *exponentially* damped at long length scales (small k).

3.1 Structure in a solid

- We have seen that correlations in positions of particles die off exponentially in liquid systems. How does this differ in solids?

- As the temperature $T \to 0$, the system adopts a configuration that minimizes the potential energy $V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$.
  - Configuration of atoms typically regular, with positions on a lattice points $\mathbf{q}^*(l, m.n) = l\mathbf{e}_1 + m\mathbf{e}_2 + n\mathbf{e}_3 = \mathbf{q}^*_{\mathbf{R}}$, where $\{l, m, n\} = \mathbf{R}$ is a triplet of integers and $\mathbf{e}_i$ are unit vectors.

- At finite temperature, there are deviations $\mathbf{u}(\mathbf{R})$ from ideal positions $\mathbf{q}^*_{\mathbf{R}}$,

$$\mathbf{q}_{\mathbf{R}} = \mathbf{q}^*_{\mathbf{R}} + \mathbf{u}(\mathbf{R}).$$

- The singlet density $\rho^{(1)}(\mathbf{r})$ is now non-uniform and periodic:

$$\rho^{(1)}(\mathbf{r}) = \sum_{\mathbf{R}} \rho(\mathbf{r} - \mathbf{q}_{\mathbf{R}} | \mathbf{q}_{\mathbf{R}})$$

- $\rho(\mathbf{r} - \mathbf{q}_{\mathbf{R}} | \mathbf{q}_{\mathbf{R}})$ is the *cell density*, taken to be zero except in the cell centered at $\mathbf{q}_{\mathbf{R}}$. At $T = 0$, $\rho(\mathbf{r} - \mathbf{q}_{\mathbf{R}} | \mathbf{q}_{\mathbf{R}}) = \delta(\mathbf{r} - \mathbf{q}^*_{\mathbf{R}})$.
- We can define a set of *reciprocal lattice vectors* $\mathbf{G}$ defined so that

$$\mathbf{G} \cdot \mathbf{q}^*_{\mathbf{R}} = 2\pi n \qquad n = \{\dots, -1, 1, 0, 1, \dots\}.$$

- Note that

$$\begin{aligned}
\rho^{(1)}(\mathbf{r}) &= \langle N(\mathbf{r}) \rangle = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) = \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{q}_{\mathbf{R}}) = \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{q}^*_{\mathbf{R}} - \mathbf{u}(\mathbf{R})) \\
\rho^{(1)}(\mathbf{k}) &= \sum_{\mathbf{R}} \left\langle e^{i\mathbf{k}\cdot\mathbf{q}_{\mathbf{R}}} \right\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{q}^*_{\mathbf{R}}} \left\langle e^{i\mathbf{k}\cdot\mathbf{u}(\mathbf{R})} \right\rangle.
\end{aligned}$$

  - If $T = 0$, $\mathbf{U}(\mathbf{R}) = 0$ and $\rho(\mathbf{k}) = \rho^{(1)}(\mathbf{k}) = \delta_{\mathbf{k},\mathbf{G}}$.
- The energetic cost of deformations in the potential energy is

$$\begin{aligned}
V(\mathbf{q}_{\mathbf{R}}) &= V^*(\mathbf{q}^*_{\mathbf{R}}) + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial^2 V}{\partial \mathbf{q}_{\mathbf{R}} \partial \mathbf{q}_{\mathbf{R}'}} \cdot \mathbf{u}(\mathbf{R}') + \cdots \\
&= V^*(\mathbf{q}^*_{\mathbf{R}}) + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} \mathbf{u}_\alpha(\mathbf{R}) \mathbf{K}_{\alpha\beta}(\mathbf{q}^*_{\mathbf{R}} - \mathbf{q}^*_{\mathbf{R}'}) \mathbf{u}_\beta(\mathbf{R}') + \cdots \\
&= V^*(\mathbf{q}^*_{\mathbf{R}}) + V^q(\mathbf{u}(\mathbf{R})) + \cdots
\end{aligned}$$

  where sums over repeated Greek indices are implied.
- Elements of the matrix $\mathbf{K}$ must satisfy symmetries of regular lattice, so $\mathbf{K}$ depends only on the difference in positions.
- The precise form of the matrix $\mathbf{K}$ is determined by microscopic interactions since it depends on the interaction potential V.
- Probability of observing a particular set of deformations is

$$P(\mathbf{u}(\mathbf{R})) = \frac{e^{-\beta V^q(\mathbf{u}(\mathbf{R}))}}{\int \prod_{\mathbf{R}} d\mathbf{u}(\mathbf{R}) e^{-\beta V^q(\mathbf{u}(\mathbf{R}))}}.$$

- Can diagonalize the interaction potential matrix by using Fourier modes,

$$\mathbf{u}_\alpha(\mathbf{r}) = \sum_{\mathbf{k}}{}' \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{N}} \mathbf{u}_\alpha(\mathbf{k})$$

  where the prime indicates a restriction over wavevectors in first Brillouin zone are included in sum.

  - The interaction potential is now:

$$V = V^* + \frac{1}{2}{\sum_{\mathbf{k}}}' \mathbf{u}_\alpha(\mathbf{k})\mathbf{K}_{\alpha\beta}(k)\mathbf{u}_\beta(\mathbf{k})^* + \cdots$$

- Example: 1-Dimensional chain with harmonic potential energy

$$V(u_i) = V^* + \frac{K_1}{2}\sum_n (u_{n+1} - u_n)^2 + \cdots .$$

  - Normal mode decomposition is

$$u_n = \frac{1}{2\pi}\int_{-\pi}^{\pi} dk e^{-ikn} u(k) \qquad \text{where} \quad u(k) = \sum_n e^{ikn} u_n$$

  - The potential energy is

$$\begin{aligned} V &= V^* + \frac{K_1}{2}\sum_n \int_{-\pi}^{\pi} \frac{dk}{2\pi}\frac{dk'}{2\pi}\left(e^{ik} - 1\right)\left(e^{ik'} - 1\right) e^{-i(k+k')n} u(k)u(k') + \cdots \\ &= V^* + \frac{K_1}{2}\int_{-\pi}^{\pi} \frac{dk}{2\pi}(2 - 2\cos(k))|u(k)|^2 + \cdots \end{aligned}$$

  - The frequency of the normal modes is therefore $\omega(k) = \sqrt{2K_1(1 - \cos k)/m}$.
  - In the limit $k \to 0$, $\omega(k) = v|k|$, with sound velocity $v = \sqrt{K_1/m}$.
  - Normal modes are called *phonons*, and k dependence of frequency ω of modes is known as the *dispersion* relation.
  - Adding second and further neighbor interactions gives

$$\begin{aligned} \frac{K(k)}{2} &= K_1(1 - \cos k) + K_2(1 - \cos 2k) + \cdots \approx \frac{\tilde{K}}{2}k^2 \quad \text{as} \quad k \to 0 \\ V &= V^* + \int_{-\pi}^{\pi} \frac{dk}{2\pi}\frac{\tilde{K}}{2}k^2|u(k)|^2 + \cdots \end{aligned}$$

- At low temperatures, only modes with $\hbar\omega(k) < kT$ are excited, so for low T, $\hbar v|k| < kT$ or $|k| < kT/(\hbar v)$.

- Typically, $\hbar v/(kT) \gg a$, where a is the lattice spacing. Thus, $ka \ll 1$, and the excitations represent distortions on length scales that are very long compared to the lattice spacing.

- Can carry out *course-graining procedure* to go over to a continuum limit: $\mathbf{u}(\mathbf{R}) \to \mathbf{u}(\mathbf{x})$ by eliminating short-lengthscale modes (large k).

  - Various correspondances:

$$\begin{aligned} \sum_{\mathbf{R}} &\to \int d\mathbf{x} \\ \int \prod_{\mathbf{R}} d\mathbf{u}(\mathbf{R}) &\to \int \mathcal{D}\mathbf{u}(\mathbf{x}) \\ P(\mathbf{u}(\mathbf{R})) &\to P(\mathbf{u}(\mathbf{x})) = \frac{e^{-\beta V[\mathbf{u}(\mathbf{x})]}}{\int \mathcal{D}\mathbf{u}(\mathbf{x}) e^{-\beta V[\mathbf{u}(\mathbf{x})]}} \\ V[\mathbf{u}(\mathbf{x})] &= \frac{1}{2}\int d\mathbf{x}d\mathbf{x}'\ \mathbf{u}_\alpha(\mathbf{x})K_{\alpha\beta}(\mathbf{x},\mathbf{x}')\mathbf{u}_\beta(\mathbf{x}'). \end{aligned}$$

- *Elasticity theory* considers the simplest long-wavelength (small k) physics consistent with symmetries of system: $V[\mathbf{u}]$ must be invariant under symmetry operations.
  - For an isotropic system, $V[\mathbf{u}] = V[\mathbf{u}']$ where $\mathbf{u}' = \mathcal{R}\cdot\mathbf{u}+\mathbf{c}$, for a rotation matrix $\mathcal{R}$ and constant vector $\mathbf{c}$.
  - For translational invariance, V must be function of derivatives of $\mathbf{u}$.
  - For rotational invariance, V must transform as a scalar.
  - Useful local quantity, the symmetric *strain field* is defined as:

    $$u_{\alpha\beta}(\mathbf{x}) = \frac{1}{2}\left(\frac{\partial \mathbf{u}_\alpha}{\partial \mathbf{x}_\beta} + \frac{\partial \mathbf{u}_\beta}{\partial \mathbf{x}_\alpha}\right)$$

    from which the most general quadratic potential functional in d-dimensions is

    $$V[\mathbf{u}(\mathbf{x})] = \int d^d\mathbf{x}\,\left[\mu\, u_{\alpha\beta}u_{\alpha\beta} + \frac{\lambda}{2}u_{\alpha\alpha}u_{\beta\beta}\right].$$
  - The elastic constants μ and λ are known as *Lame coefficients.*
  - The rotational invariance is more transparent in the Fourier basis:

    $$V[\mathbf{u}(\mathbf{k})] = \int \frac{d\mathbf{k}}{(2\pi)^d}\left[\frac{\mu}{2}k^2|\mathbf{u}(\mathbf{k})|^2 + \frac{\mu+\lambda}{2}\left(\mathbf{k}\cdot\mathbf{u}(\mathbf{k})\right)^2\right]$$
  - Note that we can differentiate between *longitudinal modes* $u_l = \hat{k}\cdot\mathbf{u}(\mathbf{k})$ which are directed along $\hat{k}$ and $d-1$ *transverse modes* u_t orthogonal to $\hat{k}$ with interactions:

    $$\begin{aligned} V_l[\mathbf{u}(\mathbf{k})] &= \frac{2\mu+\lambda}{2}\int\frac{d\mathbf{k}}{(2\pi)^d}k^2u_l(\mathbf{k})^2 \quad \to \quad v_l = \sqrt{(2\mu+\lambda)/m} \\ V_t[\mathbf{u}(\mathbf{k})] &= \frac{\mu}{2}\int\frac{d\mathbf{k}}{(2\pi)^d}k^2u_t(\mathbf{k})^2 \quad \to \quad v_t = \sqrt{2\mu/m}. \end{aligned}$$

- Note that both types of modes are *independent* and Gaussian-distributed, so

  $$\begin{aligned} \langle u_l(\mathbf{k})u_l(\mathbf{k}')\rangle &= \frac{\delta(\mathbf{k}+\mathbf{k}')}{(2\mu+\lambda)k^2} \\ \langle u_t(\mathbf{k})u_t(\mathbf{k}')\rangle &= \frac{\delta(\mathbf{k}+\mathbf{k}')}{\mu k^2} \end{aligned}$$

- Now writing $\mathbf{u}(\mathbf{k}) = \hat{k}u_l(\mathbf{k}) + \sum_{i=1}^{d-1}\hat{\mathbf{e}}_iu_t(\mathbf{k})$, we set that

  $$\begin{aligned} \langle \mathbf{u}(\mathbf{k})\mathbf{u}(\mathbf{k})^*\rangle &= \hat{k}\hat{k}\left\langle u_l^2\right\rangle + \sum_{i=1}^{d-1}\hat{\mathbf{e}}_i\hat{\mathbf{e}}_i\left\langle u_t^2\right\rangle \\ &= \mathbf{I}\left\langle u_t^2\right\rangle - \hat{\mathbf{k}}\hat{\mathbf{k}}\left(\left\langle u_t^2\right\rangle - \left\langle u_l^2\right\rangle\right) \\ &= \frac{kT}{k^2}\left[\frac{\mathbf{I}}{\mu} - \frac{\hat{k}\hat{k}}{\mu}\frac{\mu+\lambda}{2\mu+\lambda}\right] \end{aligned}$$

so that

$$\begin{aligned}
\mathbf{G}\cdot\langle\mathbf{u}(\mathbf{x})\mathbf{u}(\mathbf{x})\rangle\cdot\mathbf{G} &= \frac{kT}{(2\pi)^3}\int d\mathbf{k}\;\mathbf{G}\cdot\langle\mathbf{u}(\mathbf{k})\mathbf{u}(\mathbf{k})^*\rangle\cdot\mathbf{G} \\
&= \frac{kT}{(2\pi)^3}\int d\mathbf{k}\;\mathbf{G}\cdot\left[\frac{\mathbf{I}}{\mu k^2}-\frac{\hat{\mathbf{k}}\hat{\mathbf{k}}}{\mu k^2}\frac{\mu+\lambda}{2\mu+\lambda}\right]\cdot\mathbf{G} \\
&= \frac{kT}{(2\pi)^3}\frac{\pi}{a}\left[\frac{4\pi G^2}{\mu}-\frac{4\pi G^2}{3\mu}\frac{\mu+\lambda}{2\mu+\lambda}\right] \\
&= \frac{kTG^2}{6\pi\mu a}\left(\frac{5\mu+2\lambda}{2\mu+\lambda}\right).
\end{aligned}$$

- Now looking at $\rho(\mathbf{r})$:

$$\begin{aligned}
\rho(\mathbf{r}) &= \left(\frac{1}{2\pi}\right)^3\int d\mathbf{k}\;e^{-i\mathbf{k}\cdot\mathbf{r}}\,\langle N(\mathbf{k})\rangle = \left(\frac{1}{2\pi}\right)^3\int d\mathbf{k}\;e^{-i\mathbf{k}\cdot\mathbf{r}}\sum_{\mathbf{R}}\left\langle e^{i\mathbf{k}\cdot\mathbf{q}_{\mathbf{R}}}\right\rangle \\
&= \left(\frac{1}{2\pi}\right)^3\int d\mathbf{k}\;e^{-i\mathbf{k}\cdot\mathbf{r}}\sum_{\mathbf{R}}e^{i\mathbf{k}\cdot\mathbf{q}^*_{\mathbf{R}}}\left\langle e^{i\mathbf{k}\cdot\mathbf{u}(\mathbf{R})}\right\rangle
\end{aligned}$$

  - For Gaussian-distributed displacements in three dimensions,

$$\left\langle e^{i\mathbf{k}\cdot\mathbf{u}(\mathbf{R})}\right\rangle = e^{-\frac{1}{2}\mathbf{k}\cdot\langle\mathbf{u}(\mathbf{R})\mathbf{u}(\mathbf{R})\rangle\cdot\mathbf{k}} = e^{-\frac{kT\,k^2}{12\pi\mu a}\left(\frac{5\mu+2\lambda}{2\mu+\lambda}\right)} = \rho_{dw}(k).$$

  - $\rho_{dw}(k)$ is known as the *Debye-Waller* factor.
  - Thus, the density is

$$\begin{aligned}
\rho(r) &= \sum_{\mathbf{R}}\frac{1}{(2\pi)^3}\int d\mathbf{k}\;e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{q}^*_R)}e^{-\frac{kT\,k^2}{12\pi\mu a}\left(\frac{5\mu+2\lambda}{2\mu+\lambda}\right)} \\
&= \sum_{\mathbf{R}}\left(\frac{1}{2\pi\sigma^2}\right)^{3/2}e^{-(\mathbf{r}-\mathbf{q}^*_{\mathbf{R}})^2/2\sigma^2} \qquad \sigma^2=\frac{kT}{6\pi\mu a}\left(\frac{5\mu+2\lambda}{2\mu+\lambda}\right).
\end{aligned}$$

    - Simple elasticity theory gives Gaussian distributed density profile around each lattice point rather than delta function.
    - Width of Gaussian broadens with temperature.

- What about light scattering?

$$S(k) = \sum_{\mathbf{R},\mathbf{R}'}\left\langle e^{i\mathbf{k}\cdot(\mathbf{q}_{\mathbf{R}}-\mathbf{q}_{\mathbf{R}'})}\right\rangle = N\sum_{\mathbf{R}}\left\langle e^{i\mathbf{k}\cdot(\mathbf{q}_{\mathbf{R}}-\mathbf{q}_0)}\right\rangle = N\sum_{\mathbf{R}}e^{i\mathbf{k}\cdot(\mathbf{q}^*_{\mathbf{R}}-\mathbf{q}^*_0)}\left\langle e^{i\mathbf{k}\cdot(\mathbf{u}_{\mathbf{R}}-\mathbf{u}_0)}\right\rangle$$

  - Note that at $T=0$, $S(k)$ is a sum of delta functions at the reciprocal lattice vectors, called *Bragg peaks.*

$$S(k) = N\sum_{\mathbf{G}}\delta(\mathbf{k}-\mathbf{G}) = \frac{N}{(2\pi)^3}\sum_{G}\int d\mathbf{x}\;e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}}$$

  - At finite temperature, only get contributions near lattice vectors since oscillatory function.

- In continuum limit, defining $\delta\mathbf{u}(\mathbf{x}) = \mathbf{u}(\mathbf{x}) - \mathbf{u}(0)$,

  $$S(k) \approx N \sum_{\mathbf{G}} \int d\mathbf{x}\ e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}} \left\langle e^{i\mathbf{G}\cdot\delta\mathbf{u}(\mathbf{x})} \right\rangle$$

  Noting that

  $$\begin{aligned} \mathbf{G}\cdot\langle\delta\mathbf{u}(x)\delta\mathbf{u}(x)\rangle\cdot\mathbf{G} &= \frac{1}{(2\pi)^3}\int d\mathbf{q}\ \left(2 - 2\cos\mathbf{q}\cdot\mathbf{x}\right)\mathbf{G}\cdot\langle\mathbf{u}(\mathbf{q})\mathbf{u}(\mathbf{q})^*\rangle\cdot\mathbf{G} \\ &= \frac{2kTG^2}{12\pi\mu a}\left(\frac{5\mu+2\lambda}{2\mu+\lambda}\right)\left(1 - \frac{\sin\tilde{x}}{\tilde{x}}\right) \qquad \tilde{x} = \frac{\pi|\mathbf{x}|}{a}, \\ &= 2\eta(G)\left(1 - \frac{\sin\tilde{x}}{\tilde{x}}\right) \approx 2\eta(G), \end{aligned}$$

  where $\eta(G) = \frac{kTG^2}{12\pi\mu a}\left(\frac{5\mu+2\lambda}{2\mu+\lambda}\right)$, we have

  $$\begin{aligned} S(k) &= N\sum_{\mathbf{G}}\int d\mathbf{x}\ e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}} e^{-\frac{1}{2}\mathbf{G}\cdot\langle\delta\mathbf{u}(x)\delta\mathbf{u}(x)\rangle\cdot\mathbf{G}} \approx N\sum_{\mathbf{G}}\int d\mathbf{x}\ e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}} e^{-\eta(G)} \\ &\sim N\sum_{\mathbf{G}}\delta(\mathbf{k}-\mathbf{G})e^{-\eta(G)} \end{aligned}$$

  - Essentially delta function peaks at reciprocal lattice vectors with magnitude diminished by Debye-Waller factor.
  - Solid system shows long-ranged periodicity in X-ray scattering.

- In two-dimensions, fluctuations diverge logarithmically (*unbounded*) and

  $$\mathbf{G}\cdot\langle\delta\mathbf{u}(x)\delta\mathbf{u}(x)\rangle\cdot\mathbf{G} \sim \frac{kTG^2}{4\pi\mu}\left(\frac{3\mu+\lambda}{2\mu+\lambda}\right)\ln\frac{x}{a} = \eta(G)\ln\frac{x}{a}$$

  implying that

  $$\begin{aligned} S(k) &= N\sum_{\mathbf{G}}\int d\mathbf{x}\ e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}} e^{-\eta(G)\ln x/a} = N\sum_{\mathbf{G}}\int d\mathbf{x}\ e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{x}}\left(\frac{a}{|\mathbf{x}|}\right)^{\eta(G)} \\ &\sim N\sum_{\mathbf{G}}\frac{1}{|\mathbf{k}-\mathbf{G}|^{2-\eta(G)}}. \end{aligned}$$

  - Delta function at $\mathbf{k} = \mathbf{G}$ broadened to power law singularities.
  - Large $|\mathbf{G}|$ singularities not visible.
  - More peaks disappear as temperature increases.
  - Large scale fluctuations destroy regular periodic order, with $g(r)$ showing *algebraic* decay.
  - Mermin-Wagner theorem: no spontaneous breaking of continuous symmetry in systems with short-ranged interactions in dimensions $d \leq 2$.
  - Even though no long-ranged translational order, it can be shown that there is true long-ranged orientational order (in angle between local lattice bonds and a reference axis) in 2d solids.