Notes on an introduction to the condensed states of matter
Prof. S. Caprara

1 Condensed states of matter. Atoms and molecules (henceforth, generically particles, meant in the sense of constituents of matter) at large distances tend to attract. When the density is low and the particles are far apart, or when the temperature is high and thermal agitation predominates, the tendency to attraction is not strong enough to give rise to a condensed state and matter is found in a gaseous phase. As the density is increased (for instance, exerting an external pressure) and/or the temperature is lowered, the tendency to attraction eventually prevails and matter condenses into a liquid phase. In a liquid, the particles are loosely bound and can move quite freely, like in a gas, so that a liquid shares with a gas the property of being fluid. At even larger density and/or lower temperature, the particles are eventually trapped by their mutual interaction and are no longer free to move. They can only oscillate around their equilibrium positions and a solid phase is achieved. Depending on the conditions under which solidification occurred, the solid can be amorphous or crystalline. An amorphous solid shares with a liquid the following property: when seen from the standpoint of an individual particle, the system appears to be homogeneous at large distances. Said in other words, there is no correlation between the positions of two particles when they are far apart. In a crystalline solid, the situation is completely different. A crystal is a spatially ordered array of particles that results in an inhomogeneous and anisotropic structure. When seen from the standpoint of an individual particle, the crystal appears as a regular (periodic) arrangement of particles in any given direction. The system is characterized by the so-called long-range (i.e., long-distance) order, as opposed to the short-range order that is found in liquids and amorphous solids.

To put the previous discussion in a more quantitative perspective, let me introduce some characteristic quantities and provide numerical estimates. The average distance between two particles in a system with density (number of particles per unit volume) equal to ρ is $d = \rho^{-3}$. This must be compared with two typical length scales. The first is the de Broglie thermal wavelength Λ which is obtained assuming that the thermal energy $\kappa_B T$ (with κ_B the Boltzmann constant) is comparable to the quantum kinetic energy of a particle confined within a region of size Λ:

$$\kappa_B T = \frac{\hbar^2}{2m\Lambda^2} \quad \Rightarrow \quad \Lambda = \frac{\hbar}{\sqrt{2m\kappa_B T}}.$$

The translational motion of the particles is classical as long as $d \gg \Lambda$. At low temperatures and/or high densities the behavior of a particle is genuinely quantum mechanical. Few substances are found in a liquid phase when the quantum regime occurs. Helium is a noticeable exception, due to its light mass and to the weak interaction between helium atoms

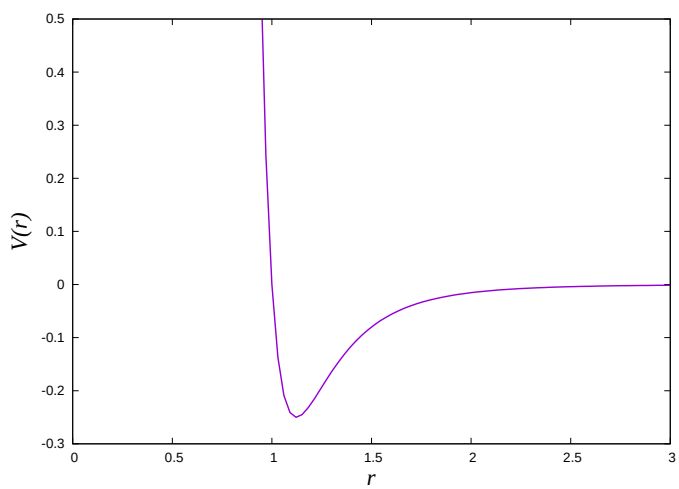

FIG. 1: Behavior of the Lennard-Jones potential. Units are such that $\epsilon = 1$, $\sigma = 1$.

The second length scale that characterizes the behavior of the system is set by the particle-particle interaction $V(r)$. There are several phenomenological forms for $V(r)$, for the sake of definiteness, I shall adopt the Lennard-Jones

potential (see Fig. 1)

$$V(r) = \epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right],$$

that was originally adopted because it captures the short-distance (hard core) repulsion and the large-distance attraction, and is suitable for computational purposes (the repulsive term is the square of the attractive term). The parameter ϵ has the dimension of an energy, while σ is a length scale. The equilibrium position corresponds to the minimum of $V(r)$ and is found at $r = r^* \equiv 2^{1/6}\,\sigma \approx 1.122\,\sigma$, where $V(r^*) = -\epsilon/4$. In the following I take $\overline{V} \equiv \epsilon/4$ as a typical energy of a particle within the potential well. The system is in the low-density regime when $d \gg \sigma$, and in the high-density regime when $d \approx \sigma$.

If $\kappa_B T \gg \overline{V}$, then the kinetic energy is too large for a particle to be trapped in the potential well and the system behaves as a gas. When $\kappa_B T \approx \overline{V}$ the condensation occurs and the system becomes a liquid. When $\kappa_B T \ll \overline{V}$ a particle can only make small oscillations around the minimum of the potential and the system is a solid.

2 The van der Waals equation of state. A perfect gas is described by the equation of state $pV = NT$, where p is the pressure V is the volume, N is the number of particles. I am using units such that the Boltzmann constant $\kappa_B = 1$. This equation ignores the interactions between the particles and provides a reasonable description of the state of matter only at sufficient low density $\rho = N/V$ and/or high temperature T. It cannot describe the condensation into a liquid phase.

The simplest model to discuss condensation is the van der Waals equation of state, in which the effect of the interactions between particles is introduced in a very crude, yet effective way. I shall not attempt a formal derivation of the van der Waals equation of state, rather provide some phenomenological arguments that motivate its form.

Let me introduce the specific volume $v = V/N = \rho^{-1}$ (the volume occupied by one particle) so that the equation of state of a perfect gas is $pv = T$. Now, it can be argued that, because of the hard-core repulsion between two particles, there is an excluded volume b (per particle), which means that two particles can never get too close, so that the volume per particle that is really accessible is $\tilde{v} = v - b$, with b determined by a characteristic length scale of the particle-particle interaction potential.

Furthermore, because of the attraction between particles, the pressure p exerted by the particles on the surface of the vessel that contains them (the one that is experimentally measured) is smaller than the pressure $\tilde{p}$ that particles would exert away from the surface of the vessel, where any individual particle is surrounded by other particles in all directions and the average attraction is zero. To estimate the effect of the attraction we must first compute the number of particles within some fixed distance from the surface of the vessel, $u\rho = u/v$, where u is the volume of a shell near the surface. Each particle within this shell will interact with all particles within a volume w set by the characteristic length scale of the particle-particle interaction potential, whose number is $w\rho = w/v$. The total effect of the interaction is then proportional to the product of these two numbers, so that one can write

$$\tilde{p} = p + \frac{a}{v^2},$$

with a suitable constant $a \propto uw$.

According to the previous arguments, the equation of state that takes into account the effect of the interactions must be written as

$$T = \tilde{p}\tilde{v} = \left(p + \frac{a}{v^2}\right)(v - b) \quad \Rightarrow \quad p = \frac{T}{v-b} - \frac{a}{v^2}.$$

The equation of state of a perfect gas is found for $a = 0,\ b = 0$.

It is easy to show that the isotherms are monotonically decreasing for $T > T^* \equiv \frac{8a}{27b}$ whereas they develop a local maximum and a local minimum, for $T < T^*$ (see Fig. 2). When $T = T^*$ the isotherm has an inflection point with horizontal tangent at $p = p^* \equiv \frac{a}{27b^2}$, $v = v^* \equiv 3b$. The interpretation is the following: for $T > T^*$ the system exists in a single phase, which is a gas. At $T \gg T^*$ the isotherms are very cose to those of a perfect gas, except when v approaches b; for $T < T^*$ the portions of the isotherm that are decreasing functions of v correspond to two different phases, a gas, for $v \gg b$, and a hardly compressible liquid for $v \approx b$. The two phases are separated by a portion of the isotherm that corresponds to unstable states, with p an increasing function of v. These states cannot be realized as equilibrium states, so the system cannot exist in a single phase in this region of parameter space. The stable state correspond to a coexistence of the two phases. In the coexistence region p is constant as a function of v and what changes is only the relative weight of the two coexisting phase, with the fraction of gas increasing for increasing v. The constant value of the pressure is determined by the equilibrium of the two coexisting phases, according to

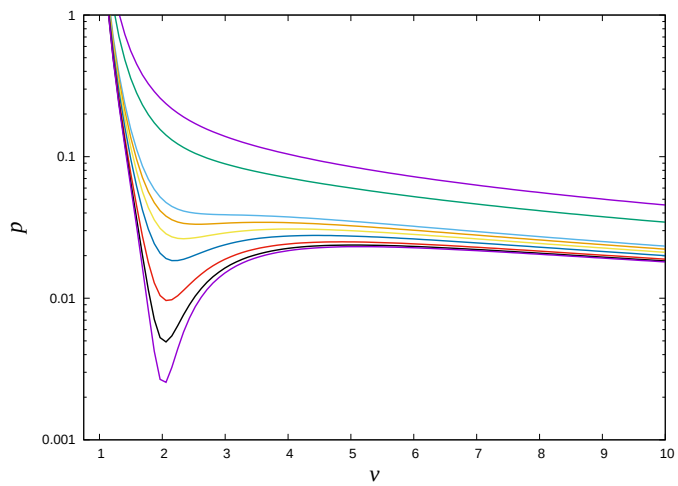

FIG. 2: Behavior of the van der Waals' isotherms. Notice the log scale on the pressure axis. Units are such that $a = 1$, $b = 1$. Temperatures are (from top to bottom) $T = 0.5, 0.4, 0.3, 0.29, 0.28.0.27, 0.26, 0.255, 0.2525$. With the chosen units the critical isotherm is found at $T = 0.2963$.

the so-called Maxwell construction: the constant pressure horizontal line must cut the corresponding van der Waal's isotherm in such a way that the areas of the portion above and below the horizontal line is the same.

3 Density correlations. Let me define the microscopic density for a system of N particles located at $\boldsymbol{r}_i$ $(i = 1, ..., N)$.

$$\hat{\rho}(\boldsymbol{r}) = \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i),$$

where δ is the Dirac delta function. This density is defined such that $\int_V \hat{\rho}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = N$ gives the total number of particles, the integral being extended over the volume V occupied by the system. However, this function is too detailed and very noisy, it is zero at all points where there is not a particle and diverges at the locations of the particles. It is more convenient to define a smoother density. This is achieved either by averaging over volumes that contain a large number of particles, so that the average is meaningful, but are still sufficiently small so that it makes sense to attribute the value of the density to a point $\boldsymbol{r}$, or performing a thermodynamical average over a statistical ensemble. The function

$$\rho(\boldsymbol{r}) = \langle \hat{\rho}(\boldsymbol{r}) \rangle,$$

where the angular brackets denote a suitable average, is still such that $\int_V \rho(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = N$, but is now a smooth function. For a translationally invariant system, the average density cannot depend on the position, hence

$$\rho(\boldsymbol{r}) = \rho = \frac{N}{V}$$

is a constant giving the number of particles per unit volume.

The average distribution of the particles in the system is not particularly insightful, however experimental techniques, like X-ray or neutron scattering experiments, can probe the correlations between the positions of the particles. Let me define the function

$$G(\boldsymbol{r}) = \frac{1}{N} \left\langle \int_V \hat{\rho}(\boldsymbol{r}')\hat{\rho}(\boldsymbol{r}' + \boldsymbol{r})\,\mathrm{d}\boldsymbol{r}' \right\rangle,$$

which is a measure of the correlation between the density at $\boldsymbol{r}'$ and the density at $\boldsymbol{r}' + \boldsymbol{r}$, integrated with respect to the position $\boldsymbol{r}'$. One can notice that, if the system is not characterized by long-range order in the position of the particles, like in a gas, in a liquid, or in an amorphous solid (as I said in Sec. 1, in a crystalline solid the situation is different),

then the densities become uncorrelated as $|\boldsymbol{r}|$ grows large. This means that the densities at points separated by a large distance $|\boldsymbol{r}|$ are statistically independent. Hence $\langle\hat{\rho}(\boldsymbol{r}')\hat{\rho}(\boldsymbol{r}'+\boldsymbol{r})\rangle \approx \langle\hat{\rho}(\boldsymbol{r}')\rangle\langle\hat{\rho}(\boldsymbol{r}'+\boldsymbol{r})\rangle = \rho^2$ and

$$G(\boldsymbol{r}) \approx \frac{1}{N}\int_V \rho^2\,\mathrm{d}\boldsymbol{r}' = \frac{V}{N}\rho^2 = \rho,$$

for large $|\boldsymbol{r}|$. In general, one has

$$G(\boldsymbol{r}) = \frac{1}{N}\left\langle \int_V \sum_{i=1}^{N}\delta(\boldsymbol{r}'-\boldsymbol{r}_i)\sum_{j=1}^{N}\delta(\boldsymbol{r}'+\boldsymbol{r}-\boldsymbol{r}_j)\,\mathrm{d}\boldsymbol{r}'\right\rangle = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N}\delta(\boldsymbol{r}+\boldsymbol{r}_i-\boldsymbol{r}_j)\right\rangle.$$

Now, there are N terms with $i=j$, hence

$$G(\boldsymbol{r}) = \delta(\boldsymbol{r}) + \frac{1}{N}\left\langle \sum_{i\neq j}\delta(\boldsymbol{r}+\boldsymbol{r}_i-\boldsymbol{r}_j)\right\rangle \equiv \delta(\boldsymbol{r}) + \rho\, g(\boldsymbol{r}),$$

where the delta-like contribution trivially represents the autocorrelation of a particle with itself, while the second contribution is a true measure of density correlations (i.e., of the probability that there are two particles separated by $\boldsymbol{r}$). The factor ρ in front of the definition of $g(\boldsymbol{r})$ is such that, since for large $|\boldsymbol{r}|$ one has $G(\boldsymbol{r})\to\rho$, then $g(\boldsymbol{r})\to 1$. In an isotropic system correlations only depend on $r=|\boldsymbol{r}|$. In Fig. 3, a typical behavior of $g(r)$ in a liquid is shown.

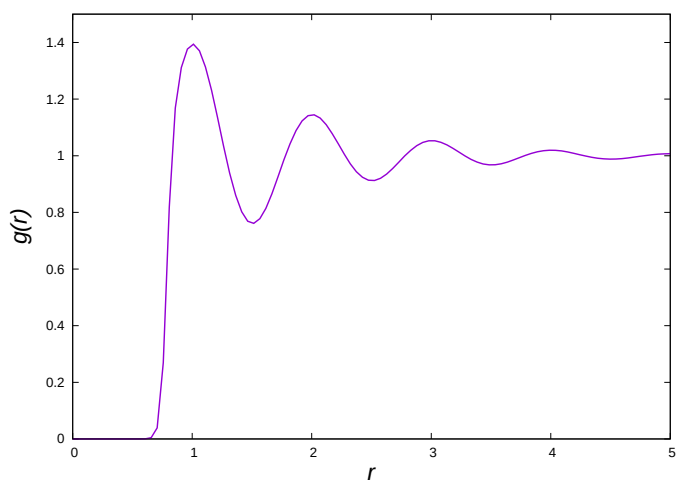

FIG. 3: Typical behavior of $g(r)$ in a liquid.

4 Correlations in reciprocal space. As I shall show in the following, X-ray or neutron scattering experiments probe correlations in reciprocal space, so that to have a picture of correlation in real space one has to Fourier transform the experimental result.

Let me introduce the Fourier transform of the density

$$\hat{\rho}_{\boldsymbol{k}} = \int \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\,\hat{\rho}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = \sum_{i=1}^{N}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}$$

and the so-called structure factor

$$S_{\boldsymbol{k}} = \frac{1}{N}\left\langle\hat{\rho}_{\boldsymbol{k}}\hat{\rho}_{-\boldsymbol{k}}\right\rangle,$$

where, again, the angular brackets denote an average. Then

$$S_{\boldsymbol{k}} = \frac{1}{N}\left\langle \sum_{j=1}^{N}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j}\sum_{i=1}^{N}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i}\right\rangle.$$

When multiplying the two sums, one finds N terms with $i = j$, hence

$$S_{\boldsymbol{k}} = 1 + \frac{1}{N} \left\langle \sum_{i \neq j} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}_j - \boldsymbol{r}_i)} \right\rangle .$$

The term within angular brackets can be rewritten as a double integral

$$S_{\boldsymbol{k}} = 1 + \frac{1}{N} \left\langle \int \int \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{r}' - \boldsymbol{r}'')} \sum_{i \neq j} \delta(\boldsymbol{r}' - \boldsymbol{r}_j) \delta(\boldsymbol{r}'' - \boldsymbol{r}_i) \, \mathrm{d}\boldsymbol{r}' \mathrm{d}\boldsymbol{r}'' \right\rangle .$$

I introduce the change of variables $\boldsymbol{r}' = \boldsymbol{r}'' + \boldsymbol{r}$ and integrate with respect to $\boldsymbol{r}''$, finding

$$S_{\boldsymbol{k}} = 1 + \frac{1}{N} \int \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \left\langle \sum_{i \neq j} \delta(\boldsymbol{r} + \boldsymbol{r}_i - \boldsymbol{r}_j) \right\rangle \mathrm{d}\boldsymbol{r} = 1 + \rho \int \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \, g(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r}.$$

This last result implies that, if one can measure the structure factor $S_{\boldsymbol{k}}$, then the correlation function is obtained by inverse Fourier transform,

$$\rho \, g(\boldsymbol{r}) = \int \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \, (S_{\boldsymbol{k}} - 1) \, \frac{\mathrm{d}\boldsymbol{k}}{(2\pi)^3}.$$

5 Measuring the structure factor. In X-ray or neutron scattering experiments a plane wave of wavevector $\boldsymbol{k}$ is scattered by the system under investigation and detected as a plane wave of wavevector $\boldsymbol{k}'$. If the scattering is elastic, then $|\boldsymbol{k}| = |\boldsymbol{k}'|$. Now, I assume that the atoms belonging to the system are seen as point-like scatterers, located at $\boldsymbol{r} = \boldsymbol{r}_i$ $(i = 1, ..., N)$, so that the potential perturbing the plane waves, that are being used as an experimental probe, is

$$U(\boldsymbol{r}) = g \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i),$$

where g is a suitable coupling constant. Then, the quantum mechanical probability of the scattering $\boldsymbol{k} \to \boldsymbol{k}'$ per unit time is proportional to the modulus squared of the matrix element of the perturbing potential between the initial and final states,

$$\mathcal{P}_{\boldsymbol{k}\to\boldsymbol{k}'} \propto \left| U_{\boldsymbol{k}\boldsymbol{k}'} \right|^2 ,$$

with

$$U_{\boldsymbol{k}\boldsymbol{k}'} \propto \int \mathrm{e}^{-\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}} \, U(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} = g \sum_{i=1}^{N} \mathrm{e}^{-\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}_i} = g \hat{\rho}_{\boldsymbol{k}-\boldsymbol{k}'}$$

and $U^*_{\boldsymbol{k}\boldsymbol{k}'} \propto g \hat{\rho}_{\boldsymbol{k}'-\boldsymbol{k}}$. Hence

$$\mathcal{P}_{\boldsymbol{k}\to\boldsymbol{k}'} \propto \hat{\rho}_{\boldsymbol{k}-\boldsymbol{k}'} \hat{\rho}_{\boldsymbol{k}'-\boldsymbol{k}}.$$

Now, this probability depends on the actual positions of the atoms. In an experiment, one measures a suitable averaged value

$$\langle \mathcal{P}_{\boldsymbol{k}\to\boldsymbol{k}'} \rangle \propto \langle \hat{\rho}_{\boldsymbol{k}-\boldsymbol{k}'} \hat{\rho}_{\boldsymbol{k}'-\boldsymbol{k}} \rangle = N S_{\boldsymbol{k}-\boldsymbol{k}'},$$

which proves the statement that a scattering experiment provides a direct measure of the structure factor.