Physics 127b: Statistical Mechanics

Lecture 1: Classical Non-ideal Gas

Partition Function

We take the Hamiltonian to be the kinetic energy plus a potential energy $U(\{\vec{r}_i\})$ that is the sum of pairwise potentials

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} u(|\vec{r}_i - \vec{r}_j|). \tag{1}$$

The factor of $1/2$ in the potential is because in the ij sum we count each interaction twice, and $i \neq j$ is because there is no self-interaction. Sometimes we will write $\frac{1}{2}\sum_{i\neq j}$ as $\sum_{i<j}$. The assumption of a pairwise potential is an *approximation*: we will not address how good the approximation is. We will also assume that the pair potential $u(r)$ is known.

The classical, canonical partition function is

$$Q_N = \frac{1}{N!}\frac{1}{h^{3N}} \int \dots \int d^{3N}r\, d^{3N}p\, e^{-\beta\sum_i p_i^2/2m}\, e^{-\beta U}. \tag{2}$$

The momentum integration can be done in the usual way, and factors out from the interaction term

$$Q_N = \left[\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\right]\left[\frac{Z_N(V,T)}{V^N}\right]. \tag{3}$$

The first term is the expression for the ideal gas (with $\lambda = (h/2\pi m k_B T)^{1/2}$), and

$$Z_N = \int \dots \int d^{3N}r\, e^{-\beta U(\{\vec{r}_i\})} \tag{4}$$

which depends on the spatial configuration $\{\vec{r}_i\}$ is called the configuration integral. (This notation follows our general one and *Pathria*, using Q_N for the partition function, and then Z_N for the configuration integral; unfortunately *Goodstein* uses exactly the reverse.) Since the interaction depends only on the difference coordinates, integration over one of the particle coordinates (e.g. $\vec{r}_1$) is trivial, and the remaining integrals can be transformed to integrals over the differences

$$Z_N = V\int \dots \int e^{-\beta\sum_{i\neq j} u(|\vec{r}_i - \vec{r}_j|)} d^3(\vec{r}_2 - \vec{r}_1)\dots d^3(\vec{r}_N - \vec{r}_1). \tag{5}$$

Radial Distribution Function

The interaction will lead to spatial *correlations*. A complete characterization of the interacting system requires knowledge of all n-particle correlation functions. However the simplest one, the pairwise correlation function, tells us the average interaction energy and the equation of state.

We measure the pairwise correlations in terms of the radial distribution function $g(\vec{r})$ which is normalized so that it is unity in the ideal gas (no correlations). It is related to the correlation function

$$C_{\rho\rho}(\vec{r}, \vec{r} + \vec{R}) = \left\langle \rho(\vec{r})\rho(\vec{r} + \vec{R})\right\rangle \tag{6}$$

where $\rho(\vec{r})$ is the density, which we can write in terms of the particle coordinates

$$\rho(\vec{r}) = \sum_i \delta(\vec{r}_i - \vec{r}) \tag{7}$$

which counts the particles at $\vec{r}$. (You can see this is the right expression for the density by integrating over the whole volume. Then each delta function integrates to unity—the particle is certainly somewhere in the volume—and the total integral is N.) For translationally invariant systems $C_{\rho\rho}$ is only a function of $\vec{R}$.

For $\vec{R} \neq 0$ different particles are at $\vec{r}$ and $\vec{r} + \vec{R}$, and so

$$C_{\rho\rho}(\vec{R} \neq 0) = \left\langle \sum_{i \neq j} \delta(\vec{r} - \vec{r}_i)\delta(\vec{r} + \vec{R} - \vec{r}_j) \right\rangle \tag{8}$$

$$= \frac{1}{V} \int d^3 r \left\langle \sum_{i \neq j} \delta(\vec{r} - \vec{r}_i)\delta(\vec{r} + \vec{R} - \vec{r}_j \right\rangle \tag{9}$$

$$= \frac{1}{V} \left\langle \sum_{i \neq j} \delta(\vec{R} + \vec{r}_i - \vec{r}_j) \right\rangle \tag{10}$$

where in the second step we have taken advantage of the fact there is no $\vec{r}$ dependence to integrate over all $\vec{r}$. The final expression counts the number of pairs separated by $\vec{R}$, and so makes sense.

Finally we fix the normalization to define g. This turns out to be slightly different in the canonical and grand canonical ensemble (so we use different symbols g_N and g), although the difference is $O(1/N)$ and can usually be ignored.

Canonical:

$$\rho g_N(\vec{R}) = \frac{1}{N-1} \left\langle \sum_{i \neq j} \delta(\vec{R} + \vec{r}_i - \vec{r}_j) \right\rangle \tag{11}$$

Grand canonical:

$$\rho g(\vec{R}) = \frac{1}{\langle N \rangle} \left\langle \sum_{i \neq j} \delta(\vec{R} + \vec{r}_i - \vec{r}_j) \right\rangle \tag{12}$$

with $\rho = \langle N \rangle / V$. In either case the normalization can be checked by integrating over all space when $N(N-1)$ delta function terms each contribute unity.

$$\rho \int [g_N(\vec{R}) - 1] d^3 R = 0. \tag{13}$$

$$\rho \int [g(\vec{R}) - 1] d^3 R = \frac{\left\langle N^2 - N \right\rangle}{\langle N \rangle} - \langle N \rangle, \tag{14}$$

$$= \frac{\left\langle N^2 - \langle N \rangle^2 \right\rangle}{\langle N \rangle} - 1. \tag{15}$$

The difference in the normalization arises because N fluctuates in the grand canonical ensemble. In the usual way these fluctuations can be related to thermodynamic quantities

$$\rho \int [g(\vec{R}) - 1] d^3 R = \rho k_B T \kappa_T - 1 \tag{16}$$

with $\kappa_T = -V^{-1}(\partial V / \partial P)_T$. As promised, the right hand side of Eq. (16) is zero for an ideal gas.

Properties of $g(\vec{R})$

I will phrase the discussion in terms of the canonical version g_N, although the results apply in general in the $N \to \infty$ limit.

1. The average in the definition of g_N in Eq. (11) is of course the usual Boltzmann average. The momentum integrals cancel in numerator and denominator, and so only the configuration integrals are left
$$g_N(\vec{R}) = \frac{V}{N(N-1)}\frac{1}{Z_N}\int\cdots\int\sum_{i\neq j}\delta(\vec{R}+\vec{r}_i-\vec{r}_j)\exp(-\beta U)d^{3N}r. \tag{17}$$
There are $N(N-1)$ identical terms in the sum, and so
$$\begin{aligned} g_N(\vec{R}) &= \frac{V}{Z_N}\int\cdots\int\delta(\vec{R}+\vec{r}_1-\vec{r}_2)\exp(-\beta U)d^3r_1\ldots d^3r_N, & (18)\\ &= \frac{V^2}{Z_N}\int\cdots\int\exp(-\beta U)d^3r_3\ldots d^3r_N, & (19)\end{aligned}$$
where in the last expression we have integrated over $\vec{r}_1$ and $\vec{r}_2$ giving a factor of V and setting $\vec{r}_2-\vec{r}_1 = \vec{R}$ in U, i.e. we integrate over $N-2$ particle coordinates holding $\vec{r}_1$ at the origin, and $\vec{r}_2$ at $\vec{R}$.

2. The average potential energy from a pairwise interaction should clearly depend just on the pairwise correlations, and so can be written in terms of g_N. The expression for the potential energy is
$$\begin{aligned}\langle U\rangle &= \frac{1}{Z_N}\int\cdots\int\frac{1}{2}\sum_{i\neq j}u(|\vec{r}_i-\vec{r}_j|)\exp(-\beta U)d^3r_1\ldots d^3r_N, & (20)\\ &= \frac{1}{Z_N}\int\cdots\int\frac{1}{2}\sum_{i\neq j}\delta(\vec{R}+\vec{r}_i-\vec{r}_j)u(R)\exp(-\beta U)d^3r_1\ldots d^3r_N d^3R, & (21)\\ &= \frac{N(N-1)}{2V}\int g_N(\vec{R})u(R)d^3R. & (22)\end{aligned}$$
For large N this reduces to
$$\langle U\rangle = \frac{1}{2}\rho^2 V\int g_N(R)u(R)d^3R. \tag{23}$$

3. The equation of state can also be expressed in terms of g_N
$$P = \rho k_B T\left[1 - \frac{\rho}{6k_BT}\int R\frac{du}{dR}g_N(R)\,d^3R\right]. \tag{24}$$
Proof: in the canonical ensemble
$$\begin{aligned} P &= k_BT\frac{\partial \ln Q_N}{\partial V} & (25)\\ &= \rho k_BT + k_BT\frac{V^N}{Z_N}\frac{\partial}{\partial V}\left(\frac{Z_N}{V^N}\right). & (26)\end{aligned}$$
To make the V dependence of Z_N clear we scale all coordinates with $V^{1/3}$, i.e. define $\vec{r}_i' = \vec{r}_i/V^{1/3}$, so that
$$Z_N = V^N\int_0^1\ldots\int_0^1 e^{-\beta/2\sum_{i\neq j}u(V^{1/3}r_{ij}')}d^{3N}r' \tag{27}$$

writing r_{ij} for $\left|\vec{r}_i - \vec{r}_j\right|$. This is easily differentiated w.r.t. V, and rewritten in terms of $\vec{R}$ gives

$$\frac{\partial}{\partial V}\left(\frac{Z_N}{V^N}\right) = \frac{1}{V^N}\int\cdots\int\left(-\frac{\beta}{6}\sum_{i\neq j}\frac{\partial u(r_{ij})}{\partial r_{ij}}\frac{r_{ij}}{V}\right)e^{-\beta U}\,d^{3N}r, \tag{28}$$

$$= -\frac{(N)(N-1)}{6k_BTV^2}\frac{Z_N}{V^N}\int R\frac{du}{dR}g_N(R)\,d^3R, \tag{29}$$

where Eq. (11) has been used. Now take N large to reproduce Eq. (24).

4. The radial distribution function is related to the structure factor $S(\vec{Q})$ which is the quantity measured in Xray scattering

$$S(\vec{Q}) - 1 = \rho\int e^{i\vec{Q}\cdot\vec{R}}[g_N(\vec{R}) - 1]d^3R. \tag{30}$$

Nearly-ideal Gas

In the nearly ideal gas the pair correlations are directly given by the pairwise interaction, since there will be no other particle nearby to affect these correlations

$$g_N(R) = e^{-\beta u(R)}. \tag{31}$$

We then have a complete expression for the equation of state

$$P = \rho k_BT\left[1 - \frac{\rho}{6k_BT}\int_0^\infty R\frac{du}{dR}e^{-\beta u(R)}\,d^3R\right] \tag{32}$$

$$= \rho k_BT\left[1 + \frac{\rho}{2}\int_0^\infty\left(1 - e^{-\beta u(R)}\right)\,d^3R\right] \tag{33}$$

with the second expression given by integration by parts. These are the zeroth and first terms in the *virial expansion*

$$P = \rho k_BT\left[1 + B(T)\rho + C(T)\rho^2\cdots\right] \tag{34}$$

which is an expansion in low densities and/or weak interaction.

It is interesting to evaluate the equation of state for a simple model of the interaction potential consisting of a hard core repulsion of radius r_0 (equal to the atomic diameter) and a weak attraction for $r > r_0$. Then

$$\frac{1}{2}\int_0^\infty\left(1 - e^{-\beta u(R)}\right)\,d^3R \simeq \frac{2}{3}\pi r_o^3 + \frac{1}{2k_BT}\int_{r_0}^\infty u(R)\,d^3R, \tag{35}$$

where we can expand $1 - \exp(-\beta u(R))$ in small βu for the attraction term (obviously this would not work for the infinite repulsion!). This gives the equation of state

$$P = \rho k_BT\,[1 + \rho b - \rho a/k_BT] \tag{36}$$

with

$$b = \frac{2}{3}\pi r_o^3, \tag{37}$$

$$a = \frac{1}{2}\int_{r_0}^\infty u(R)\,d^3R. \tag{38}$$

Writing $\rho^{-1} = v$, and approximating $(1 + \rho b)^{-1}$ as $(1 - \rho b)$ gives the Van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = k_BT, \tag{39}$$

with a clear understanding of the parameters a and b.