Density Functional Theory: The Classical Hard-Core Gas

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Model

Set-up

We have a number of particles N with positions $x_i \in \Lambda \subset \mathbb{R}^d$ and momentum $p_i \in \mathbb{R}^d$.
For convenience we define

$$X_N = (x_1, \ldots, x_N) \in \Lambda^N$$
$$P_N = (p_1, \ldots, p_N) \in \mathbb{R}^{dN}$$

and

$$\beta = \frac{1}{k_B T}.$$

The Hamiltonian

$$H^V_{\Lambda^N}(X_N, P_N) = \underbrace{\sum_{1\leq i<j\leq N} W(x_i - x_j)}_{\text{inter-particle interaction U}} + \underbrace{\sum_{i=1}^{N} V(x_i)}_{\text{external potential}} + \underbrace{\sum_{i=1}^{N} \frac{p_i^2}{2m}}_{\text{Kinetic part}}$$

Canonical Gibbs Ensemble

characterised by $\gamma^{\beta}_{\Lambda,N} \in \mathcal{P}(\Lambda, \mathcal{B}_{\Lambda})$ with density

$$\rho^{\beta}_{\Lambda,N}(X_N, P_N) = \frac{\exp[-\beta H^{V}_{\Lambda^N}(X_N, P_N)]}{N! Z_{\Lambda}(\beta, N)}$$

with respect to the Lebesgue measure, where $\mathcal{B}_{\Lambda}$ is the Borel σ -algebra on Λ.

Here $Z_{\Lambda}(\beta, N)$ is a normalisation factor known as the **Partition Function**.

Partition Functions

$$Z_\Lambda(\beta, N) = \underbrace{\left(\int_{\mathbb{R}^d} \exp\left[-\beta \frac{p^2}{2m}\right] \mathrm{d}p\right)^N}_{\text{kinetic partition function}}$$

$$\times \underbrace{\frac{1}{N!} \int_{\Lambda^N} \prod_{i=1}^{N} \exp[-\beta V(x_i)] \prod_{1 \le i < j \le N} \exp[-\beta W(x_i - x_j)] \mathrm{d}X_N}_{Z_{\Lambda,con}(\beta, V) \text{ configurational partition function}} .$$

Average Energy

We define

$$E = \frac{\int_{\mathbb{R}^{dN}} \int_{\Lambda^N} H^V_{\Lambda^N}(X_N, P_N) \exp[-\beta H^V_{\Lambda^N}(X_N, P_N)] \mathrm{d}X_N \mathrm{d}P_N}{N! Z_\Lambda(\beta, N)}.$$

Free Energy

Helmholtz Free Energy

Free energy is minimised at equilibrium if temperature is held constant.

$$A_\beta^{\Lambda^N}[V] = E - TS_\Lambda.$$

We can also show

$$\begin{aligned}
A_\beta^{\Lambda^N}[V] &= -\beta^{-1}\ln[Z_\Lambda(\beta, N)] \\
&= \underbrace{-\beta^{-1}\ln\left[\prod_{i=0}^{N}\int_{\mathbb{R}^d}\exp\left[-\beta\frac{p_i^2}{2m}\right]\mathrm{d}p_i\right]}_{\text{Kinetic free energy}} \\
&\quad + \underbrace{-\beta^{-1}\ln\left[\frac{1}{N!}\int_{\Lambda^N}\prod_{i=1}^{N}\exp[-\beta V(x_i)]\prod_{1\le i<j\le N}\exp[-\beta W(x_i - x_j)]\mathrm{d}X_N\right]}_{A_{\beta,con}^{\Lambda^N}[V]\text{ configurational free energy}}.
\end{aligned}$$

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Free Energy per Particle

For use in the thermodynamic limit (where $N \to \infty$). We need free energy per particle

$$\mathcal{F}_{\beta}^{\Lambda^N}[V] = \frac{1}{N} A_{\beta}^{\Lambda^N}[V]$$

and we can similarly define $\mathcal{F}_{\beta,con}^{\Lambda^N}[V]$.

One-particle Density

One-particle Density

Three ways of doing this

- Integrating out $N-1$ Variables

$$\rho^{(1)}_{\Lambda^N}(x) = \frac{N \int_{\mathbb{R}^d} \int_{\Lambda^{N-1}} \exp\left[-\beta H^V_{\Lambda^N}(X_N, P_N)\right] \mathrm{d}x_2 \ldots \mathrm{d}x_N \mathrm{d}P_N}{N! Z_\Lambda(\beta, N)}$$

- Average over δ-functions

$$\rho^{(1)}_{\Lambda^N}(x) = \left\langle \sum_{i=0}^{N} \delta(x - x_i) \right\rangle_C$$

$$= \frac{1}{N! Z_\Lambda(\beta, N)}$$

$$\times \int_{\mathbb{R}^d} \int_{\Lambda^N} \sum_{i=0}^{N} \delta(x - x_i) \exp\left[-\beta H^V_{\Lambda^N}(X_N, P_N)\right] \mathrm{d}X_N \mathrm{d}P_N$$

- Functional Derivative

$$\rho^{(1)}_{\Lambda^N}(x) = \frac{\delta A^{\Lambda^N}_\beta[V]}{\delta V(x)}.$$

Introduction to Density Functional Theory

Introduction to DFT

We want to express free energy as the sum of a functional of one-particle density only and another term.

$V(x)$ is a conjugate variable to the one-particle density $\rho^{(1)}_{\Lambda^N}(x)$. Since free energy is a functional of the external potential, we can use a Legendre transform to re-write the free energy.

$$A^{\Lambda^N}_{\beta}[V] = F_{HK}\left[\rho^{(1)}_{\Lambda^N}(x)\right] + \int_{\Lambda} V(x)\rho^{(1)}_{\Lambda^N}(x)\mathrm{d}x$$

F_{HK} is known as the Hohnberg-Kohn functional.

Ideal Gas

Ideal Gas

In this case the internal potential is zero

$$Z_\Lambda(\beta, N) = \frac{1}{N!}\left(\int_\Lambda \exp[-\beta V(x)]\mathrm{d}x\right)^N \left(\int_{\mathbb{R}^d} \exp\left[\frac{-\beta p_1^2}{2m}\right]\mathrm{d}p_1\right)^N.$$

We introduce the notation

$$z_\beta(\mathrm{d}x_i) = \mathrm{d}x_i \exp[-\beta V(x_i)]$$

and

$$z(\Lambda)^N = \left(\int_\Lambda z_\beta(\mathrm{d}x)\right)^N.$$

Ideal Gas: Free Energy

We can re-write the partition function as

$$Z_\Lambda(\beta, N) = \frac{1}{N!}\left(\frac{z(\Lambda)}{\lambda^d}\right)^N \qquad \lambda = \left(\frac{\beta}{2\pi m}\right)^{\frac{1}{2}}$$

which allows us to write

$$A_\beta^{\Lambda^N}[V] = \beta^{-1}\left(\ln[N!] + Nd\ln[\lambda] - N\ln[z(\Lambda)]\right).$$

Density Functional Form

We seek to re-write the free energy in a density functional form.

Using the functional derivative of the free energy we can find the one-particle density

$$\rho^{(1)}_{\Lambda^N}(x) = \frac{N \exp[-\beta V(x)]}{z(\Lambda)}.$$

Re-arranging we can find an expression for the external potential

$$V(x) = -\beta^{-1} \ln \left[\frac{\rho^{(1)}_{\Lambda^N}(x) z(\Lambda)}{N} \right].$$

We therefore find

$$\int_{\Lambda} \rho^{(1)}_{\Lambda^N}(x) V(x) \mathrm{d}x = -\beta^{-1} \int_{\Lambda} \rho^{(1)}_{\Lambda^N}(x) \ln\left[\rho^{(1)}_{\Lambda^N}(x)\right] \mathrm{d}x - \beta^{-1} N \ln\left[\frac{z(\Lambda)}{N}\right].$$

We recall a generalisation of Stirling's approximation

$$\sqrt{2\pi N}\left(\frac{N}{e}\right)^N \exp\left[\frac{1}{12N+1}\right] \leq N! \leq \sqrt{2\pi N}\left(\frac{N}{e}\right)^N \exp\left[\frac{1}{12N}\right].$$

Using this and that $\int_{\Lambda} \rho^{(1)}_{\Lambda^N}(x) dx = N$ we can re-write the free energy as

$$A^{\Lambda^N}_{\beta}[V] = \beta^{-1} \int_{\Lambda} \rho^{(1)}_{\Lambda^N}(x) \left(\ln[\rho^{(1)}_{\Lambda^N}(x)] + d \ln \lambda - 1\right) \mathrm{d}x$$
$$+ \int_{\Lambda} \rho^{(1)}_{\Lambda^N}(x) V(x) \mathrm{d}x + O(\ln N).$$

Hard-Core Gas

Hard-Core Potential

$$\begin{cases} W_a(x_i - x_j) & = 0 \quad \|x_i - x_j\| > a \\ W_a(x_i - x_j) & = \infty \quad \|x_i - x_j\| \leq a \end{cases}$$

Given that $a < a_{cp}$ where a_{cp} is the close-packing density.

Then our internal potential is

$$U = \sum_{1 \leq i < j \leq N} W_a(x_i - x_j).$$

1D Free Energy

Here we are in one dimension $\Lambda = L$ and we can write

$$\begin{aligned} Z_{\Lambda,con}(\beta, V) &= \mathfrak{Z}(L) \\ &= \frac{1}{N!}\int_0^L \cdots \int_0^L \prod_{1\le i<j\le N} \exp\left[-\beta W_a(x_i - x_j)\right] \\ &\times \prod_{i=1}^{N} \exp[-\beta V(x_i)]\mathrm{d}x_1 \ldots \mathrm{d}x_N. \end{aligned}$$

Since we are in one dimension we can order the particles so that there positions lie between 0 and L

$$0 < x_1 \le x_2 \cdots \le x_N < L.$$

Convolution form

We can use two changes of variables

$$y_j^a = x_j - (j-1)a \qquad l^a = L - (N-1)a$$
$$\lambda_N^a = l^a - y_N^a \qquad \lambda_i^a = y_{i+1}^a - y_i^a$$

and that the potential is translation invariant

$$V(x_j) = V(y_j^a).$$

To re-write the configurational partition function

$$\mathfrak{Z}(L) = \int_0^{l^a} \mathrm{d}\lambda_N^a \exp\left[-\beta V\left(l^a - \lambda_N^a\right)\right] \int_0^{l^a - \lambda_N^a} \mathrm{d}\lambda_{N-1}^a$$
$$\times \exp\left[-\beta V\left(l^a - \lambda_N^a - \lambda_{N-1}^a\right)\right] \dots \int_0^{l^a - \sum_{i=2}^{N} \lambda_i^N} \mathrm{d}\lambda_1^a$$
$$\times \exp\left[-\beta V\left(l^a - \sum_{i=1}^{N} \lambda_i^a\right)\right].$$

Laplace Transform

Since $\mathfrak{Z}(l^a)$ when $V = 0$ is a convolution we write the Laplace transform

$$
\begin{aligned}
Z(s) &= \int_0^\infty \exp[-s l^a]\mathfrak{Z}(l^a)\mathrm{d}l^a \\
&= s^{-(N+1)}
\end{aligned}
$$

since

$$
\int_0^\infty \exp[-s\lambda^a]\mathrm{d}\lambda^a = \frac{1}{s}.
$$

Thus using the inverse transform we find

$$
\mathfrak{Z}(l^a) = \frac{1}{2\pi i}\oint_C \exp[s l^a] s^{-(N+1)} ds
$$

where C is the Bromwich contour.

The Saddle-point

We write the integrand of our integral as the exponential of $g(s)$.

$$g(s) = l^a s - (N+1)\ln s$$

this is clearly complex differentiable and has a minimum on the real-axis so has a saddle-point.

Using the saddle-point condition $g'(s_0) = 0$ we have at the saddle-point

$$s_0 = \frac{N+1}{L - a(N-1)}.$$

We also find the second derivative

$$g''(s_0) = \frac{(N+1)}{s_0^2}.$$

Saddle-point Approximation

We now expand $g(s)$ around the saddle-point and alter the contour to give an approximation of the configurational partition function

$$\begin{aligned}
\mathfrak{Z}(l^a) &= \frac{1}{2\pi i}\oint_C \exp[g(s)]\mathrm{d}s \\
&\approx \frac{1}{2\pi i}\exp[g(s_0)]\int_{x_0-i\infty}^{x_0+i\infty}\exp\left[\frac{g''(s_0)(s-s_0)^2}{2}\right]\mathrm{d}s \\
&\approx \frac{1}{2\pi}\exp[g(s_0)]\int_{-\infty}^{\infty}\exp\left[\frac{g''(s_0)y^2}{2}\right]\mathrm{d}y \quad s-s_0=iy \\
&\approx \frac{\exp[g(s_0)]}{\sqrt{2\pi g''(s_0)}}\left(1+O\left(\frac{1}{N}\right)\right).
\end{aligned}$$

Thus we can see

$$A_{\beta,con}^{\Lambda^N}[V] \approx -\beta^{-1}\left(g(s_0)-\frac{1}{2}\ln[2\pi g''(s_0)]+\ln\left[1+O\left(\frac{1}{N}\right)\right]\right).$$

The Zero Hard-Core Limit

Using the values of $g(s_0)$ and $g''(s_0)$ we find

$$A_a^{N,L} \approx -\beta^{-1}\left(N + 1 - N\ln[N+1] + N\ln[L - a(N-1)] - \frac{1}{2}\ln[2\pi] - \frac{1}{2}\ln[N+1] + \ln\left[1 + O\left(\frac{1}{N}\right)\right]\right).$$

The zero hard-core limit is

$$\lim_{a\to 0} A_a^{N,L} \approx -\beta^{-1}\left(N + 1 - N\ln\left[\frac{N+1}{L}\right] - \frac{1}{2}\ln[2\pi] - \frac{1}{2}\ln[N+1] + \ln\left[1 + O\left(\frac{1}{N}\right)\right]\right).$$

The Ideal Gas Case

From above we have an ideal gas expression for the configurational energy and using Stirling's approximation we have

$$A_0^{N,L} = -\beta^{-1}\left(N - N\ln\left[\frac{N}{L}\right] - \frac{1}{2}\ln[2\pi] - \frac{1}{2}\ln N\right) + O\left(\frac{1}{N}\right)$$

the free energy per particle in this case is

$$\mathcal{F}_0^{N,L} = -\beta^{-1}\left(1 - \ln\left[\frac{N}{L}\right] - \frac{1}{2N}\ln[2\pi] - \frac{1}{2N}\ln N\right) + O\left(\frac{1}{N^2}\right).$$

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Comparison

We take the thermodynamic limit in both cases and note that $\rho = N/L$.

For the ideal gas

$$\begin{aligned}\mathcal{F}_0^{th} &= \lim_{\substack{N\to\infty \\ L\to\infty}} \mathcal{F}_0^{N,L} \\ &= -\beta^{-1}\left(1 - \ln[\rho]\right)\end{aligned}$$

whereas in the thermodynamic and zero hard-core limit of the hard-core case we have

$$\begin{aligned}\lim_{\substack{N\to\infty \\ L\to\infty}} \lim_{a\to 0} \mathcal{F}_a^{N,L} &= \lim_{\substack{N\to\infty \\ L\to\infty}} \frac{\lim_{a\to 0} A_a^{N,L}}{N} \\ &= -\beta^{-1}\left(1 - \ln[\rho]\right)\end{aligned}$$

Further Work

Further Work

- My Website
- Grand Canonical Ensemble
- Quantum Problems

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