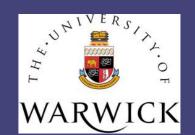# Density Functional Theory: The Ideal Gas

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Motivation

Density Functional Theory (DFT) is a widely used technique in both chemistry and in physics. In my MSc thesis we start from the canonical ensemble of statistical mechanics and use this as a motivation for the formulation of DFT. We then give the free energy of the ideal gas as a simple example of the DFT formalism.

Once the ideal gas formula has been achieved we hope to use similar methlodgy consider more complicated potentials, initially considering the hard-core potential.

Statistical Mechanics Model

We initially consider a statistical mechanical model in the canonical ensemble. We have a constant number of particles N with positions $x_i \in \Lambda \subset \mathbb{R}^d$ and momentum $p_i \in \mathbb{R}^d$. For convience we define a vector of particle positions and momenta

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

Then the Hamiltonian of our system is given by

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

Canonical Ensemble

The canonical Gibbs ensemble is characterised by the probability measure $\gamma_{\Lambda,N}^{\beta} \in \mathcal{P}(\Lambda, \mathcal{B}_{\Lambda})$ with density

$$\rho_{\Lambda,N}^{\beta}(X_N, P_N) = \frac{\exp\left[-\beta H_{\Lambda^N}^V(X_N, P_N)\right]}{N! Z_{\Lambda}(\beta, N)}$$

with repect to the Lebesgue measure, where $\mathcal{B}_{\Lambda}$ is the Borel σ-algebra.[1]

$Z_{\Lambda}(\beta, N)$ is a normalisation factor known as the partition function and

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

The partition function can be split into the product of an integral over space variables and an integral over momentum variables . Since the momentum integrals are all identically Gaussians they can be integrated to give a constant λ^{-1}. We can thus write the partition function as

$$Z_{\Lambda}(\beta, N) = \frac{1}{N! \lambda^{dN}} \int_{\Lambda^N} \prod_{i=1}^{N} \exp[-\beta V(x_i)] \prod_{1 \leq i < j \leq N} \exp[-\beta W(x_i - x_j)] dX_N \quad (1)$$

Helmholtz Free Energy

The Helmholtz free energy is known to be minimised at equilibrium and can be given by [1]

$$A_{\beta}^{\Lambda^N}[V] = -\beta^{-1} \ln[Z_{\Lambda}(\beta, N)]. \quad (2)$$

Using the definition of the partition function given above (1) we have

$$A_{\beta}^{\Lambda^N}[V] = \beta^{-1} \left(Nd \ln \lambda + \ln N! \right.$$
$$\left. - \ln\left[\int_{\Lambda^N} \prod_{i=1}^{N} \exp[-\beta V(x_i)] \prod_{1 \leq i < j \leq N} \exp[-\beta W(x_i - x_j)] dX_N \right] \right).$$

One Particle Density

The fundamental quantity of interest in density functional theory is the one particle density. There are three ways of doing this:

1. Integrating out the momentum variables and $N-1$ spatial variables of the Gibbs measure

$$\rho_{\Lambda^N}^{(1)}(x) = \frac{N \int_{\mathbb{R}^d} \int_{\Lambda^{N-1}} \exp\left[-\beta H_{\Lambda^N}^V(X_N, P_N)\right] dx_2 \ldots dx_N dP_N}{N! Z_{\Lambda}(\beta, N)}$$

2. Taking the canonical average of N δ-functions centered at the positions of each particle

$$\rho_{\Lambda^N}^{(1)}(x) = \frac{\int_{\mathbb{R}^d} \int_{\Lambda^N} \sum_{i=0}^{N} \delta(x - x_i) \exp\left[-\beta H_{\Lambda^N}^V(X_N, P_N)\right] dX_N dP_N}{N! Z_{\Lambda}(\beta, N)}$$

3. Taking the functional derivative of the free energy

$$\rho_{\Lambda^N}^{(1)}(x) = \frac{\delta A_{\beta}^{\Lambda^N}[V]}{\delta V(x)}. \quad (3)$$

Introduction to DFT

The external potential $V(x)$ is a conjugate variable to the one particle density. We can use the Legendre transform to find a pure functional of density (the Hohenberg-Kohn functional)

$$F_{HK}\left[\rho_{\Lambda^N}^{(1)}(x)\right] = \inf_{\rho_{\Lambda^N}^{(1)}(x)} \left\{ A_{\beta}^{\Lambda^N}[V] - \int_{\Lambda} V(x)\rho_{\Lambda^N}^{(1)}(x) dx \right\}.$$

Since the Hohenberg-Kohn functional is minimised at the equilibrium density $\rho_{\Lambda^N, eq}^{(1)}(x)$, we can write the free energy at equilibrium as

$$A_{\beta}^{\Lambda^N}[V] = F_{HK}\left[\rho_{\Lambda^N, eq}^{(1)}(x)\right] + \int_{\Lambda} V(x)\rho_{\Lambda^N, eq}^{(1)}(x) dx.$$

The Ideal Gas

We consider the ideal gas as a motivating example. This is the case where there is no interaction between particles i.e. $W = 0$. Using (1) and that the spatial integrals can be seperated out we have

$$Z_{\Lambda}(\beta, N) = \frac{1}{N! \lambda^{dN}} \underbrace{\left(\int_{\Lambda} \exp[-\beta V(x)] dx. \right)^N}_{z(\Lambda)^N}$$

Using (2) we have that the free energy is

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

Density Functional Form

We want to re-write the free energy in a density functional form. We find the one-particle density using (3)

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

Re-arranging to find $z(\Lambda)$ and using that the integral of $\rho_{\Lambda^N}^{(1)}(x)$ is N we have

$$A_{\beta}^{\Lambda^N}[V] = \beta^{-1}\left(\ln[N!] - N \ln[N] + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln\left[\lambda^d \rho_{\Lambda^N}^{(1)}(x)\right] dx \right)$$
$$+ \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx.$$

A generalisation of Stirling's formula [2] allows us to re-write the free energy

$$A_{\beta}^{\Lambda^N}[V] = \beta^{-1} \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \left(\ln\left[\lambda^d \rho_{\Lambda^N}^{(1)}(x)\right] - 1 \right) dx$$
$$+ \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx + O(\ln N).$$

Outlook

1. MSc Thesis
   - Tonks Gas
   - 1D Hard-Core Gas
   - Mayer Expansion
2. PhD
   - Deriving Phase Field Crystal (PFC) Model from DFT
   - Numerics for PFC

Acknowledgements

References

1. S. Adams, Communications of the Dublin Institute for Advanced Studies, Series A (Theoretical Physics), No. 30, 2006.
2. H. Robbins, The American Mathematical Monthly, 62, No. 1,1955.