1 Theory

We define $r = \|\boldsymbol{r} - \boldsymbol{r}'\|$, and $\Delta n(\boldsymbol{r}) = n(\boldsymbol{r}) - n_0$, and n_0 the density (given in dft.in) of the homogeneous fluid of reference, e.g., 0.0332891 molecule per Å^3 for water.

We also define $n(\boldsymbol{r}) = \int \rho(\boldsymbol{r}, \boldsymbol{\Omega}) \mathrm{d}\boldsymbol{\Omega}$. We have

$$F_{exc} = -\frac{1}{2} k_B T \iint \Delta n(\boldsymbol{r}) \Delta n(\boldsymbol{r}') c(r) d\boldsymbol{r} d\boldsymbol{r}', \tag{1}$$

Now, we consider the convolution in the right hand side of the equation, $\gamma \equiv (\Delta n * c)$, that can be computed much efficiently than in $O(N^2)$ by fast Fourier transform in $O(N \log N)$.

2 Algo

Algorithm 1 energy_nn_cs.f90

Inputs:

- $\rho(\boldsymbol{r}, \Omega)$
- $c_s(k)$, with $k \equiv \|\boldsymbol{k}\|$
- functions to Fast Fourier Transform (FFT) and inverse Fast Fourier Transform (FFT^{-1})
- n_0, the density of the homogeneous fluid of reference
- T the temperature in Kelvin
- k_B the Boltzmann constant.

Output:

- F_{exc}, The part of the excess free energy that is due to the density-density coupling.

$$\Delta n(\boldsymbol{r}) \leftarrow \int \rho(\boldsymbol{r}, \boldsymbol{\Omega}) \mathrm{d}\boldsymbol{\Omega} - n_0 \tag{2}$$

$$\hat{\Delta n} \leftarrow FFT[\Delta n] \tag{3}$$

$$\hat{\gamma} \leftarrow \hat{\Delta n} \cdot \hat{c} \tag{4}$$

$$\gamma \leftarrow FFT^{-1}[\hat{\gamma}] \tag{5}$$

$$F_{exc} \leftarrow -\frac{1}{2} k_B T \int \Delta n(\boldsymbol{r}) \cdot \gamma(\boldsymbol{r}) d\boldsymbol{r} \tag{6}$$