Classical density functional theory: Exact density distribution of hard rods between walls in 1D

Martin Oettel

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1. Introduction

Introductory statistical physics, as taught in the *Basic Module Thermodynamics and Statistical Mechanics* mostly deals with homogeneous systems, and applications to real systems are restricted essentially to the equation of state of ideal classical and quantum gases. Beyond the classical ideal gas, real gases are treated with a perturbative treatment via the virial expansion and the mean-field approximation. Some aspects of phase transitions in homogeneous systems are introduced in a thermodynamic manner.

In projects 5 and 6 you will learn more about simulations addressing the phemonenon of phase transitions with the examples of the Ising model and the hard rod model.

However, there is a large class of theoretically and practically relevant phenomena in statistical physics which occur in inhomogeneous systems, i.e. systems where the averaged number density of particles is not constant throughout space. Inhomogeneities always occur when there is a fixed external potential acting on the particles of the system, such as a confining boundary or wall or an inhomogeneous external field such as electric/magnetic fields. But also without external fields inhomogeneous systems are possible in equilibrium: think of the interface between a vapor and a liquid phase at coexistence. Experimentally relevant phenomena in inhomogeneous systems are the adsorpotion at surfaces and consequently the appearance of surface tensions, the adsorption in small pores and the ensuing possible shifts

of phase coexistence (capillary condensation), the appearance of wetting transitions at flat walls and many more.

For the description of the equilibrium state of inhomogeneous systems, the framework of Statistical Mechanics (as taught in the *Basic Module*) is fully applicable. In view of the technical difficulties which you encountered when applying the various ensembles to simple model systems you might wonder whether it is an impossible task to calculate e.g. an inhomogeneous number density profile $\rho(\mathbf{r})$ for a given system (specified by a certain interatomic potential) in a given external field. Fortunately, there exists a theoretical approach which simplifies this taks: *Density Functional Theory (DFT)*. In short, DFT states that there exists a unique functional for the grand potential, depending on $\rho(\mathbf{r})$, which upon minimization gives the equilibrium value of the grand potential and the associated density profile is indeed the equilibrium profile. With this information at hand, all other properties can be calculated.

The drawback of DFT is that for most systems (i.e. most types of interatomic potential) this unique functional is only known approximately. For systems in one dimension (1D) with a nearest-neighbor interaction potential, the exact functional can be derived. In this project, you will treat such a 1D system (for simplicity defined on a lattice, i.e. on discrete points on a line) of rodlike particles which mutually interact with a hard potential. The equilibrium density profile near a hard wall will be numerically computed, as well as surface tensions and adsorptions. These can be compared to exact, analytical results. The numerics involves a simple form of techniques which appear in many classical DFT calculations: evaluation of free energy functionals with weighted densities and their functional derivatives, as well as the solution of nonlinear integral equations by iteration.

1.1. REMINDER OF THE GRAND CANONICAL ENSEMBLE FOR HOMOGENEOUS SYSTEMS

DFT is formulated in the grand canonical ensemble (GCE) which we briefly review. The GCE assumes the existence of a huge reservoir in which the actual system (with fixed volume V) is embedded. The reservoir and the system may freely exchange heat and particles. Therefore the control parameters, set by the reservoir and determining the equilibrium state of the system, are the chemical potential μ and the temperature T. The associated thermodynamic potential of the GCE is the grand potential $\Omega(\mu, V, T)$ depending on its natural variables $\{\mu, V, T\}$. Remember that the grand potential and the free energy $F(N, V, T)$ of a homogeneous system are connected by a Legendre transformation

$$\Omega(\mu, V, T) = F(N, V, T) - \mu N. \tag{1.1}$$

In the GCE, the grand potential follows from the grand partition function Z_{gc}

$$\Omega(\mu, V, T) = -kT \ln Z_{\text{gc}}, \tag{1.2}$$

where k is Boltzmann's constant. For a homogeneous system of isotropic (spherical) particles with coordinates $\mathbf{r}_i$ and momenta $\mathbf{p}_i$, the grand partition function is defined by

$$
\begin{aligned}
Z_{\text{gc}}(\mu, V, T) &= \sum_{N=0}^{\infty} \frac{1}{h^{dN} N!} \int d^d r_1 ... \int d^d r_N \int d^d p_1 ... \int d^d p_N \exp(-\beta H_N + \beta \mu N) \quad (1.3) \\
&=: \text{Tr}_{\text{cl}} \, \exp(-\beta H_N + \beta \mu N), \tag{1.4}
\end{aligned}
$$

where d is the dimension of the system and $\beta = 1/(kT)$. The symbol Tr_{cl} signifies "classical trace" and abbreviates the sum over N and the position and momentum integrals. (In that way the expression for Z_{gc} is formally identical in classical and quantum systems.) H_N is the (classical) Hamiltonian which for N particles with mass m interacting with pair potentials $u(\mathbf{r})$ reads

$$
\begin{aligned}
H_N &= K_N + U_N \,, && (1.5) \\
&= \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{\substack{i,j \\ i<j}}^{N} u(\mathbf{r}_i - \mathbf{r}_j) \,. && (1.6)
\end{aligned}
$$

Recall that in the expression for Z_{gc} the integrals over momenta can be done straightforwardly with the result:

$$
Z_{\text{gc}}(\mu, V, T) = \sum_{N=0}^{\infty} \frac{1}{\lambda^{dN} N!} \int d^d r_1 ... \int d^d r_N \exp(-\beta U_N + \beta \mu N) \,, \qquad (1.7)
$$

$$
(1.8)
$$

where $\lambda = h/\sqrt{2\pi m k T}$ is the thermal de Broglie wavelength (h is Planck's constant).
For an arbitrary pair potential u, further simplification is in general not possible. Thus, the actual problem of classical statistical mechanics lies in the position dependencies of the classical trace (the "configuration integral"). It is worth, however, to recall the calculable case of the ideal gas ($u = U_N = 0$) for which we find:

$$
\begin{aligned}
Z_{\text{gc,id}}(\mu, V, T) &= \sum_{N=0}^{\infty} \frac{1}{\lambda^{dN} N!} V^N \exp(\beta \mu N) && (1.9) \\
&= \exp\left(\frac{V}{\lambda^d} \exp(\beta \mu) \right) \rightarrow && (1.10) \\
\Omega_{\text{id}}(\mu, V, T) &= -kT \frac{V}{\lambda^d} \exp(\beta \mu) \,. && (1.11)
\end{aligned}
$$

All thermodynamics is contained in Ω_{id}. Consider:

$$
\begin{aligned}
-N &= \frac{\partial \Omega_{\text{id}}}{\partial \mu} = -\frac{V}{\lambda^d} \exp(\beta \mu N) \rightarrow && (1.12) \\
\mu = \mu_{\text{id}} &= kT \ln \frac{N \lambda^d}{V} && (1.13)
\end{aligned}
$$

and

$$
\begin{aligned}
p_{\text{id}} &= -\frac{\Omega}{V} = \frac{kT}{\lambda^d} \exp(\beta \mu) && (1.14) \\
&= kT \frac{N}{V} = kT \rho \,, && (1.15)
\end{aligned}
$$

where we used Eq. (1.13) and have recovered the ideal gas equation of state with $\rho = N/V$ being the particle number density.

1.2. INHOMOGENEOUS SYSTEMS

For inhomogenous systems, there is only a slight change. The volume V as a natural variable does not make sense any more since the occupied volume of the system is governed by the external potential. Z_{gc} is defined as before

$$Z_{\mathrm{gc}}(\mu, T) = \mathrm{Tr}_{\mathrm{cl}} \exp(-\beta H_N + \beta \mu N) \tag{1.16}$$

but the classical Hamiltonian has an additional piece due to the external potential

$$H_N \quad = \quad K_N + U_N + V_N\,, \tag{1.17}$$
$$V_N \quad = \quad \sum_i V^{\mathrm{ext}}(\mathbf{r}_i)\,. \tag{1.18}$$

The external contribution is simply the sum over contributions from a space–dependent external potential $V^{\mathrm{ext}}(\mathbf{r})$ acting on each particle individually (one calls this a *one body potential*). As discussed, this external potential makes the density distribution inhomgeneous. An inhomogenous density profile $\rho(\mathbf{r})$ can be expressed as a grand canonical average of a density operator $\hat{\rho}$

$$\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle \tag{1.19}$$

with

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)\,. \tag{1.20}$$

The meaning is clear: the operator is only nonzero when any of the particles is at position $\mathbf{r}$. The average over positions and momenta is defined via

$$\langle ... \rangle := \frac{1}{Z_{\mathrm{gc}}} \mathrm{Tr}_{\mathrm{cl}} \exp(-\beta H_N + \beta \mu N)... = \mathrm{Tr}_{\mathrm{cl}} f_0 ... \tag{1.21}$$

which defines the grand canonical equilibrium phase space density $f_0 = \frac{1}{Z_{\mathrm{gc}}} \exp(-\beta H_N + \beta \mu N)$. It is normalized, i.e. $\mathrm{Tr}_{\mathrm{cl}} f_0 = 1$. Note that this definition of a density profile is consistent with a modification of the the thermodynamic identity (1.12):

$$-N = \frac{\partial \Omega}{\partial \mu} \quad \rightarrow \quad -\rho(\mathbf{r}) = \frac{\delta \Omega}{\delta(\mu - V^{\mathrm{ext}}(\mathbf{r}))} \tag{1.22}$$

which links the density profile $\rho(\mathbf{r})$ to a functional derivative of Ω.

It is again instructive to solve the case of an ideal gas in an external potential. Quite analogous to the derivation of Eq. (1.11) we find

$$Z_{\mathrm{gc,id}}(\mu, T) \quad = \quad \sum_{N=0}^{\infty} \frac{1}{\lambda^{dN} N!} \left(\int d^d r \exp(\beta(\mu - V^{\mathrm{ext}}(\mathbf{r}))) \right)^N \tag{1.23}$$

$$= \quad \exp\left(\frac{1}{\lambda^d} \int d^d r \exp(\beta(\mu - V^{\mathrm{ext}}(\mathbf{r}))) \right) \rightarrow \tag{1.24}$$

$$\Omega_{\mathrm{id}}(\mu, T) \quad = \quad -kT \frac{1}{\lambda^d} \int d^d r \exp(\beta(\mu - V^{\mathrm{ext}}(\mathbf{r})))\,. \tag{1.25}$$

Then the density profile becomes

$$\rho(\mathbf{r}) = -\frac{\delta\Omega_{\text{id}}}{\delta(\mu - V^{\text{ext}}(\mathbf{r}))} = \frac{1}{\lambda^d}\exp(\beta(\mu - V^{\text{ext}}(\mathbf{r}))). \tag{1.26}$$

We can get rid of the chemical potential μ if we assume that at some reference point in the system (where $V^{\text{ext}} = 0$) the density is give by ρ_0. Then according to Eq. (1.13) we have $\exp(\beta\mu) = \rho_0\lambda^d$ and thus

$$\rho(\mathbf{r}) = \rho_0\exp(-\beta V^{\text{ext}}(\mathbf{r})). \tag{1.27}$$

This is the barometric law!

The connection between free energy and grand potential via the Legendre transformation (1.1) can also be generalized:

$$\begin{aligned}
\mathscr{F}[\rho(\mathbf{r}), T] &= \Omega(\mu, T) + \int d^d\mathbf{r}(\mu - V^{\text{ext}}(\mathbf{r}))\rho(\mathbf{r}) \tag{1.28} \\
&= -kT\frac{1}{\lambda^d}\int d^d r\exp(\beta(\mu - V^{\text{ext}}(\mathbf{r}))) + \int d^d\mathbf{r}(\mu - V^{\text{ext}}(\mathbf{r}))\rho(\mathbf{r}) \tag{1.29}
\end{aligned}$$

The proper conjugate variable to μ is not N anymore but the density profile $\rho(\mathbf{r})$. Therefore, the free energy is a *functional* rather than a function, and we empahsize this by using a special font. From Eq. (1.26) we have $\mu - V^{\text{ext}}(\mathbf{r}) = kT\ln[\rho(\mathbf{r})\lambda^d]$ and therefore

$$\mathscr{F}_{\text{id}}[\rho(\mathbf{r}), T] = kT\int d^d r\rho(\mathbf{r})\left(\ln[\rho(\mathbf{r})\lambda^d] - 1\right). \tag{1.30}$$

This is the ideal gas free energy functional. Note that it is independent of the external potential (that is the purpose of the Legendre transform!) and thus it is an *intrinsic* property of the system.

1.3. DENSITY FUNCTIONAL THEORY (DFT)

Consider a particular system, characterized by its specific pair potential. For a certain external potential, the equilibrium phase space density is given by f_0 (see Eq. (1.21). The formulation of DFT rests on the following lemma and two theorems:

Lemma: *Minimum property for Ω:*

We introduce a functional $\Omega[f]$ where f is an arbitrary phase space density:

$$\Omega[f] = \text{Tr}_{\text{cl}}\, f\,(H_N - \mu N + kT\ln f). \tag{1.31}$$

Note that for $f = f_0 = \frac{1}{Z_{\text{gc}}}\exp(-\beta H_N + \beta\mu N)$, $\Omega[f]$ becomes the equilibrium grand potential Ω_0 of the system:

$$\begin{aligned}
\Omega[f_0] &= \text{Tr}_{\text{cl}}\, f_0\,(-kT\ln Z_{\text{gc}}) = -kT\ln Z_{\text{gc}} \tag{1.32} \\
&= \Omega_0. \tag{1.33}
\end{aligned}$$

Then:

$$\Omega[f] \geq \Omega_0 \,, \tag{1.34}$$

i.e. in equilibrium the grand potential is minimized.

We expect this to hold since it is nothing but the maximum entropy principle, applied to the GCE.

Theorem 1: *Uniqueness of $\mathscr{F}[\rho]$:*

For a particular fluid, $\mathscr{F}[\rho]$ is a unique functional of the equilibrium density profile.

Theorem 2: *Grand potential functional of the density $\Omega[n]$:*

Let $n(\mathbf{r})$ be some average of the microscopic density associated with a nonequilibrium phase space probability f_n. Then the generalized grand potential functional introduced in the Lemma is

$$\Omega[f_n] \equiv \Omega[n] = \mathscr{F}[n] + \int d\mathbf{r}\, n(\mathbf{r})\, V^{\text{ext}}(\mathbf{r}) - \mu \int d\mathbf{r}\, n(\mathbf{r}) \tag{1.35}$$

and acquires its minimum at equilibrium, $n = \rho$, with $\Omega[\rho] = \Omega_0$.

The proof of the lemma and the two theorems can be found in Appendix A. Further details can be found in the lecture notes by Roland Roth [1], Sec. 1–2.

Traditionally, the yet unknown but unique free energy functional is decomposed as

$$\mathscr{F}[\rho] \quad = \quad \mathscr{F}_{\text{id}}[\rho] + \mathscr{F}_{\text{ex}}[\rho] \tag{1.36}$$

where the ideal gas part

$$\mathscr{F}_{\text{id}}[\rho] \quad = \quad kT \int d^d r\, \rho(\mathbf{r}) \Big(\ln[\rho(\mathbf{r})\lambda^d] - 1 \Big) . \tag{1.37}$$

was computed in the previous section. The second part is called excess part (meaning "excess over ideal") and this part is in general unknown and theoretical insights are needed to determine or to approximate it.

Using this decomposition, we can use **theorem 2** to write down an equation for the equilibrium density profile $\rho(\mathbf{r})$:

$$\left. \frac{\delta \Omega}{\delta n(\mathbf{r})} \right|_{n(\mathbf{r})=\rho(\mathbf{r})} \quad = \quad \left. \frac{\delta \mathscr{F}}{\delta n(\mathbf{r})} \right|_{n(\mathbf{r})=\rho(\mathbf{r})} + V^{\text{ext}}(\mathbf{r}) - \mu \tag{1.38}$$

$$= \quad \left. \frac{\delta \mathscr{F}_{\text{id}}}{\delta n(\mathbf{r})} \right|_{n(\mathbf{r})=\rho(\mathbf{r})} + \left. \frac{\delta \mathscr{F}_{\text{ex}}}{\delta n(\mathbf{r})} \right|_{n(\mathbf{r})=\rho(\mathbf{r})} + V^{\text{ext}}(\mathbf{r}) - \mu_{\text{id}} - \mu_{\text{ex}} \tag{1.39}$$

$$= \quad 0 \,. \tag{1.40}$$

Here we split the chemical potential μ in an ideal gas part and in an excess part as well. Using $\mu_{\text{id}} = kT \ln[\rho_0 \lambda^d]$ (from Eq. (1.13), ρ_0 is a reference density where $V^{\text{ext}} = 0$ and the density

profile is locally flat) and the functional derivative of $\mathcal{F}_{\mathrm{id}}$ we find

$$kT\ln[\rho(\mathbf{r})\lambda^d] + \left.\frac{\delta\mathcal{F}_{\mathrm{ex}}}{\delta n(\mathbf{r})}\right|_{n(\mathbf{r})=\rho(\mathbf{r})} + V^{\mathrm{ext}}(\mathbf{r}) - kT\ln[\rho_0\lambda^d] - \mu_{\mathrm{ex}} = 0 \qquad \rightarrow \tag{1.41}$$

$$\rho(\mathbf{r}) = \rho_0 \exp\left(-\beta V^{\mathrm{ext}}(\mathbf{r}) + \beta\mu_{\mathrm{ex}} - \beta\left.\frac{\delta\mathcal{F}_{\mathrm{ex}}}{\delta n(\mathbf{r})}\right|_{n(\mathbf{r})=\rho(\mathbf{r})}\right) \tag{1.42}$$

This is an implicit, highly nonlinear equation for $\rho(\mathbf{r})$. There is no dependence on the thermal de Broglie wavelength λ anymore, owing to the introduction of the reference density ρ_0.

2. Hard rods in 1D on a lattice

Investigating lattice models has often helped in formulating general concepts in statistical physics, if not initiating them. Additionally, lattice models often take up the role of a simplified version of a continuum model of interest, in the hope they retain the basic physics, e.g. the type of phase transition. One of the most popular examples is the lattice gas model (equivalent to the Ising model) to explore the phase transitions (see project 5).
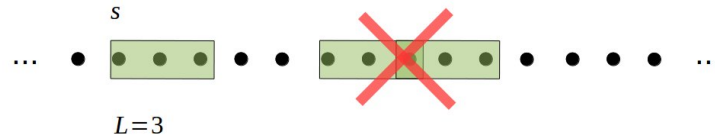

Figure 2.1: Lattice model for hard rods in 1D.

Here we consider a 1D lattice, formed by discrete points on a line. On this lattice, a hard rod of length L covers L consecutive points and configurations of hard rods which overlap are forbidden (see Fig. 2.1 for an example with $L = 3$). We define densities ρ_s as number of particles per lattice point s. We adopt the following convention: For a rod with left–most point fixed at s, the density is $\rho_s = 1$, otherwise zero. Since the densities are ensemble–averaged quantities, they can take continuous values but with the obvious constraint $\rho_s \in [0,1]$. (We are in the GCE: the system is connected to a reservoir with chemical potential μ and may freely exchange particles with it. Therefore the occupation of a lattice point s by a rod may change and what we record in ρ_s is an average occupation.) Since a rod covers L consecutive points, it makes sense to define a local packing fraction by

$$n_s^{(1)} = \sum_{s'=s-L+1}^{s} \rho_{s'}. \tag{2.1}$$

It sums the densities over $L-1$ preceding points to s and s itself. Rods which sit at these points also cover s. Therefore, we have the same constraint as for the densities, $n_s^{(1)} \in [0,1]$. The local packing fraction is an example of a *weighted density* which is formed of the density profile convoluted with a weight function. Such weighted densities are very important in classical DFT.

Without proof, we state that the free energy functional for this system is given by

$$\mathscr{F}[\rho] \quad = \quad \mathscr{F}_{\text{id}}[\rho] + \mathscr{F}_{\text{ex}}[\rho] \qquad \text{with} \tag{2.2}$$

$$\beta \mathscr{F}^{\text{id}}[\rho] = \sum_s \rho_s (\ln \rho_s - 1) , \tag{2.3}$$

$$\beta \mathscr{F}^{\text{ex}}[\rho] = \sum_s \left(\Phi^{0D}(n_s^{(1)}) - \Phi^{0D}(n_s^{(0)}) \right) , \tag{2.4}$$

$$\Phi^{0D}(\eta) = \eta + (1 - \eta) \ln(1 - \eta) , \tag{2.5}$$

$$n_s^{(0)} = \sum_{s' = s - L + 1}^{s-1} \rho_{s'} . \tag{2.6}$$

and consequently the grand potential functional is

$$\Omega[\rho] \quad = \quad \mathscr{F}[\rho] + \sum_s (V_s^{\text{ext}} - \mu) \rho_s . \tag{2.7}$$

$$\tag{2.8}$$

A very essential property of this functional is the so-called *0D limit*: When you restrict the system to a cavity of length S such that only one particle fits in (i.e. $S = L..2L - 1$), then the excess free energy of such a cavity times β is $\Phi^{0D}(\eta)$ where η is the average occupancy (packing fraction) in the cavity. In 1D, the requirement of the correct *0D limit* is enough to arrive at the exact functional, in higher dimensions it leads to very good approximations. The derivation of the functional can be found in [2] (excerpt of a talk by M. Oettel).

2.1. COMPUTATIONAL PROBLEM: DENSITY PROFILE BETWEEN HARD WALLS

We will numerically compute the density profile and the surface tension of 1D hard rods of length L at a hard wall. The computation will be done on a grid with $M \gg L$ points in a slit geometry with *two* hard walls. The setup is depicted in Fig. 2.2.
Notation: Tasks to be performed are in blue and important equations for the solution are in red.

boundary condition:
$$\rho_1, ..., \rho_L = 0 \quad \text{and} \quad \rho_{M-L+1}, ..., \rho_M = 0$$

Figure 2.2: Numerical setup.

The equilibrium density profile is found by the variational derivative

$$\frac{\delta \Omega}{\delta \rho} = 0 \qquad \rightarrow \qquad \frac{\partial \Omega}{\partial \rho_s} = 0 , \tag{2.9}$$

which in the discrete lattice model amounts to the partial derivative with respect to all density points. Performing this derivative (**check!**), we find

$$\ln \rho_s + \beta \mu_s^{\text{ex}} + \beta V_s^{\text{ext}} - \beta \mu \; = \; 0 \qquad \text{or} \tag{2.10}$$

$$\rho_s \; = \; \exp(\beta[\mu - \mu_s^{\text{ex}}]) \exp(-\beta V_s^{\text{ext}}) \qquad \text{with} \tag{2.11}$$

$$\mu_s^{\text{ex}} = \left(\frac{\delta \mathscr{F}_{\text{ex}}}{\delta \rho} \right)_s . \tag{2.12}$$

$$\exp(-\beta V_s^{\text{ext}}) = \begin{cases} 0 & \text{(rod inside wall)} \\ 1 & \text{(otherwise)} \end{cases} \tag{2.13}$$

The functional derivative of the excess free energy, evaluated at point s, is (**check!**)

$$\beta \mu_s^{\text{ex}} \; = \; \sum_{s'=s}^{s+L-1} \Phi^{\text{0D}'}(n_{s'}^{(1)}) - \sum_{s'=s+1}^{s+L-1} \Phi^{\text{0D}'}(n_{s'}^{(0)}) \tag{2.14}$$

$$\Phi^{\text{0D}'}(\eta) = \frac{d\Phi^{\text{0D}}(\eta)}{d\eta} = -\ln(1-\eta) . \tag{2.15}$$

Note that e.g. both summands in $\beta \mu_s^{\text{ex}}$ are nonzero in the interval $[2, M-1]$ (*inside both walls*), however, the local excess chemical potential is zero there (**why?**). One sees that the minimizing equation ((2.11) together with (2.14)) corresponds to a strongly non–linear, coupled set of equations for the ρ_s. The bulk chemical potential μ is an input parameter which implicitly determines the bulk density ρ_0 in the middle of the (sufficiently large) slit. The corresponding bulk packing fraction is $\eta_0 = L\rho_0$.

The numerically easiest way to solve the minimizing equation to get the equilibrium profile ρ_{eq_s} is by Picard iteration with mixing. For that, define a suitable starting density profile $\rho_{s,0}$ and iterate the equation according to

$$\rho_{s,i}^{\text{new}} \; = \; \exp(\beta[\mu - \mu_s^{\text{ex}}[\rho_{s,i}]]) \exp(-\beta V_s^{\text{ext}}) , \tag{2.16}$$

$$\rho_{s,i+1} \; = \; (1-\alpha)\rho_{s,i} + \alpha \rho_{s,i}^{\text{new}} , \tag{2.17}$$

where $\alpha < 1$ is a parameter which ensures that the iteration does not lead to divergence. With increasing η_0 it should be chosen smaller and smaller. Convergence is achieved if $\rho_{s,i+1}$ and $\rho_{s,i}$ do not differ anymore, as expressed, e.g., by the criterion

$$\sum_s (\rho_{s,i}^{\text{new}} - \rho_{s,i})^2 < \epsilon , \tag{2.18}$$

where ϵ is a small parameter. More information on these type of Picard iterations can be found in the review by Roland Roth [1].

Having obtained ρ_{eq}, the surface tension between the lattice fluid and the hard wall can be determined in the following way. In 1D, the surface tension is actually a "point" tension. Thermodynamically, this is the excess grand potential,

$$\gamma \; = \; \Omega[\rho_{\text{eq}}] - \Omega(\rho_0), \tag{2.19}$$

which is the difference between the grand potential (2.7) of the equilibrium profile near *one* wall and the bulk grand potential. The bulk grand potential is simply

$$\Omega(\rho_0) = -p(\rho_0)V = -p(\rho_0) \sum_{s_{\text{wall}}}^{\infty} 1,$$

(2.20)

so the value of γ depends on where one defines the location of the wall, i.e. from which point s_{wall} onwards the fluid domain starts. In our slit geometry we have *two* hard walls, so we find

$$2\gamma = \Omega[\rho_{\text{eq}}] - \Omega(\rho_0) = \Omega[\rho_{\text{eq}}] + p(\rho_0) \sum_{s_{\text{wall},1}}^{s_{\text{wall},2}} 1 = \Omega[\rho_{\text{eq}}] + p(\rho_0)(s_{\text{wall},2} - s_{\text{wall},1} + 1),$$

(2.21)

For our problem, it makes sense to assign the fluid domain to those points where the density is nonzero, i.e. $s_{\text{wall},1} = L+1$ and $s_{\text{wall},2} = M-L$.

In 1D, one can determine the surface tension also analytically, with the following argument. Consider a bulk fluid with density ρ_0 and occupying the volume V. The excess chemical potential $\mu^{\text{ex}}(\rho_0)$ in the fluid is actually the excess grand potential of an inserted rod at a fixed location, i.e the difference between the grand potential of the fluid with the fixed rod and the bulk grand potential $-p(\rho_0)V$ *(Widom's insertion trick)*. The equilibrium density profile of the fluid with the fixed rod corresponds to a hard wall profile "left" and "right" from the fixed rod. Thus this excess grand potential is just twice the hard wall surface tension, minus the bulk grand potential for those points around the fixed rod where the density is zero:

$$\mu^{\text{ex}}(\rho_0) = 2\gamma + (2L-1)p(\rho_0).$$

(2.22)

2.2. Tasks:

- Consider the hard rod system at the constant reference density ρ_0 (in the middle of the slit). From the functional, calculate analytically $p(\rho_0) = -\Omega/V$, $\mu^{\text{ex}}(\rho_0) = \partial F_{\text{ex}}/\partial N$ and $\gamma(\rho_0)$ (from Eq. (2.22)) in terms of the bulk weighted densities $n^{(1)} = \rho_0 L$ and $n^{(0)} = \rho_0(L-1)$.

- Check all blue items in the previous section.

- Write a code which solves the minimizing equation (2.11) for $L = 3$ and $L = 10$ and for bulk packing fractions $\eta_0 = 0.1, 0.2, ..., 0.9$, respectively.

- Plot the density profiles ρ_{eq_s} at one wall in a suitable manner.

- Compute the surface tension numerically from the excess grand potential. Check that it agrees with the analytical result.

- Compute the excess adsorption Γ through

$$2\Gamma = \sum_{s_{\text{wall},1}}^{s_{\text{wall},2}} (\rho_{\text{eq}_s} - \rho_0) \,. \tag{2.23}$$

Check that Gibbs' adsorption equation $\Gamma = -d\gamma/d\mu$ is fulfilled. Incidentally, integrating the adsorption equation with respect to μ is the most popular method to determine surface tensions in simulations.

- (∗) For the surface tension, you must have determined the grand potential of the equilibrium profile which can be written as a sum over lattice points of a grand potential density ω_s, $\Omega[\rho_{\text{eq}}] = \sum_s \omega_s[\rho_{\text{eq}}]$. Verify that ω_s is actually *not symmetric under reflections around the slit midpoint.* How can you determine γ unambiguously, if you want to use only half of the profile, i.e. the density profile at one wall?

REFERENCES

[1] Lecture notes *Introduction to Density Functional Theory of Classical Systems: Theory and Applications* by Prof. Roland Roth (U Tübingen). Provided as .pdf

[2] Lattice density functional theory. Excerpt from a talk by M. Oettel. Provided as .pdf.

A. PROOF OF THE LEMMA AND THE TWO THEOREMS OF DFT

Remember the equilibrium phase space probability of a microstate in the grand canonical ensemble:

$$f_0(\Gamma) = \frac{1}{Z_{gc}} \exp(-\beta H_N + N\beta\mu) . \tag{A.1}$$

Summation over N and integration over position–momentum of N particles is termed *classical trace*:

$$\text{Tr}_{cl}(\dots) := \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int (\dots) \, d\mathbf{r}_1 d\mathbf{p}_1 \dots d\mathbf{r}_N d\mathbf{p}_N \tag{A.2}$$

With this new notation

$$Z_{gc} = \text{Tr}_{cl} \exp(-\beta H_N + N\beta\mu), \qquad \text{Tr}_{cl} f_0 = 1 . \tag{A.3}$$

We may regard a generalized (non–equilibrium) grand potential $\Omega[f]$ as a functional of a general phase space probability f. From thermodynamics we expect that $\Omega[f_0] \equiv \Omega$ is a minimum, i.e. $\Omega[f] \geq \Omega[f_0]$.

- Lemma: Minimum property of $\Omega[f]$:

$$\Omega[f] = \text{Tr}_{cl} f(\beta^{-1}\ln f + H_N - N\mu) = \text{Tr}_{cl} f(\beta^{-1}\ln f - \beta^{-1}\ln(Z_{gc} f_0)) \tag{A.4}$$

Check

$$\Omega[f_0] = \text{Tr}_{cl} f_0(\beta^{-1}\ln f_0 - \beta^{-1}\ln(Z_{gc} f_0)) = -\beta^{-1}\ln Z_{gc} = \Omega , \tag{A.5}$$

as it should be. For the minimum property, consider

$$\Omega[f] - \Omega[f_0] = \beta^{-1} \left[\text{Tr}_{cl} f \ln f - \text{Tr}_{cl} f \ln f_0 \right] \tag{A.6}$$

$$= \beta^{-1} \text{Tr}_{cl} f_0 \left[\frac{f}{f_0} \ln \frac{f}{f_0} - \frac{f}{f_0} + 1 \right] \tag{A.7}$$

This holds since $\text{Tr}_{cl} f_0 = \text{Tr}_{cl} f = 1$. Since $x \ln x \geq x - 1 \ (x > 0)$, we immediately find

$$\Omega[f] - \Omega[f_0] \geq 0 . \tag{A.8}$$

- Theorem 1:
  For some specific fluid, $\mathcal{F}[\rho]$ is a unique functional of the equilibrium density profile.
  Note that the free energy does not depend explicitly on $V^{\text{ext}}(\mathbf{r})$ but only through $\rho(\mathbf{r})$. To
  see that, remember $V_N = \int d\mathbf{r}\hat{\rho}\, V^{\text{ext}}$ and $H_N = K_N + U_N + V_N$ with K_N, U_N – kinetic and
  potential energy. Then (with $\psi(\mathbf{r}) = \mu - V^{\text{ext}}(\mathbf{r})$):

$$
\begin{aligned}
\mathcal{F} &= \Omega[\psi(\mathbf{r})] + \int d^3\mathbf{r}\rho(\mathbf{r})[\mu - V^{\text{ext}}(\mathbf{r})] & \text{(A.9)} \\
&= \text{Tr}_{\text{cl}}\left[f_0(\beta^{-1}\ln f_0 + \mathcal{H}_N - N\mu) + f_0(N\mu - V_N)\right] & \text{(A.10)} \\
&= \text{Tr}_{\text{cl}}\, f_0(\beta^{-1}\ln f_0 + K_N + U_N) & \text{(A.11)}
\end{aligned}
$$

Since

$$
f_0(\Gamma) = \frac{1}{Z_{\text{gc}}}\exp(-\beta(K_N + U_N + V_N) + N\beta\mu)\,, \tag{A.12}
$$

we have $f_0 \equiv f_0[V^{\text{ext}}]$, i.e. the equilibrium phase space probability is a functional of the
external potential. Since

$$
\rho(\mathbf{r}) = \text{Tr}_{\text{cl}}\, \hat{\rho}\, f_0\,, \tag{A.13}
$$

we have $\rho \equiv \rho[f_0[V^{\text{ext}}]]$.
**If we can show a one–to–one correspondence $\rho(\mathbf{r}) \leftrightarrow V^{\text{ext}}(\mathbf{r})$, then also $f_0 \equiv f_0[\rho]$ and
thus also $\mathcal{F} \equiv \mathcal{F}[\rho]$.**
We define the following Hamiltonians, equilibrium phase space densities and grand
potentials

$$
\begin{aligned}
H_1 &= K_N + U_N + V_{N,1}, & H_2 &= K_N + U_N + V_{N,2} \\
f_{0,1} &= f_0[V_1^{\text{ext}}], & f_{0,2} &= f_0[V_2^{\text{ext}}] \\
\Omega_1 &= \Omega_{H_1}[f_{0,1}] & \Omega_2 &= \Omega_{H_2}[f_{0,2}]
\end{aligned}
$$

Assume now $\rho[V_1^{\text{ext}}] = \rho[V_2^{\text{ext}}]$, i.e. that two different external potentials lead to the same
density profile. The minimum property of Ω entails

$$
\begin{aligned}
\Omega_2 < \Omega_{H_2}[f_{0,1}] &= \text{Tr}_{\text{cl}}\, f_{0,1}(H_2 - N\mu + \beta^{-1}\ln f_{0,1}) & \text{(A.14)} \\
&= \Omega_1 + \text{Tr}_{\text{cl}}\,[f_{0,1}(V_{N,2} - V_{N,1})] & \text{(A.15)} \\
&= \Omega_1 + \int d\mathbf{r}\,\rho(\mathbf{r})[V_2^{\text{ext}}(\mathbf{r}) - V_1^{\text{ext}}(\mathbf{r})] & \text{(A.16)}
\end{aligned}
$$

We may exchange subscripts $_{1\leftrightarrow 2}$:

$$
\Omega_1 < \Omega_2 + \int d\mathbf{r}\,\rho(\mathbf{r})[V_1^{\text{ext}}(\mathbf{r}) - V_2^{\text{ext}}(\mathbf{r})] \tag{A.17}
$$

and add the two inequalities:

$$
\Omega_2 + \Omega_1 < \Omega_1 + \Omega_2\,, \tag{A.18}
$$

which contradicts the assumption $\rho[V_1^{\text{ext}}] = \rho[V_2^{\text{ext}}]$. Thus, different V^{ext} lead to different
ρ and thus there is a one–to–one correspondence between V^{ext} and ρ.

- Theorem 2:
  Let $n(\mathbf{r})$ be some average of the microscopic density associated with a nonequilibrium phase space probability f_n. Then the generalized grand potential functional is

  $$\Omega[n] = \mathscr{F}[n] + \int d\mathbf{r}\, n(\mathbf{r})\, V^{\text{ext}}(\mathbf{r}) - \mu \int d\mathbf{r}\, n(\mathbf{r}) \tag{A.19}$$

  and acquires its minimum at equilibrium, $n = \rho$, with $\Omega[\rho] = \Omega$.

Given the above points, the proof is trivial:

$$
\begin{aligned}
\Omega[f_n] &= \text{Tr}_{\text{cl}}\, f_n(\beta^{-1}\ln f_n + K_N + U_N \quad + V_N - N\mu) \tag{A.20}\\
&= \mathscr{F}[n] + \int d\mathbf{r}\, n(\mathbf{r})\, V^{\text{ext}}(\mathbf{r}) - \mu \int d\mathbf{r}\, n(\mathbf{r}) \equiv \Omega[n] \tag{A.21}
\end{aligned}
$$

We have shown already that $\Omega[f_0] \le \Omega[f_n]$, thus also $\Omega[\rho] \le \Omega[n]$.
These theorems are called the *Hohenberg–Kohn–Mermin theorems*. The practical importance lies in the following:

- There exists a *unique* free energy functional $\mathscr{F}[n]$ due to $(n =)\rho(\mathbf{r}) \leftrightarrow V^{\text{ext}}(\mathbf{r})$. The minimization of the associated $\Omega[n]$ determines the equilibrium density profile ρ:

  $$0 = \left. \frac{\delta \mathscr{F}}{\delta n(\mathbf{r})} \right|_{n(\mathbf{r})=\rho(\mathbf{r})} + V^{\text{ext}}(\mathbf{r}) - \mu . \tag{A.22}$$

- Although the precise form of $\mathscr{F}[n]$ is unknown for most systems (except the ideal gas and one–dimensional systems), one may construct trial functionals $\mathscr{F}'[n]$ whose equilibrium density profiles are given by $\delta\Omega'[n]/\delta n)_{n=\rho'} = 0$. That the grand potential is bounded from below, i.e.

  $$\Omega[\rho'] \ge \Omega[\rho] . \tag{A.23}$$

  is not of help since one does not know the correct functional form of $\Omega[n]$.
  Rather it gives the straightforward possibility to define a model system by $\mathscr{F}'[n]$ and exploit its implications through the functional formulation of liquid state physics.
  Unfortunately, it is difficult to constrain $\mathscr{F}'[n]$ such that it gives an internally consistent model of a fluid with two–body potentials.