

# Free Energy for an Anisotropic and Inhomogeneous Fluid of Spherocylinders

J. Mulia and J. Orozco

Facultad de Ciencias

Instituto Literario 100 Ote

50000, Toluca, Méx.

## Abstract

One of the most powerful and useful theories use in different work to determine the internal energy of non-uniform fluids is the density functional. Our goal is determine the form of the free energy corresponding to a anisotropic and inhomogeneous fluid of spherocylinders molecules, with positions and orientations given the complete information of posicional description. This kind of molecules are widely used to model with great successful liquid crystals. However, we not use a hard potential to describe the interaction between molecules. The determination of the free energy can be done from the internal energy and the computation of the statistical entropy through the Helmholtz relation,  $a = u - Ts$ . For the determination of the free energy  $U$  and the statistical entropy  $S$ , the distribution and canonical functions are expressed in terms of the lineal and angular momentum, orientational positions and potential energy. For a homogeneous fluid, the free energy reduce to the well-know result of Onsager free energy for low densities, which is given in terms of the orientational distribution function.

The liquid structure is determined by the repulsive part of the pair potential between particles. For the case of liquid crystals, Onsager was the first to show that in a system of elongated particles a isotropic-nematic phase transition can be observed[1]. Typical molecules of a thermotropic and liotropic liquid crystal are represented by rigid rods with length between 20 to 30 Å and width between 4 to 5 Å. To this work we will consider a system made of  $N$  spherocylinders. Each spherocylinder has a coordinate in the phase space given by[2]  $(r, \mathbf{p}, \mathbf{l}, J)$ , where  $r$  is the position of the center of mass of the spherocylinder,  $\mathbf{p}$  is its linear momentum,  $\mathbf{l}$  is the orientation of the spherocylinder given by the Euler angles, and  $J$  is the angular momentum. The last two variables gives new information to the internal energy and entropy of the system.

The distribution function is denoted by  $P^N(\mathbf{r}^N, \mathbf{p}^N, \mathbf{l}^N, J^N, t)$  with the usual meaning. The normalization condition, for this case, is

$$\int P^N(\mathbf{r}^N, \mathbf{p}^N, \mathbf{l}^N, J^N, t) d\mathbf{r}^N d\mathbf{p}^N d\mathbf{l}^N dJ^N = \int P^N(\mathbf{i}^N, t) d\mathbf{i}^N = 1 \quad (1)$$

A system made of elongated rigid molecules (ellipsoids or spherocylinders) presents several phases[3, 4, 5], this can be show determining the free energy of the system using the density functional theory[4, 5]. For the determination of the free energy  $f$  per particle we start from the thermodynamic relation

$$a = u - Ts, \quad (2)$$

where  $u$  is the internal energy per particle,  $T$  is the temperature, and  $s$  is the entropy per particle. This is a different approach by those used by Onsager[1] and others[3, 4, 5, 6] to study phase transitions in the kind of systems considered in this work. We use the

Gibbs postulate to define the entropy per molecule respect to its equilibrium value, which is determined for the following expression[7]

$$s = \int k P^{(N)}(\mathbf{i}^N, t) \ln \frac{P^{(N)}(\mathbf{i}^N, t)}{P_{eq}^{(N)}(\mathbf{i}^N)} d\mathbf{i}^N + s_{eq}$$

where  $k$  is the Boltzmann's constant,  $P_{eq}^{(N)}(\mathbf{i}^N) = P^{(N)}(\mathbf{r}^N, \mathbf{p}^N, \omega^N, \mathbf{J}^N)$  is equilibrium distribution function of the system, and  $s_{eq}$  is the equilibrium entropy, where the extra variables  $\mathbf{i}$  and  $\mathbf{J}$  are considered,

$$s_{eq} = \int k P_{eq}^{(N)}(\mathbf{i}^N) \ln P_{eq}^{(N)}(\mathbf{i}^N) d\mathbf{i}^N. \quad (3)$$

Now we assume that  $P_{eq}^{(N)}(\mathbf{i}^N)$  satisfy the mesoscopic continuity equation, when the Hamiltonian of the system is given by

$$H^N = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=1}^N \sum_{l=x,y,z} \frac{J_{il}^2}{2I_l} + \frac{1}{2} \sum_{i \neq j} V(\mathbf{r}_i, \mathbf{r}_j, \mathbf{i}_i, \mathbf{i}_j) \quad (4)$$

In the same way that in equilibrium[8, 9, 10], we assume that we can factor the non-equilibrium distribution function  $P^{(N)}(\mathbf{i}^N)$  in terms of the dynamic correlation function  $g^{(N)}(\mathbf{r}^N, \mathbf{i}^N)$  as

$$\begin{aligned} P^{(N)} &= P^{(N)}(\mathbf{r}^N, \mathbf{p}^N, \omega^N, \mathbf{J}^N) \\ &= P^{(1)}(1)P^{(1)}(2) \dots P^{(1)}(N)g^{(N)}(\mathbf{r}^N, \mathbf{i}^N). \end{aligned} \quad (5)$$

Here, the reduced distribution function is represented by  $P^{(s)} = P_{1,2,\dots,s}^{(s)}$ . When  $s = 1$ , we use the short notation  $P^{(1)}(i)$ . Beside, we also assume that the dynamic correlation

function  $g^{(N)}(\mathbf{r}^N, \omega^N, t)$  can be factor in several correlation functions as

$$g^{(N)}(\mathbf{r}^N, \omega^N, t) = g^{(2)}(1, 2) \dots g^{(2)}(N-1, N) \\ \times \delta g^{(3)}(1, 2, 3) \dots \delta g^{(3)}(N-2, N-1, N) \dots,$$

where  $g^{(3)}(1, 2, 3) = \delta g^{(3)}$  is defined through the relation

$$g^{(3)}(1, 2, 3) = g^{(2)}(1, 2) g^{(2)}(1, 3) g^{(2)}(2, 3) \delta g^{(3)}(1, 2, 3).$$

In the factors of  $g^{(N)}$  we have  $N(N-1)/2$  pairs,  $N(N-1)(N-2)/3!$  triplets, etc., and applying the logarithm to expression (5), we have

$$\ln P^{(N)} = \sum_{i=1}^N \ln P^{(1)}(i) + \ln g^{(N)}(\mathbf{r}^N, \omega^N, t) \\ = N \ln P^{(1)}(i) + \frac{N}{2} (N-1) \ln g^{(2)}(\mathbf{r}^2, \omega^2, t) \\ + \frac{N}{3!} (N-1)(N-2) \ln \delta g^{(3)} + \dots \quad (6)$$

For local equilibrium we have the same result but with the distribution functions evaluated in equilibrium,

$$\ln P_{eq}^{(N)} = N \ln P_{eq}^{(1)}(i) + \frac{N}{2} (N-1) \ln g^{(2)}(\mathbf{r}^2, \omega^2, t) + \dots \quad (7)$$

Using expressions (6) and (7) in the Gibbs postulate, eq. (3), we obtain

$$s = \sum_i \frac{1}{kN} \ln \frac{P^{(1)}(1)}{P_{eq}^{(1)}(1)} d\mathbf{r} d\mathbf{p} d\mathbf{J} \\ + \sum_i \frac{N(N-1)}{2} \frac{1}{k} \ln \frac{g^{(2)}}{g_{eq}^{(2)}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{J}_1 d\mathbf{J}_2 + s_{eq} + \dots$$

being  $s_{eq}$

$$s_{eq} = \sum_i \frac{1}{k} \ln P_{eq}^{(1)}(1) + \sum_{i < j} \frac{1}{k} \ln g_{eq}^{(2)}(r_{ij}, \Omega_{ij}) + \dots \quad (8)$$

In particular, when the system is in thermodynamic equilibrium, and according to [6], we only take into account the pair correlation function  $g_{eq}^{(2)}$ , and the one,  $P_{eq}^{(1)}$ , and two particles,  $P_{eq}^{(2)}$ , distribution function. From the Hamiltonian (4), we can factor the one particle distribution function as [2]

$$\begin{aligned} P_{eq}^{(1)}(1) &= P_{eq}^{(1)}(r_1, \mathbf{p}_1, \mathbf{J}_1) \\ &= P(\mathbf{p}_1)P(\mathbf{J}_1)P(r_1, \Omega_1). \end{aligned} \quad (9)$$

Here,  $P(\mathbf{p}_1)P(\mathbf{J}_1)$  and  $P(r_1, \Omega_1)$  are the linear momentum, angular momentum, and position-orientation distribution function respectively, and the appropriate normalized.

In equilibrium  $g_{eq}^{(2)}(r^2, \Omega^2)$  correspond to the pair correlation function, and when pair potentials are considered, it depends of the centers of mass distance and the orientations,

$$g_{eq}^{(2)}(r^2, \Omega^2) = g_{eq}^{(2)}(r_{12}, \Omega_1, \Omega_2). \quad (10)$$

Also, in equilibrium,  $P_{eq}^{(2)}$  the distribution function can be writing as

$$P_{eq}^{(2)} = P_{eq}^{(1)}(1)P_{eq}^{(1)}(2)g_{eq}^{(2)}(r_{12}, \Omega_1, \Omega_2).$$

If expressions (9) and (10) are used, and the appropriate normalizations too, the integrations over momentums, linear and angular, gives the following relation for the

equilibrium entropy

$$\begin{aligned}
 s_{eq} = & \int \int k P(r_1, \omega_1) \ln [ \int P(r_1, \omega_1) ]^{-1} g dr_1 d\omega_1 \\
 & + \int \int k P(r_1, \omega_1) P(r_2, \omega_2) g_{eq}^{(2)}(r_{12}, \omega_1, \omega_2) \\
 & - \ln g_{eq}^{(2)}(r_{12}, \omega_1, \omega_2) dr_1 dr_2 d\omega_1 d\omega_2
 \end{aligned} \tag{11}$$

where  $\lambda$  is the de Broglie's wavelength, where the inertia moments are considered. Expression (11) can be considered as the entropy for an anisotropic and inhomogenous fluid consisting of non-spherical molecules.

According to the free energy relation (2), the internal energy has to be determined. For this we will use the canonical ensemble, where the expression for the internal energy is[2]

$$u = \int \int \frac{1}{2} V(r_{12}, \omega_1, \omega_2) P_{eq}^{(2)} dr_1 dr_2 d\omega_1 d\omega_2.$$

Thus, the free energy of the system is given by

$$\begin{aligned}
 A = & \int kT P(r_1, \omega_1) \ln [ \int P(r_1, \omega_1) ]^{-1} g dr_1 d\omega_1 \\
 & + kT \int \int P_{eq}^{(2)}(r, \omega) \ln g_{eq}^{(2)} dr_1 dr_2 d\omega_1 d\omega_2 \\
 & + \int \int \frac{1}{2} V(r_{ij}, \omega_1, \omega_2) P_{eq}^{(2)} dr_1 d\omega_1 dr_2 d\omega_2.
 \end{aligned}$$

Because of the internal degrees of freedom, the all the terms of the above expression includes additional contributions, respect to the spherical case, but the meaning of each one is similar to the spherical case.

For the case of a homogenous fluid, the one and two particles distribution functions do not depend of the position and can be written as  $P(r, \omega) = \frac{1}{2} P(\omega)$ , where  $\frac{1}{2}$  is the

numerical density. For this, the free energy is

$$\frac{A}{NkT} = \frac{A^{(r,\omega)}}{N} + \ln \left( \frac{1}{\Omega} \right) + \frac{1}{2} \int \int V(r_{12}, \omega_1, \omega_2) P(\omega_1) P(\omega_2) d\omega_1 d\omega_2$$

The above expression is known as free energy Onsager's approximation, without the first term  $A^{(r,\omega)}/N$ . In a homogenous fluid,  $P(r_1, \omega_1)$  is constant, and its value is  $N/V\Omega$  ( $\Omega = 4\pi$  for linear molecules,  $\Omega = 8\pi^2$  for nonlinear molecules), and  $A^{(r,\omega)}/N$  is given by

$$\frac{A^{(r,\omega)}}{N} = \frac{kT\Omega^2}{N} \int \int g_{eq}^{(2)}(r_{12}, \omega_1, \omega_2) \ln g_{eq}^{(2)}(r_{12}, \omega_1, \omega_2) dr_1 dr_2 d\omega_1 d\omega_2 \quad (12)$$

To evaluate the last expression we assume that the pair correlation function can be split into a positional and a orientational parts[11],

$$g_{eq}^{(2)}(r_{12}, \omega_1, \omega_2) = g^r(r) g^{\omega}(r/\omega^2) \quad (13)$$

The first factor in the above expression represents the radial distribution function for an arbitrary site in the molecule, i.e.,

$$g^r(r) = \frac{1}{\Omega^2} \int \int g_{eq}^{(2)}(r_{12}, \omega_1, \omega_2) d\omega_1 d\omega_2$$

The second one is the distribution function of the relative orientations of two molecules at a distant  $r$ , and is known as orientational distribution function, and its normalized as

$$\frac{1}{\Omega^2} \int \int g^{\omega}(r/\omega^2) d\omega_1 d\omega_2 = 1.$$

Using (13) into (12), and using the above normalization, the free energy  $A^{(r,\omega)}$  becomes

$$A^{(r,\omega)} = \int_0^Z \frac{k\lambda^2}{2} g^r(r) \ln g^r(r) dr + \int_0^Z \frac{k\lambda^2}{2} g^r(r) S^{or}(r) dr$$

where

$$S^{or}(r) = \sum_{d=1}^Z g^i(r/\omega^2) \ln g^i(r/\omega^2) d!^{-1} d!^{-2}$$

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