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## Contact theorems for anisotropic fluids near a hard wall.

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In this paper, from the Born-Green-Yvon (BGY) equation, we formulate a general expression for the contact value of the singlet distribution function for anisotropic fluids near a hard wall. This expression consists of two separate contributions. One is related to the bulk partial pressure for a given orientation of the molecules. The second is related to the anchoring phenomena and is characterized by the direct interaction between the molecules and the wall. Given this relation, we formulate the contact theorems for the density and order parameter profiles. The results are illustrated by the case of a nematic fluid near a hard wall.

## I. INTRODUCTION

The contact theorem (CT) for a fluid near a hard wall is one of the few exact theoretical relations describing a fluid at an interface. According to this theorem, for a simple fluid, the contact value of the density profile (DP)  $\rho(z)$  near a hard wall at position  $z = 0$  (i.e. at the wall) is determined by the bulk pressure  $P$  of the fluid

$$\rho(z = 0) = \beta P \quad (1)$$

where  $z$  is the normal distance from the wall and  $\beta = 1/(k_B T)$  with  $k_B$  the Boltzmann constant and  $T$  the absolute temperature.

In the case of ionic fluids near a charged hard wall, eq. (1) should be corrected by adding to the pressure  $P$  the electrostatic Maxwell tensor contribution<sup>1,2</sup>. The CT for the charge profile in ionic fluids next to a charged hard wall has also been formulated<sup>3-5</sup>. In contrast to the CT for the DP, we showed that the CT for the charge profile has a non local character. In particular for the symmetrical electrolyte, the contact value of the charge profile includes the spatial integral of the DP multiplied by the gradient of the mean electric potential.

In anisotropic fluids such as nematic liquid crystals or anisotropic dipolar fluids, in contrast to simple and ionic fluids, the singlet distribution function (SDF) has a more complex dependence than the distance  $z$ . It depends on both the orientation of the molecules (for instance molecule 1) against the preferred orientational direction (director  $n$ )  $\Omega_{1n} = (\theta_{1n}, \phi_{1n})$  and the orientation of the wall against the director  $\Omega_{wn}$ . Due to the orientational ordering, anisotropic fluids next to a hard wall have a far richer behaviour than simple and ionic fluids. For instance, we point out the tensorial character of the order parameter (OP), the wall-induced biaxiality and the anchoring phenomena, whereby the surface induces a specific orientation of the director against the surface orientation<sup>6</sup>. In this study, we consider anisotropic fluids with exclusively orientational ordering leaving aside for instance smectic type phases where spatial ordering is also present.

In this paper, starting from the BGY equation for the SDF:  $\rho(z, \Omega_{1n}, \Omega_{wn})$ , as for ionic fluids<sup>3,7</sup>, we formulate the CT for an anisotropic fluid next to a hard wall. From the relation obtained, we will then formulate the CTs for the DP

$$\rho(z, \Omega_{wn}) \equiv \int d\Omega_{1n} \rho(z, \Omega_{1n}, \Omega_{wn}) \quad (2)$$

and for the OP profile

$$S_{l\mu}(z, \Omega_{wn}) \equiv \int d\Omega_{1n} \rho(z, \Omega_{1n}, \Omega_{wn}) Y_{l\mu}(\Omega_{1n}) \quad (3)$$

where  $d\Omega_{1n} = \frac{1}{4\pi} \sin(\theta_{1n}) d\theta_{1n} d\phi_{1n}$  is the normalized angle element for the orientation of the molecules against the director.  $Y_{l\mu}(\Omega_{1n})$  is the corresponding spherical harmonic for the orientation of the molecule against the director<sup>8</sup>. Usually the important spherical harmonics refer to  $l = 1$  for dipolar fluids and  $l = 2$  for nematic fluids.

## II. DERIVATION OF THE CONTACT THEOREM

In order to take into account anchoring effects, we assume molecules interact with the wall using the potential  $V(z, \theta_{1w})$  which is dependent on the distance  $z$  to the wall and on  $\theta_{1w}$ , the angle between the molecule and the wall. As a result the BGY equation for anisotropic fluids next to a hard wall is

$$\nabla_1 \rho(1) = -\beta \nabla_1 V(1) \rho(1) - \beta \rho(1) \int d2 \rho(2) g(12) \nabla_2 U(12) \quad (4)$$

where 1 and 2 stand for the position and orientation of the corresponding molecules and  $U(12) = U(r_{12}, \Omega_{1n}, \Omega_{2n})$  is the intermolecular interaction potential.  $r_{12}$  denotes the distance between molecules 1 and 2,  $\Omega_{1n}$  and  $\Omega_{2n}$  are the respective orientations of the molecules and  $g(12)$  is the pair distribution function.

After integration of eq. (4) with respect to  $z$ , the inhomogeneous part of the pair distribution function  $g^{inh}(12)$  vanishes<sup>3,7</sup> due to the symmetry of the pair interaction potential ( $\nabla_1 U(12) = -\nabla_2 U(12)$ ). As a result,

$$\begin{aligned} \rho(z=0, \Omega_{1n}, \Omega_{wn}) &= \beta \int_0^\infty dz_1 \frac{\partial V(z_1, \Omega_{1n}, \Omega_{wn})}{\partial z_1} \rho(z_1, \Omega_{1n}, \Omega_{wn}) \\ &+ \rho_b(\Omega_{1n}) \left[ 1 - \frac{1}{6} \int d\mathbf{r}_{12} d\Omega_{2n} g_b(r_{12}, \Omega_{1n}, \Omega_{2n}) \rho_b(\Omega_{2n}) r_{12} \frac{\partial U(12)}{\partial r_{12}} \right] \end{aligned} \quad (5)$$

where  $\rho_b(\Omega_{1n})$  and  $g_b(r_{12}, \Omega_{1n}, \Omega_{2n})$  are correspondingly the singlet and pair distribution functions for the anisotropic fluid in the bulk phase.

The last term in eq. (5) can be treated as the bulk partial pressure for molecules with a given orientation  $\Omega_{1n}$

$$\beta P(\Omega_{1n}) \equiv \rho_b(\Omega_{1n}) \left[ 1 - \frac{1}{6} \int d\mathbf{r}_{12} d\Omega_{2n} g_b(r_{12}, \Omega_{1n}, \Omega_{2n}) \rho_b(\Omega_{2n}) r_{12} \frac{\partial U(12)}{\partial r_{12}} \right]. \quad (6)$$

In consequence, the CT for the SDF  $\rho(z, \Omega_{1n}, \Omega_{wn})$  can be presented in the form

$$\rho(z = 0, \Omega_{1n}, \Omega_{wn}) = \beta \int_0^\infty dz_1 \frac{\partial V(z_1, \Omega_{1n}, \Omega_{wn})}{\partial z_1} \rho(z_1, \Omega_{1n}, \Omega_{wn}) + \beta P(\Omega_{1n}). \quad (7)$$

The above equation constitutes the principal result of this paper.

Clearly, the contact value of the SDF depends on  $\Omega_{wn}$  exclusively via the first term which accounts for the direct interaction between the wall and the particles. In the absence of this interaction the contact value of the SDF does not depend on  $\Omega_{wn}$  and is set only by the partial pressure, hence

$$\rho(z = 0, \Omega_{1n}, \Omega_{wn}) = \beta P(\Omega_{1n}). \quad (8)$$

This means that we may omit  $\Omega_{wn}$  in eq. (8).

After integration of eq. (7) on all possible orientations of molecule 1, i.e. integration over  $\Omega_{1n}$ , using definition eq. (2), we obtain the CT for the DP

$$\rho(z = 0, \Omega_{wn}) = \beta \int_0^\infty dz_1 d\Omega_{1n} \frac{\partial V(z_1, \Omega_{1n}, \Omega_{wn})}{\partial z_1} \rho(z_1, \Omega_{1n}, \Omega_{wn}) + \beta P \quad (9)$$

where

$$\beta P = \int d\Omega_{1n} P(\Omega_{1n}) \quad (10)$$

is simply the bulk pressure of the anisotropic fluid.

We must mention that, in the absence of anchoring effects, i.e. when  $V(z, \Omega_{1n}, \Omega_{wn}) = 0$ , the CT eq. (9) coincides exactly with the CT eq. (1) for the DP of a simple fluid. Therefore the contact value  $\rho(z = 0, \Omega_{wn})$  is independent from the angle  $\Omega_{wn}$  between the wall and the director. This has previously been illustrated<sup>9</sup> in the mean field approximation (MFA) for a nematic fluid near a hard wall in the Maier-Saupe model<sup>10,11</sup>.

Multiplying eq. (7) by  $Y_{l\mu}(\Omega_{1n})$ , integrating over  $\Omega_{1n}$  and using definition eq. (3), we can formulate the CT for the order parameter tensor

$$\begin{aligned} S_{l\mu}(z = 0, \Omega_{wn}) &= \beta \int_0^\infty dz_1 d\Omega_{1n} Y_{l\mu}(\Omega_{1n}) \frac{\partial V(z_1, \Omega_{1n}, \Omega_{wn})}{\partial z_1} \rho(z_1, \Omega_{1n}, \Omega_{wn}) \\ &+ \beta \int d\Omega_{1n} Y_{l\mu}(\Omega_{1n}) P(\Omega_{1n}) \end{aligned} \quad (11)$$

In the absence of anchoring interaction:  $V(z, \Omega_{1n}, \Omega_{wn}) = 0$ , we have the simpler relation

$$S_{l\mu}(z = 0, \Omega_{wn}) = \beta \int d\Omega_{1n} Y_{l\mu}(\Omega_{1n}) P(\Omega_{1n}). \quad (12)$$

Here again,  $S_{l\mu}(z = 0, \Omega_{wn})$  does not depend on the angle  $\Omega_{wn}$  and if  $P(\Omega_{1n})$  has no azimuthal dependence,

$$S_{l\mu}(z = 0, \Omega_{wn}) = 0 \quad \text{for } \mu \neq 0. \quad (13)$$

### III. THE CASE OF NEMATIC FLUIDS

To illustrate the role of anchoring on the CTs, we take a simple model of a nematic fluid near a hard wall obeying the wall-nematic interaction introduced in<sup>12,13</sup>

$$V(z, \Omega_{1n}, \Omega_{wn}) = V_0(z) + V_2(z)P_2(\cos[\theta_{1w}]) \quad (14)$$

where the first and second term are relative to the direct isotropic and anisotropic interactions of the molecules with the wall and  $P_2(\cos(\theta_{1w})) = (1/2)[3\cos^2(\theta_{1w}) - 1]$  is the second order Legendre polynomial.

With the above potential, using definitions (2) and (3), and relations (9) and (11), the CTs for the DP and the order parameter can be presented as

$$\begin{aligned} \rho(z=0, \Omega_{wn}) = & \beta \int_0^\infty dz_1 \frac{\partial V_0(z_1)}{\partial z_1} \rho(z_1, \Omega_{wn}) \\ & + \beta \sum_{\mu} Y_{2\mu}(\Omega_{wn}) \int_0^\infty dz_1 \frac{\partial V_2(z_1)}{\partial z_1} S_{2\mu}(z_1, \Omega_{wn}) \\ & + \beta P, \end{aligned} \quad (15)$$

$$\begin{aligned} S_{2\mu}(z=0, \Omega_{wn}) = & \beta \int_0^\infty dz_1 \frac{\partial V_0(z_1)}{\partial z_1} S_{2\mu}(z_1, \Omega_{wn}) \\ & + \beta \sum_{\mu'} Y_{2\mu'}(\Omega_{wn}) \int_0^\infty dz_1 \frac{\partial V_2(z_1)}{\partial z_1} S_{2\mu\mu'}(z_1, \Omega_{wn}) \\ & + \beta \int d\Omega_{1n} Y_{2\mu}(\Omega_{1n}) P(\Omega_{1n}) \end{aligned} \quad (16)$$

where

$$S_{2\mu\mu'}(z, \Omega_{wn}) = \int d\Omega_{1n} \rho(z, \Omega_{1n}, \Omega_{wn}) Y_{2\mu}(\Omega_{1n}) Y_{2\mu'}(\Omega_{1n}). \quad (17)$$

In contrast to the CT eq. (7) for the SDF, the presence of an orientationally dependent interaction between molecules and wall (anchoring phenomenon) leads to a non closed set of integral equations in the CTs for both the density and the order parameters profiles. It implies that the calculation of the contact value of the DP requires the knowledge of the density and order parameter profiles. And the calculation of the contact value of the order parameter requires the knowledge of the order parameter profile as well as the higher order parameter  $S_{2\mu\mu'}(z, \Omega_{wn})$  profile.

## IV. CONCLUSION.

In this paper, we show the exact expression for the contact value of the SDF near a hard wall of an anisotropic fluid characterized by orientational ordering in the bulk. The expression has two separate contributions. One is related to the partial pressure  $P(\Omega_{1n})$  for a given orientation  $\Omega_{1n}$  of the molecules. The second contribution is connected with the direct interaction of the molecules with the wall, typical of the so called anchoring phenomenon – which can be distance and orientationally dependent.

From this relation, we elaborate the CT for the density and the OP irrespective of the molecule’s orientation. We then show the fundamental role of the orientational dependent interaction of the molecules with the wall on the tensorial character of the OP near the wall. In the absence of molecule-wall interaction, the contact values of the density and of the OP profiles do not depend on the angle between the wall and the director. Consequently for dipolar or nematic liquids for instance, since their partial pressure  $P(\Omega_{1n})$  has no azimuthal orientational dependence, the contact values of the SDF will likewise not have any azimuthal dependence. Hence, the contact value of the order parameter will not have an azimuthal component for  $\mu \neq 0$  spherical harmonics.

Finally, we illustrate the CT with a simple model of a nematic fluid near a hard wall. The set of equations has a non closed form.

We believe that these exact relations at a surface can be used to verify the accuracy of results from numerical simulations or else to improve DP approximations based on state of the art approximations for the bulk pressure – easier to calculate. We have adopted this procedure for isotropic fluids<sup>14</sup> and intend to apply it to nematic fluids.

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## REFERENCES

<sup>1</sup>D. Henderson and L. Blum, J. Chem. Phys. **69**, 5441 (1978).

- <sup>2</sup>D. Henderson, L. Blum, and J. Lebowitz, *J. Electroanal. Phys.* **102**, 315 (1979).
- <sup>3</sup>M. Holovko, J. P. Badiali, and D. di Caprio, *J. Chem. Phys.* **123**, 234705 (2005).
- <sup>4</sup>M. Holovko, J. P. Badiali, and D. di Caprio, *J. Chem. Phys.* **127**, 014106 (2007).
- <sup>5</sup>M. Holovko and D. di Caprio, *J. Chem. Phys.* **128**, 174702 (2008).
- <sup>6</sup>B. Jérôme, *Rep. Prog. Phys.* **54**, 391 (1991).
- <sup>7</sup>S. L. Carnie and D. Y. C. Chan, *J. Chem. Phys.* **74**, 1293 (1981).
- <sup>8</sup>Note that  $S_{l\mu}(z, \Omega_{wn})$  for  $\mu \neq 0$  is complex, it is usual to introduce the following real quantities  $S_{l\mu}^+ = (S_{l\mu} + S_{l\mu}^*)/2$  and  $S_{l\mu}^- = (S_{l\mu} - S_{l\mu}^*)/(2i)$  where \* denotes the complex conjugate.
- <sup>9</sup>M. Holovko, I. Kravtsiv, and D. di Caprio, *Cond. Matter. Phys.* **16**, 14002 (2013).
- <sup>10</sup>W. Maier and A. Saupe, *Z. Naturforsch.* **A14**, 882 (1959).
- <sup>11</sup>W. Maier and A. Saupe, *Z. Naturforsch.* **A15**, 287 (1960).
- <sup>12</sup>T. G. Sokolovska, R. O. Sokolovskii, and G. N. Patey, *Phys. Rev. Lett.* **92**, 185508 (2004).
- <sup>13</sup>T. G. Sokolovska, R. O. Sokolovskii, and G. N. Patey, *J. Chem. Phys.* **122**, 034703 (2005).
- <sup>14</sup>I. Kravtsiv, T. Patsahan, M. Holovko, and D. di Caprio, in preparation (2015).