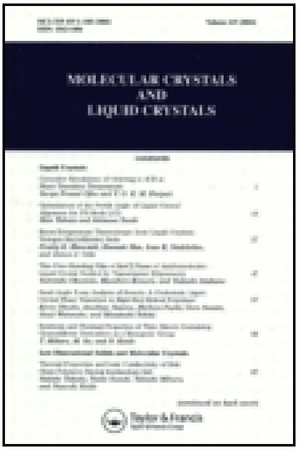
This article was downloaded by: [University of California, San Diego]
On: 22 August 2012, At: 09:24
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Magnetic Susceptibility Studies on a Lyotropic Nematic System

D. Vijayaraghavan [a] & K. A. Suresh [a]

[a] Raman Research Institute, Bangalore, India

Version of record first published: 31 Jan 2007

To cite this article: D. Vijayaraghavan & K. A. Suresh (2005): Magnetic Susceptibility Studies on a Lyotropic Nematic System, Molecular Crystals and Liquid Crystals, 434:1, 281/[609]-290/[618]

To link to this article: http://dx.doi.org/10.1080/15421400590954362

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

Mol. Cryst. Liq. Cryst., Vol. 434, pp. 281/[609]–290/[618], 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590954362

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

Magnetic Susceptibility Studies on a Lyotropic Nematic System

D. Vijayaraghavan
K. A. Suresh
Raman Research Institute, Bangalore, India

We have carried out magnetic susceptibility studies on a lyotropic system, cesium perfluorooctanoate (CsPFO) in water for various concentrations of CsPFO. This system exhibits isotropic, nematic and lamellar phases on cooling for a range of concentrations. The structural unit in all the three phases is a disk shaped micelle with positive diamagnetic anisotropy. We find small discontinuous jumps in the magnetic susceptibility values in the vicinity of the isotropic-nematic transition temperatures for various concentrations. The susceptibility decreases initially with increasing CsPFO concentration and then increases. These observed changes can be attributed to the changes in the sizes and shapes of the micelles. We have also studied the temperature dependence of the diamagnetic anisotropy in the nematic phase. We discuss our results with those reported in the literature for lyotropic systems.

Keywords: lyotropic nematic; magnetic susceptibility; micelles

1. INTRODUCTION

The nematic micellar phase consisting of binary or ternary amphiphilic-water system has drawn considerable interest since its discovery in 1967 [1]. The orientationally ordered micellar nematic phase can be considered as an intermediate state between the translationally ordered lamellar and the disordered micellar system. Depending on their orientation in a magnetic field, the nematic phase can be classified into type I phase (positive diamagnetic anisotropy) or type II phase (negative diamagnetic anisotropy) [2]. Cesium perfluorooctanoate (CsPFO)/water (H_2O) system exhibits a diamagnetically positive, discotic nematic phase that is stable over a wide range of

Address correspondence to Dr. D. Vijayaraghavan, Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bangalore 560 080, India. E-mail: vijay@rri.res.in

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

temperature and concentration [3]. The nematic order parameter of this system has been studied using birefringence measurements [4]. Magnetic-field birefringence measurements in the nematic phase close to the nematic-isotropic (N-I) transition has been carried out to study the nematic order parameter susceptibility exponents [5,6].

Stefanov and Saupe have reported the susceptibility measurements on a ternary micellar nematic system consisting of decylammonium chloride/ammonium chloride/water for two different concentrations [7]. In this system the micelles were disk shaped and in the nematic phase it exhibited negative diamagnetic anisotropy. They measured the principle susceptibility perpendicular to the optical axis. Apart from this work, there has been no direct measurement of magnetic susceptibility in the surfactant based lyotropic liquid crystals. Hence, it is of interest to study the magnetic properties of CsPFO/H_2O system. Here, we report our magnetic susceptibility measurements on this system for four different concentrations. We find small discontinuous jump in the susceptibility values in the vicinity of the N-I transition.

2. EXPERIMENTAL

We used the lyotropic liquid crystal system CsPFO dissolved in de-ionised millipore water. The measurements were carried out for four different concentrations of CsPFO namely, CsPFO/H_2O = 40/60 wt% (sample A), CsPFO/H_2O = 45/55 wt% (sample B), CsPFO/H_2O = 50/50 wt% (sample C) and CsPFO/H_2O = 55/45 wt% (sample D). The nematic-isotropic transition temperatures (T_{NI}) were 309 K, 312 K, 320 K and 330.6 K for the samples A,B,C and D respectively and the corresponding nematic-lamellar transition temperatures (T_{NL}) were 304 K, 307 K, 315 K and 326.6 K. For the susceptibility measurements, oxygen was removed from the millipore water by bubbling dry nitrogen gas through it for several hours. This water was added to CsPFO under a nitrogen atmosphere and the components were mixed thoroughly. Typically about 5.2 mg of the sample was taken in a Perkin Elmer DSC sample cup and sealed to prevent evaporation of water using standard procedure.

The diamagnetic susceptibility $\boldsymbol{\chi}$ relates the induced magnetic moment **M** (per unit mass), and the applied field **H** [8]:

$$\mathrm{M}_\alpha = \chi_{\alpha\beta}\mathrm{H}_\beta;\ \ \alpha,\beta = \mathrm{x,y,z} \tag{1}$$

where $\chi_{\alpha\beta}$ denotes an element of the susceptibility tensor $\boldsymbol{\chi}$. Choosing the z-axis along the director, the tensor corresponding to the nematic

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

phase is given by

$$\chi = \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{pmatrix} \tag{2}$$

where the subscripts $_{\parallel}$ and $\perp$ refer to the directions parallel and perpendicular to the director, respectively. The average mass susceptibility is given by

$$\bar{\chi} = \frac{1}{3}\sum_{\gamma}\chi_{\gamma\gamma} = \frac{1}{3}(\chi_\parallel + 2\chi_\perp) \tag{3}$$

The average mass susceptibility is equal to the isotropic phase susceptibility and hence the magnetic anisotropy can be defined as

$$\Delta\chi = \chi_\parallel - \chi_\perp = 3/2(\chi_\parallel - \bar{\chi}) \tag{4}$$

We measured the magnetic susceptibility by the classical Faraday-Curie method. The energy U of the sample of mass m and magnetic susceptibility χ when kept in a horizontal magnetic field H_x is given by

$$U = -(m\chi H_X{}^2)/2 \tag{5}$$

The vertical force F_z exerted on this sample is given by

$$F_z = \chi m H_x \left(\frac{dH_x}{dH_z}\right) \tag{6}$$

$F_z = \Delta Mg$ where ΔM can be considered as the extra mass measured by the balance due to the force exerted by the field gradient, and g is the acceleration due to gravity. For $\Delta\chi > 0$, the field causes a uniform alignment of the director along the direction of the field, and χ can be measured. A measurement of χ in the isotropic phase gives the value of $\bar{\chi}$.

A schematic diagram of the experimental set up is shown in Figure 1. A continuous flow cryostat (CF1200, Oxford instruments) was held between the pole pieces of an electro magnet (Oxford instruments). The pole tips were shaped to give a constant value of $H_x(dH_x/dH_z)$ in the sample region (about $15 \times 12 \times 12\,\mathrm{mm}^3$). The sample was top loaded through an access port on top of the cryostat. This port was sealed by a plug against an O ring. The force exerted on the sample was measured using a Sartorious balance (model S3DV) which has a maximum capacity of 3 g and sensitivity of 0.1 µg. The temperature of the sample was monitored by an Oxford instruments controller (ITC4) with a resolution of 0.1 K. A chromel-alumel thermocouple was used to measure the temperature of the sample.

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

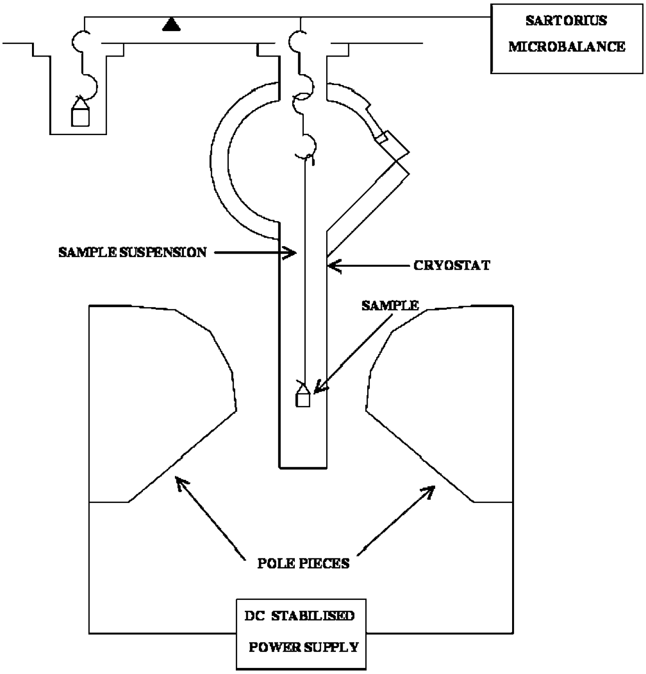


FIGURE 1 A schematic diagram of the experimental set up used in the magnetic susceptibility measurements.

The sample cup susceptibility was determined by the following method. The sample cup was modified into a pan by using a pair of 40 gauge copper wires (of negligible mass with respect to the mass of the cup) of length 0.5 cm and suspended from one end of the 62 cms length (124 microns thick) quartz fiber (supplied by Oxford instruments). The other end of the quartz fiber was hooked to the sample port of the balance. The advantage of using a quartz fiber is that its susceptibility and temperature variation of the susceptibility are very low. Weights were added to the weighing port of the balance until the balance reading was nearly zero (M_0). The cryostat was evacuated and then slowly filled with dry helium gas (for better thermal conductivity). The magnetic field was applied on the sample cup (pan) and the balance reading M_c was taken. The difference between the two values $M_c - M_0 (= \Delta M_c)$ is related to the susceptibility through Equation (6):

$$\Delta M_c g = \chi m H_x \left(\frac{dH_x}{dH_z}\right) \tag{7}$$

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

where

g - acceleration due to gravity = 980 cm/sec^2,
m - mass of the sample,
H_x - magnetic field strength = 11 kilo Gauss,
dH_x/dH_z magnetic field gradient at the sample region.

The value of $H_x(dH_x/dH_z) = K$ was obtained from the manufacturer's chart; 10.895×10^6 gauss^2/cm for a 11 Kilo Gauss field with a pole gap of 42 mm.

By measuring ΔM_c and knowing the mass of the pan, the sample cup susceptibility (χ_{cup}) can be calculated. The room temperature susceptibility of the sample cup was found to be $+0.65 \times 10^{-6}$ cgs and it was found to decrease linearly by about 5% at 373 K.

For calibration, measurements were carried on heptyl cyanobiphenyl (7CB) liquid crystalline sample ($T_{NI} = 315.5$ K). About 10 mg of the sample was taken in a DSC cup and sealed. This sealed cup was put in the pan described above and hooked to the balance. The ΔM for the present set up (ΔM_{total}) was measured as the difference between the balance readings corresponding to zero field and 11 kilo Gauss field.

Using the relations,

$$\chi_{total}\ m_{total} = \chi_{cup}\ m_{cup} + \chi_{sample}\ m_{sample} \tag{8}$$

and

$$\Delta M_{total}\ g = \chi_{total}\ m_{total}\ K \tag{9}$$

we get

$$\Delta M_{total}\ g = \chi_{cup} m_{cup}\ K + \chi_{sample} m_{sample}\ K. \tag{10}$$

Thus χ_{sample} can be determined.

Here, m_{cup} refers to the total mass of the pan and the empty DSC cup. Measurements were made by heating the sample to 333 K and cooling it slowly in the presence of the magnetic field in 1 K step. The results on 7CB were in good agreement with those reported in reference 9. In a similar way, the measurements were carried out on the CsPFO in water micellar system.

3. RESULTS AND DISCUSSION

The mass diamagnetic susceptibility as a function of temperature for four different concentrations of CsPFO in water are shown in

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

Figure 2. We find a small discontinuous jump at the isotropic-nematic transition temperatures in all the cases.

The diamagnetic anisotropy in these micellar nematic system was positive. The experiment gives, therefore, the principle susceptibility parallel to the director. In micellar systems, the mean diamagnetic susceptibility has a temperature dependence which has to be taken into account [7]. The mean susceptibility $\bar{\chi}$ can be obtained by linear extrapolation from the isotropic phase [7]. The diamagnetic anisotropy $\Delta\chi$ can be evaluated from Eq. (4).

Stefanov and Saupe attributed the temperature dependence of the mean susceptibility in the isotropic phase to the mass diamagnetic susceptibility of bulk (pure) water, arising due to the temperature dependence of the number of hydrogen bonds between water molecules [7,10]. They found the susceptibility value to be 7.5×10^{-7} cgs in the isotropic phase. They suggested that the number of hydrogen bonds also depend on the ion concentration and could be affected by a change in the micellar structure. They observed only a weak dependence of susceptibility on concentration and temperature. In contrast, we find a strong

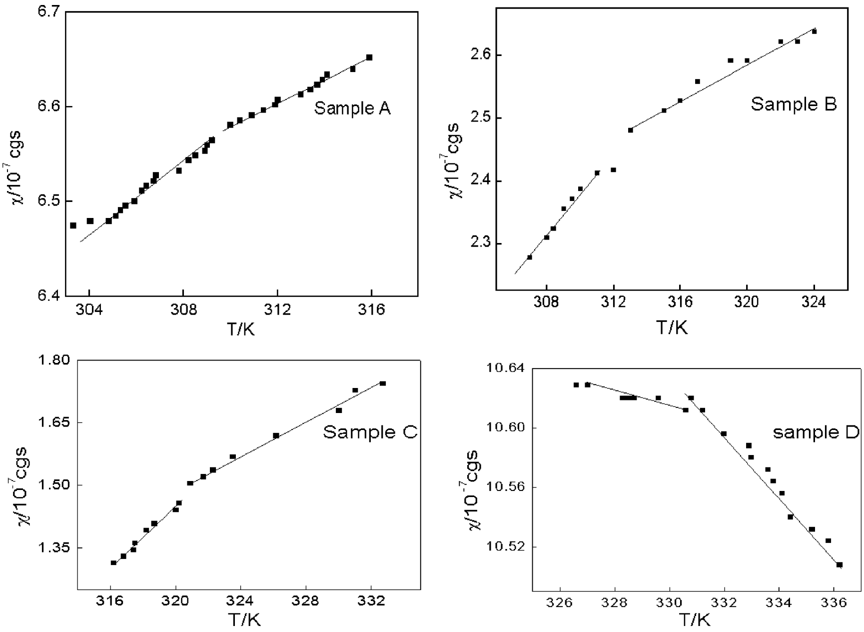


FIGURE 2 Mass diamagnetic susceptibility (χ) as a function of temperature (T/K) for samples A (40/60 wt%), B (45/55 wt%), C (50/50 wt%) and D (55/45 wt%) of CsPFO/H_2O system. The solid lines are guide to the eyes.

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

dependence of the susceptibility on concentration and temperature (Fig. 2). The isotropic susceptibility values for various concentrations are found to exhibit marked deviations from the water susceptibility. This can be explained using the concentration-temperature dependence of the size and shape of the micelles as observed in CsPFO/^2H_2O system by Holmes *et al.* [11]. Figure 3 shows the mass diamagnetic susceptibility plotted as a function of weight percentage of CsPFO in water at fixed temperatures. Holmes *et al.* have reported the variation of the aggregation number of the oblate ellipsoidal micelles with weight fraction of CsPFO in ^2H_2O at fixed temperatures. From these results we can infer that the diamagnetic susceptibility has an inverse relation to the aggregation number or the size of the micelles. Since, the aggregation number decreases with increasing temperature at a rate which is roughly inversely proportional to the axial ratio (thickness to diameter ratio) of the micelles, we can expect the temperature dependence of the susceptibility to depend on the axial ratio or the shape of the micelles. In the nematic phase, the variations in the susceptibility also depend on the orientational ordering of the micelles.

Interestingly, for the high concentration of CsPFO (55 wt%; sample D), we find a different behaviour. Here, the susceptibility in the isotropic phase is found to increase weakly with decrease in temperature. We expect a small decrease of susceptibility with decrease

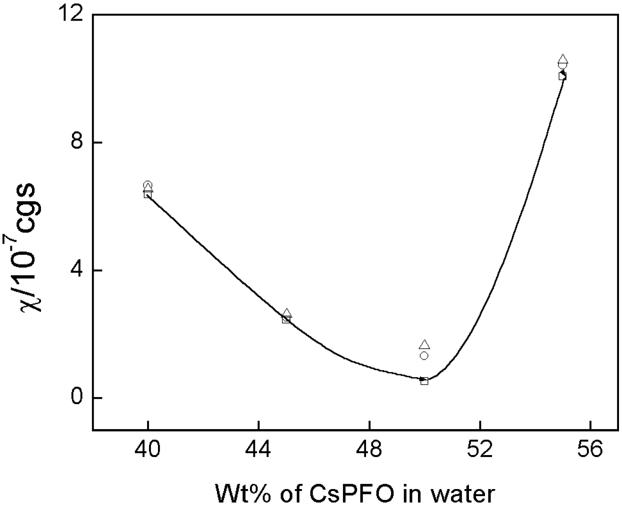


FIGURE 3 Mass diamagnetic susceptibility (χ) as a function of weight percentage of CSPFO in water (H_2O) at fixed temperatures, 303 K (squares), 316 K (circles) and 324 K (triangles). The solid line is a guide to the eyes.

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

in temperature based on the results of Holmes *et al.* [11]. The reported molecular simulation study in this system suggests the presence of bound water [12,13]. Based on this suggestion, the observed slight increase in the susceptibility with decrease in temperature can be related to the free to bound water ratio. The bound water in this system may depend on many factors like the number of bound water molecules per surfactant molecule, the ratio of the number of surfactant molecules to the water molecules and the time over which the water molecules may bound to the surfactant molecule as reported in a protein-bound water system [14].

The diamagnetic anisotropy ($\Delta\chi$) as a function of temperature in the nematic phase for the four different concentrations of CsPFO in water are shown in Figure 4. The order of magnitude of the $\Delta\chi$ values for 40 and 55 wt% CsPFO are close to the values obtained for the micellar nematic system [7]. However, we find the $\Delta\chi$ values at T_{NI} to be nearly 2 times larger for 45 and 50 wt% CsPFO compared to their system. Interestingly, our values are in reasonable agreement with the estimated value for the diamagnetic anisotropy derived from light scattering and magnetic birefringence studies on $DACl/NH_4Cl/H_2O$ system [15].

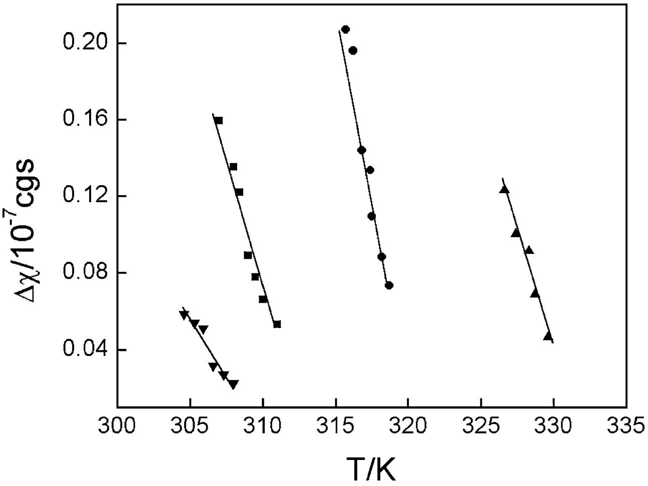


FIGURE 4 Diamagnetic anisotropy ($\Delta\chi$) in the nematic phase as a function of temperature (T/K) for sample A (40/60 wt%) (inverted triangles), sample B (45/55 wt%) (squares), sample C (50/50 wt%) (circles) and sample D (55/45 wt%) (triangles) for the $CsPFO/H_2O$ system. The solid lines are guide to the eyes.

The nematic order parameter for the CsPFO/H_2O system has been studied using optical birefringence measurements [4]. The ratio of the order parameter values at T_{NL} and T_{NI} is approximately equal to 2.5. If we assume that the diamagnetic anisotropy is propotional to the nematic order parameter (as observed in thermotropic systems), then one expects the value of the ratio of the diamagnetic anisotropy at T_{NL} and in the vicinity of T_{NI} to be of the order of 2.5. However, our studies yield the average ratio to be about 3. The nematic order parameter for the CsPFO/^2H_2O system of 55 wt% CsPFO measured using electrical conductivity studies show the ratio to be about 2 which agrees well with our results at the same concentration of CsPFO [16]. We find the diamagnetic anisotropy values in the vicinity of T_{NL} depends markedly on CsPFO concentration (fig. 4). Such a dependence in nematic order parameter has also been observed in water self diffusion studies on CsPFO/^2H_2O system using NMR techniques [17].

4. CONCLUSION

We have carried out mass diamagnetic susceptibility measurements on the micellar isotropic and micellar nematic phase of CsPFO/H_2O system for four different concentrations of CsPFO. The strong concentration and temperature dependence of the mass diamagnetic susceptibility is attributed to the changes in the micellar sizes and shapes reported for the CsPFO/^2H_2O system. The temperature dependence of the diamagnetic anisotropy of the micellar nematic phase for different concentrations was derived from the susceptibility data. We have discussed our diamagnetic anisotropy data with those of a micellar nematic system reported in the literature.

REFERENCES

[1] Lawson, K. D. & Flautt, T. J. (1967). *J. Am. Chem. Soc.*, *89*, 5489.
[2] Hendrikx, Y. & Charvolin, J. (1981). *J. de Physique.*, *42*, 1427.
[3] Boden, N., Jackson, P. H., McMullen, K., & Holmes, M. C. (1979). *Chem. Phys. Lett.*, *65*, 476.
[4] Larson, B. D. & Litster, J. D. (1984). *Mol. Cryst. Liq. Cryst.*, *113*, 13.
[5] Charles Rosenblatt., Satyendra Kumar, & Litster, J. D. (1984). *Phys. Rev. A.*, *29*, 1010.
[6] Charles Rosenblatt (1985). *Phys. Rev. A.*, *32*, 1115.
[7] Stefanov, M. & Saupe, A. (1984). *Mol. Cryst. Liq. Cryst.*, *108*, 309.
[8] Buka, A. & de Jeu, W. H. (1982). *J. Physique.*, *43*, 361.
[9] Picken, S. J. (1999). Physical properties of liquid crystals: Nematics. Dunmur, D. A., Fukuda, & Luckhurst, G. R. (Eds.), United Kingdom: INSPEC, Hertz, 97.
[10] Cini, R. & M. Torrini, M. (1968). *J. Chem. Phys.*, *49*, 2826.

Downloaded by [University of California, San Diego] at 09:24 22 August 2012

[11] Michael C. Holmes, David J. Reynolds, & Neville Boden (1987). *J. Phys. Chem.*, *91*, 5257.

[12] Subrata Pal, Sundaram Balasubramanian, & Biman Bagchi (2003). *Phys. Rev.*, E *67*, 061502.

[13] Subrata Pal, Sundaram Balasubramanian, & Biman Bagchi (2002). *J. Chem. Phys.*, *117*, 2852.

[14] Alexandra Van-Quynh, Steven Willson, & Robert G. Bryant (2003). *Biophysical Journal*, *84*, 558.

[15] Satyendra Kumar, S., Litster, J. D., & Charles Rosenblatt (1983). *Phys. Rev. A.*, *28*, 1890.

[16] Boden, N., Corne, S. A., Holmes, M. C., Jackson, P. H., Parker, D., & Jolley, K. W. (1986). *J. Physique.*, *47*, 2135.

[17] Haukur Johannesson, Istvan Furo, & Bertil Halle (1996). *Phys. Rev.*, E. *53*, 4904.

Downloaded by [University of California, San Diego] at 09:24 22 August 2012