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ON THE SWITCHING FROM THREE TO ONE DIMENSIONAL BEHAVIOR IN A MODEL LIQUID CRYSTAL

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A Monte Carlo study of a Lebwohl-Lasher lattice model with anisotropic interaction is presented. Six different values of out of plane to the in-plane coupling ratio have been taken into account. Comparison with mean field prediction and with analytic results, when possible, are made.

Keywords: Computer Simulations; Monte Carlo; Phase Transitions; Liquid Crystals.

1. Introduction

Computer simulations represent a useful tool to study phase transitions.[1] In particular they have been extensively applied to investigate the physics of anisotropic fluids (model liquid crystals) where the prototype nearest neighbours model is that originally due to Lebwohl and Lasher (LL).[2] In this model the particles are placed at the sites of a cubic lattice and interact through a pair potential:

$$U_{ij}(\beta) = -\epsilon_{ij} P_2(\cos\beta_{ij}) \tag{1}$$

where ϵ_{ij} is a positive constant that takes the value ϵ if i and j are nearest neighbours and 0 otherwise; P_2 is the second Legendre polynomial and β_{ij} is the angle between the symmetry axis of the ith and jth particles. The LL model is well studied and it has been found to give a weakly first order orientational phase transition at the reduced temperature[3] $kT/\epsilon = 1.1232$ with characteristics similar to those of real nematics.

Some time ago we studied an anisotropic version of this model where the potential differs in strength for the four horizontal and the two vertical neighbours.[4] We considered various values of the out of plane to the in-plane coupling ratio

$\delta = \epsilon_{\parallel}/\epsilon_{\perp}$ starting from a LL model ($\delta = 1$) to reach the limiting situation of a two-dimensional lattice, for which a true phase transition does not exist. This system has recently received a great deal of attention from various researchers.[5–7]

In this work we wish to study the other limiting case where the interactions in the plane decrease and eventually tend to zero. This model could be appropriate to columnar systems formed by a central core surrounded by a suitable number of alkyl chains of a given length. The interaction between molecules in different columns becomes weaker and weaker as the chain length increases and the interacting cores are more spaced (Fig. 1). In the limit the system reduces to a set of one-dimensional lattices for which an analytical solution, showing the absence of a phase transition, has been obtained by Vuillermot and Romerio.[8] This one-dimensional solution has also been verified by a MC study of the orientational pair correlations of the model and their size dependence.[9]

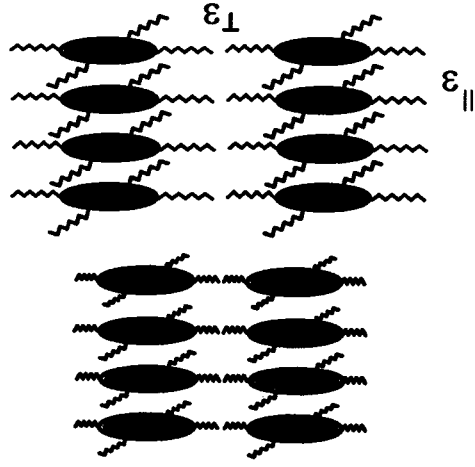

Fig. 1. A schematic representation of a lattice model of a columnar system. The interaction in the plane, denoted by the coupling constant $\epsilon_{\perp}$, is inversely proportional to the chain length.

In the present simple model system with anisotropic second rank interactions we have the following N particle hamiltonian:

$$-U_N = \sum_{(i,j)_p} (\epsilon_{\perp})_{ij} P_2(\cos\beta_{ij}) + \sum_{(i,j)_s} (\epsilon_{\parallel})_{ij} P_2(\cos\beta_{ij}) \qquad (2)$$

where we consider a simple cubic lattice and the sums are extended, respectively, to nearest neighbours in the same laboratory horizontal plane (i.e. with interparticle vector $\vec{r}_{ij} \parallel X, Y$) and to neighbours along the vertical, Z axis. The parameter $\xi = \epsilon_{\perp}/\epsilon_{\parallel}$ gives the relative strength of the two interactions and when $\xi = 1$ the model reduces to the usual LL one. Decreasing ξ we have a weakening of the in-plane

coupling and at the limit $\xi = 0$ the lattice becomes, as already mentioned, a collection of independent linear chains, that is a set of one-dimensional LL lattices.[8,9]

In this paper we briefly discuss the mean field theory predictions for the model, followed by the results of a set of MC simulations for six different values of the coupling anisotropy ξ. Comparisons are made with available simulations[3,9] and with mean field theory.

2. Mean Field Theory

The potential of mean torque acting on a particle by effect of all the others in the system is obtained from Eq. (2) in a standard way[10] as:

$$U(\beta) = -(2\epsilon_{\parallel} + 4\epsilon_{\perp})\langle P_2\rangle P_2(\cos\beta) \tag{3}$$

where β is the angle between the molecule and the director and we have assumed $\langle P_2\rangle$ to be homogeneous throughout the sample. We can rewrite Eq. (3) as:

$$\frac{U(\beta)}{kT} = -\frac{\epsilon_{\parallel}}{kT}(2 + 4\xi)\langle P_2\rangle P_2(\cos\beta) \tag{4}$$

where $\xi = \epsilon_{\perp}/\epsilon_{\parallel} = 1/\delta$. This compares with the LL potential, i.e.:

$$\frac{U(\beta)}{kT} = -\frac{z\epsilon}{kT}\langle P_2\rangle P_2(\cos\beta) \tag{5}$$

where z (here $z = 6$) is the coordination number and we can observe that at molecular field theory level the effect of changing the in-plane coupling is just a renormalization of the temperature. We have an effective $z' = 2 + 4\xi$ and, instead of kT/ϵ, an effective temperature:

$$(T^*)_{\xi} = \frac{kT}{\epsilon_{\parallel}}\frac{(2 + 4\xi)}{6} \tag{6}$$

then

$$(T^*_{NI})_{\xi} = (T^*_{NI})_{LL}\left(\frac{2 + 4\xi}{6}\right) = 0.1872(2 + 4\xi)\ . \tag{7}$$

Apart from this renormalization all the properties of the transition, including the first order character are predicted to be unchanged by simple mean field theory.

3. Monte Carlo Simulations

We have studied a system of $N = 10 \times 10 \times 10$ particles for six different values of ξ, i.e. $\xi = 0.01, 0.02, 0.05, 0.1, 0.2, 0.5$.

The simulations were meant to be completely independent, so in each case the run at the lowest temperature studied has been initiated from a completely aligned system. The calculations at the other temperatures have been started from an equilibrium configuration at the nearest lower temperature.

The updating procedure of the lattice follows the standard Metropolis prescriptions[11] employing periodic boundary condition and a controlled evolution step so to have a rejection rate not too far from 0.5.[12] We have used at least 22000 equilibration cycles far from the transition and 30000 in the pseudo critical region. Apart from equilibration, production runs were also of varying length, according to the distance from the transition. Close to the pseudo phase change sequences as long as 20 Kcycles have been used. Each calculation was divided in chains of 1000 to 2000 cycles. Statistical errors were estimated as standard deviations from the average over these runs. During the production run various observables have been calculated in addition to the internal energy and second rank order parameters calculated at every cycle as already described. Each property of interest, A, is evaluated at every cycle. After a certain number of cycles m_J (typically between 1000 and 2000) an average A^J is calculated thus providing an effective coarse graining of the trajectory. A further grand average is then computed as the weighted average over M such supposedly uncorrelated segments. The attendant weighted standard deviation from the average σ_A is also calculated and gives the error estimates shown in the figures.

4. Main Results

We have calculated, for each simulation, the energy, specific heat and second and fourth rank order parameters. Pair correlation coefficients, again of second and fourth rank, have been calculated, at selected temperatures, as described in Ref. 11.

4.1. *Energy*

The energy of the system is computed at every cycle because it is the essential information needed for the Monte Carlo procedure. In Fig. 2 the dimensionless single particle energy $U^* = \langle U_N \rangle / N\epsilon_{\|}$ versus the reduced temperature $T^* = kT/\epsilon_{\|}$ is shown.

The curves are well separated for the higher values of ξ starting, of course, from their respective minimum energy configurations corresponding to completely aligned systems. Indeed the average energy per particle for the simple cubic lattice is:

$$U^* = -\frac{(2+4\xi)}{2}\sigma_2 \tag{8}$$

in terms of the short-range-order parameter $\sigma_2 = \langle P_2(\cos\beta_{ij}) \rangle$ with i,j nearest neighbours. We notice that the results for $\xi = 0.01$ are quite close to the analytic solution for the one-dimensional lattice.

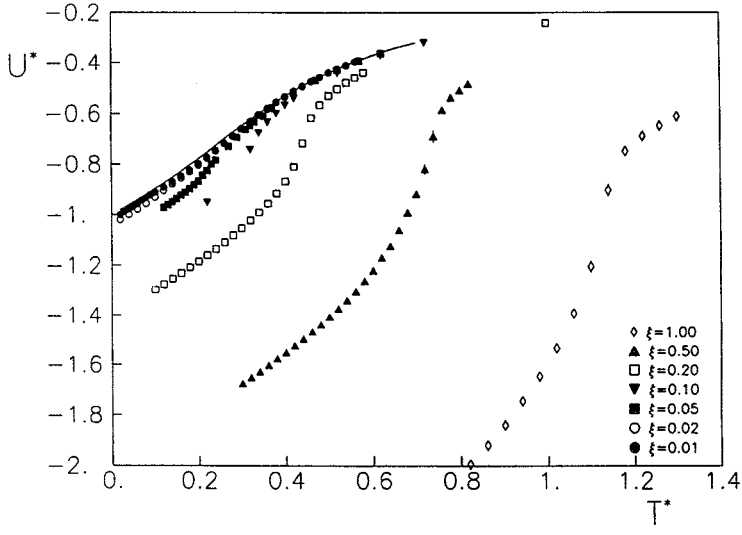

Fig. 2. The energy vs. temperatures for the various system studied. The continuous line is the analytic result for $\xi = 0$.[8]

4.2. *Heat capacity*

The dimensionless heat capacity, C_V^*, is obtained by differentiating the average energy with respect to temperature as previously described.[4] In brief, the energy values are interpolated and smoothed using a five point orthogonal formula before performing the numerical differentiation with an inversion method on the energy written as an integral of the heat capacity with respect to temperature.

For the case $\xi = 0.$, i.e. the linear lattice, the analytic formula for C_V^* has been obtained by Vuillermot and Romerio[8]:

$$\frac{C_v}{Nk} = \frac{1}{2} - \frac{3}{4T^*}\sqrt{\frac{3}{2T^*}}\left[\frac{T^*}{3} - 1\right] D^{-1}\left(\sqrt{\frac{3}{2T^*}}\right) - \frac{3}{8T^*} D^{-2}\left(\sqrt{\frac{3}{2T^*}}\right) \qquad (9)$$

where $D(x)$ is the Dawson function[13] and is plotted as the continuous line in Fig. 3. We also report in Fig. 3 the heat capacity C_V^* results vs. the reduced temperature for the cases studied. We notice that the peaks of the heat capacity, occurring at T^*_C, become less pronounced as the strength of the interactions on the plane decreases. The curve assumes the same behavior of the analytic result when $\xi = 0.01$[8] and, in particular, it is very similar to that obtained by a Monte Carlo simulation of a one-dimensional lattice with 100 particles.[9]

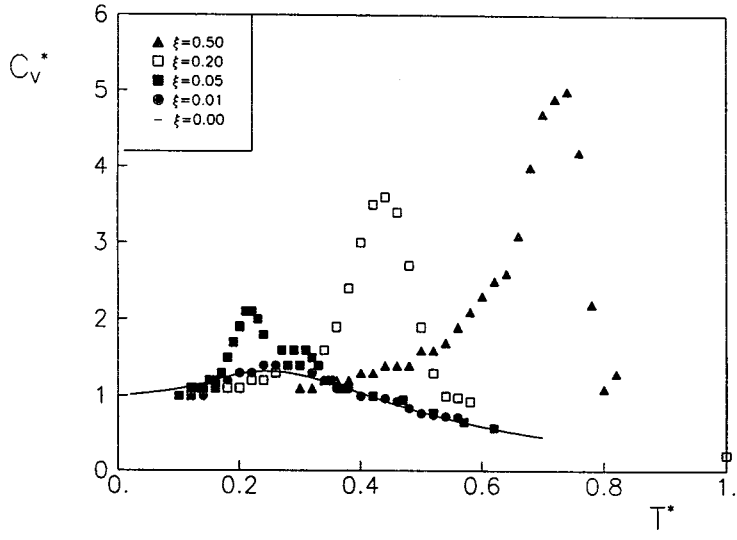

Fig. 3. The temperature dependence of the heat capacity C_V^* for the model as obtained from PBMC on a 10 x 10 x 10 lattice for the various ξ. The symbols used are as in Fig. 2. As a comparison we report the analytic results[8] for $\xi = 0$ (continuous line).

4.3. *Order parameters*

The second rank order parameter defined with respect to the instantaneous director (i.e. $\langle P_2 \rangle_\lambda$) is calculated by diagonalization of a suitably defined ordering matrix.[11] The calculation of the fourth rank order parameter $\langle P_4 \rangle_\lambda$ has been performed according to the algorithm we have previously proposed[3]; it shows a behavior similar to that of $\langle P_2 \rangle_\lambda$ and is not reported here for reasons of space.

In Fig. 4 the $\langle P_2 \rangle_\lambda$ results vs. T^*/T^*_C are shown. We have used this dimensionless unit to compare the curves for the different values of ξ since changing the strength of the interactions corresponds to a change of the heat capacity maximum. In such a way all the curves should be superimposable if the orientational transitions had the same characteristics. We notice that only for $\xi = 0.01$ and $\xi = 0.02$ the $\langle P_2 \rangle_\lambda$ curve is significantly shifted from the other.

As a comparison we report in Fig. 5 $\langle P_2 \rangle_\lambda$ for $\xi = 0.01$ and the correspondent results obtained from computer simulations of a one-dimensional lattice with 100 and 1000 particles.[9] We remind that the limiting situation to which the potential in Eq. (2) tends upon decreasing the parameter ξ to zero is a a set of 100 independent one-dimensional lattices with 10 molecules. So, looking at Fig. 5, we can notice that the results for the second rank order parameter for $\xi = 0.01$ are in good agreement with the previous simulations. In particular the behavior of the curve is similar to the results obtained with 100 particles at low temperatures and becomes superimposable to the $N = 1000$ data at higher temperatures.

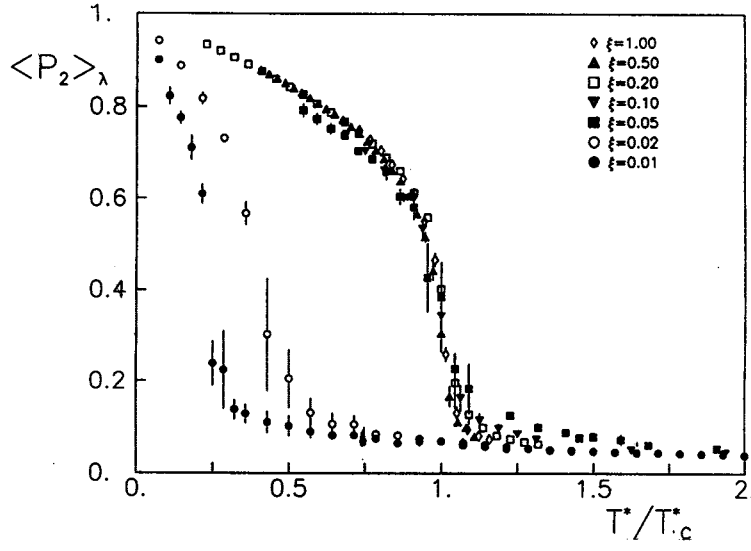

Fig. 4. The second rank order parameters $\langle P_2 \rangle_\lambda$ vs. T^*/T^*_C.

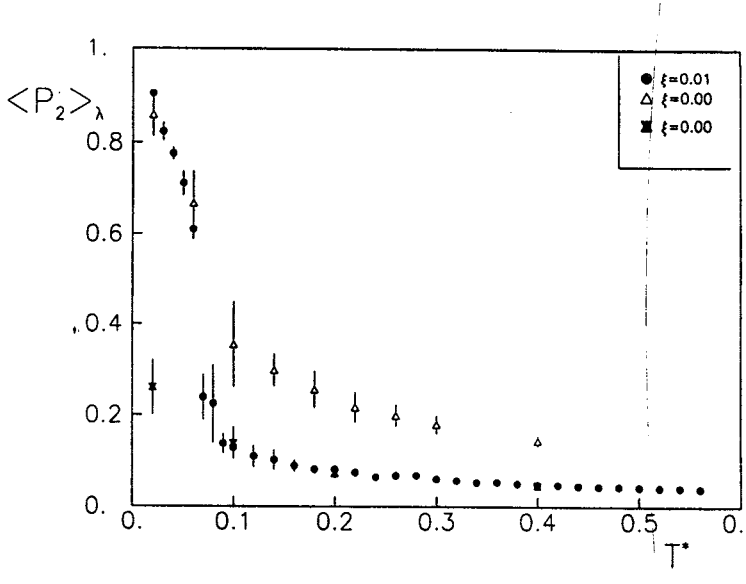

Fig. 5. The second rank order parameters $\langle P_2 \rangle_\lambda$ vs. T^* for $\xi = 0.01$ (full circles) and for a one dimensional lattice with 100 (empty triangles), and 1000 particles (hourglasses).

4.4. *Orientational pair correlations*

The two particle angular correlation coefficients $G_L(r)$ are expansion coefficients of the rotationally invariant pair distribution.[11] They give the correlation between the orientation ω_{12} of two particles separated by a distance r. We calculate the first two angular pair correlation coefficients G_2 and G_4 for all the temperatures. To do that we select a number of particles as origins and calculate for each particle j falling within a certain distance r the Legendre polynomial $P_L(\cos\beta_{ij})$ with respect to the origin particle i. Here we have also calculated the $G_L(r)$ for the three different directions X, Y, Z and in Fig. 6 the results for three sample cases are presented at a temperature $T^* = 0.22$. We also report the analytic results at that temperature for the one-dimensional lattice. We notice that, for $\xi = 0.5$, the pair correlation function $G_2(r)$ along the three different directions gives similar results for the X and Y axes and that these are not much lower than the vertical component. Decreasing ξ the coupling in the plane is reduced and the difference becomes more evident ($\xi = 0.2$) and eventually an absence of correlation in the plane ($\xi = 0.01$) is obtained.

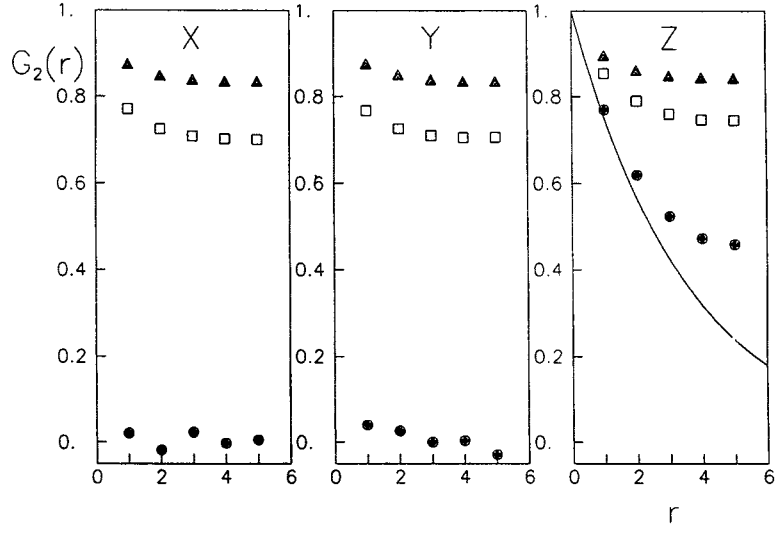

Fig. 6. The three cartesian components of the second rank pair correlation coefficient $G_2(r)$ plotted against the distance r in lattice units at $T^* = 0.22$. The results are for $\xi = 0.5$ (full triangles), $\xi = 0.2$ (squares) and $\xi = 0.01$ (full circles). The continuous line plotted in the Z plate represents the analytic solution for the one-dimensional lattice.[8]

The large difference between the analytic results and the experimental ones for $\xi = 0.01$ is probably due to the fact that in the computer simulations data $G_L(r)$ have been obtained summing the contribution of linear chains constituted of only ten particles.[9]

5. Conclusions

We have studied an anisotropic version of the Lebwohl-Lasher lattice model with varying strength of interaction for the four horizontal neighbours while keeping the interaction with the two vertical ones fixed .

Decreasing the value of the parameter ξ we have performed six independent simulations of the model so as to approach a situation where the interactions in the plane are absent and the system reduces to a set of independent one dimensional lattices.

We have shown that changing the parameter ξ in Eq. (2) not only corresponds to a renormalization of the temperature as predicted for instance by molecular field theory (Fig. 7) but also to a change of the characteristics of the orientational transition. The effect is not observable up to a 1/20 in the value of the out of plane to the in-plane coupling ratio.

Acknowledgments

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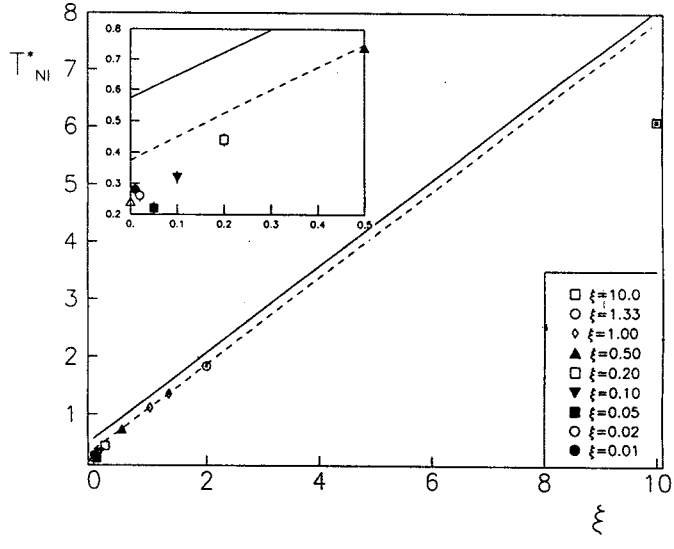

Fig. 7. A plot of the temperatures where the heat capacity is a maximum, i.e. the pseudo transition temperatures. The continuous line is the molecular field prediction, the dashed line is rescaled so that it is exact at $\xi = 1$.

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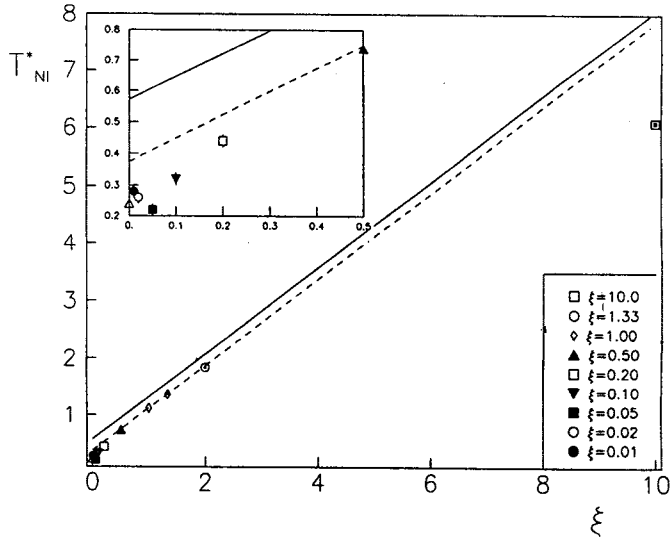

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Table 1. The values of the heat capacity peaks from the energy derivative $(C_v^*)_D$ and the temperatures at which they occur. For the case $\xi = 1.0$ we report the results of simulations performed on[14] a $20 \times 20 \times 20$ and[3] $30 \times 30 \times 30$ lattices. Simulations[9] for $\xi = 0$ are for $N = 40$ and $N = 100$ (in brackets).

ξ	$(C_v^*)_D$	$(T^*)_D$	Ref.
0.00	1.32213	0.24	Ref. 8
0.00	1.28 (1.35)	0.24	Ref. 9
0.01	1.42	0.28	This work
0.02	1.44	0.26	This work
0.05	2.1	0.22	This work
0.10	3.3	0.30	This work
0.20	3.7	0.44	This work
0.50	5.1	0.74	This work
1.00	17.87	1.127	Ref. 14
1.00	24.44	1.1232	Ref. 3

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