
POLARIZATION PARAMETER IN THE ISING MODEL AND ITS INFLUENCE ON THERMODYNAMIC PROPERTIES OF AN EPITROPIC LIQUID-CRYSTALLINE SYSTEM

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A modified one-dimensional Ising model, which describes an orientationally ordered state in a near-surface epitropic liquid-crystalline (ELC) layer, has been considered. The modification consists in introducing the parameter of "polarization" α into the intermolecular potential. The spatial alignment distribution in the layer and the thermodynamic properties of such a model, in particular, the heat capacity, have been obtained. A comparison of those properties with the thermodynamic properties of the earlier considered model, which takes into account the orientational influence of the layers on one another through an "internal" field with a characteristic parameter γ^* , has been made.

1. Introduction

In liquid layers adjacent to a solid phase, there arise polymolecular orientationally ordered ELC layers [1]. They are capable to change the rheological, optical, and thermodynamic characteristics of systems.

In a number of cases, the Ising model is used to describe statistical systems. Among the exactly solvable models with an external field, we mention a one-dimensional Ising model and a two-dimensional "hexagonal" one (the model of ice) [2].

The one-dimensional "chain" model [3, 4] was used to describe an orientationally ordered state of anisometric molecules of the ELC phase stabilized by a substrate [5, 6]. In this approach, liquid "molecules" with a small anisotropic interaction, which is not sufficient for their organization into a bulk mesophase, are in the field of one [5] or two [6] plane substrates.

A more complicated "hexagonal" model, where the results of the theory of molecular potential are not accounted for, gives rise mainly to the same results as the one-dimensional model does, except for the behavior of the heat capacity. If one makes allowance for the "interchain" coupling in the one-dimensional model, a new property of the simulated ensemble of elements appears, namely, the opportunity to transform it into a mesogen phase [7]. The

properties of this model were studied in more details in work [8].

2. The ELC Model of a Layer with Interacting "Chains" and Mesomorphism

Using the simplest ideas concerning the noninteracting "chains" of elements in a semiconfined medium, the Ising model made it possible to qualitatively describe the emergence of an alignment in the near-surface layer and its absence in the bulk, as well as the orientational melting of an ELC layer, the phase transition heat, and the temperature dependence of the heat capacity [9, 10]. In this approximation, the axis direction of an anisotropic molecule of a liquid was simulated by spin. An element can be oriented in parallel or perpendicularly to the surface field of the substrate. The orientationally ordered (with the order parameter Q) near-surface layer was considered as a system of i_Q sets of the closed (a periodic boundary condition) chains of elements, being parallel to one another and to the substrate and located equidistantly from the substrate and above it. Owing to a decrease of the field potential induced by the substrate surface (proportionally to i^{-3} , where i is the number of the chain) the order parameter also decreases.

The introduction of "interchain" coupling [7] allowed the so-called "relay-race" (according to the terminology of B.V. Deryagin, one of the authors of work [11]) mechanism of orientational ordering translation to be realized, starting from the chains adjacent to the substrate and possessing a high degree of alignment to the next layers, which are more distant from the substrate. In this case, every chain is located not only in the field of the substrate but also in the "internal" field of the neighbor chains proportional to the average value of their order parameters. It allowed the peculiarities of the ELC state to be taken into account more correctly and an agreement with experiment to be improved.

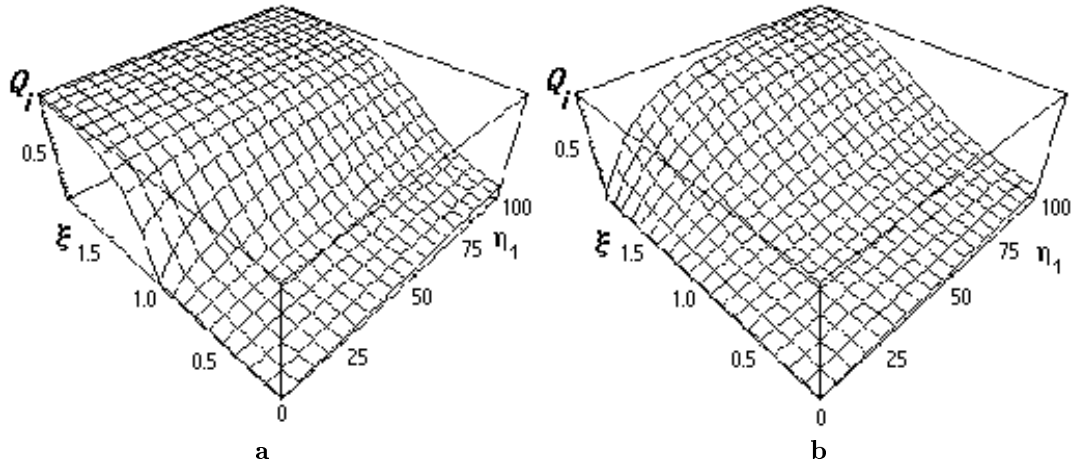


Fig. 1. Dependence of the alignment degree Q_i in the 10-th chain on the intensity of intermolecular interactions ξ and the potential of the surface forces on the substrate η_1 for a system of interacting ($\gamma = 0.14$) (a) and noninteracting ($\gamma = 0$) (b) chains. The relative temperature $\theta = 1$

Similarly to the elementary one-dimensional model, the system with “interacting chains” is a lattice, every site of which is occupied by an element in either of two states, i.e. its discrete spin variable can accept two values $\sigma_k = \pm 1$. The Hamiltonian of the separate i -th chain, as before, looks like

$$H_i = - \sum_{p=1}^N [J\sigma_p\sigma_{p+1} + h_i\sigma_p], \quad (1)$$

where the first term describes the energy of interaction between two adjacent elements, and the second one does the energy of interaction between the p -th element and an external field of the strength h_i

The potential of the surface force field was considered constant within every i -th chain. The following dimensionless parameters were used: the field potential η ($\eta_1 = h_1/3kT$ for a chain positioned directly on the substrate) and the intermolecular interaction intensity $\xi = J/kT$. The statistical sum was determined using the transfer-matrix method [3].

In the approach, which takes into account the orientating action of the preceding intermolecular layer upon the next one, the potential of the internal field which affects the elements of the i -th chain is assumed proportional to $\langle Q_{i-1} \rangle$. But due to the fact that $\langle Q_i \rangle$ changes weakly in the nearest neighborhood of the i -th chain, $\langle Q_{i-1} \rangle \approx \langle Q_i \rangle \approx \langle Q_{i+1} \rangle$. Then, the potential of the effective field is defined by the expression

$$\eta_i = \eta_1/i^3 + \gamma Q_i, \quad (2)$$

where γ is the dimensionless parameter of the field potential which characterizes the intensity of interchain

coupling for a completely aligned chain ($Q = 1$) on the substrate, and Q_i is the order parameter of the i -th chain in the first approximation. We note that the substitution of the external field by a certain averaged one, which takes into account the internal structure of the substance, was made earlier too (see, e.g. [12]). But form (2) for the potential is simpler in both mathematical and physical senses, because it does not split the energy of the field into parallel and perpendicular components.

The average value of the order parameter of the i -th chain was determined numerically by solving the transcendental equation

$$Q_i = \frac{\sinh(\eta_1/i^3 + \gamma Q_i)}{\sqrt{[\sinh(\eta_1/i^3 + \gamma Q_i)]^2 + \exp(-4\xi)}}. \quad (3)$$

Making allowance for the interchain coupling in the approximation where the parameters ξ and η were constant resulted not only in the order parameter Q increasing in all chains, but also in a qualitative transformation of the form of the surface $Q_i(\eta_1, \xi)$ (see Fig. 1). The displayed surfaces were calculated according formula (2) at the temperature $\theta = T/T_0 = 1$.

Fig. 1, a shows that, starting from a certain value $\xi \approx 1$, the elements in the near-surface chain are already aligned even at small η_1 . If ξ is rather large (e.g., $\xi \geq 1.5$ for the case analyzed in Fig. 1 of the 10-th chain and at the specified value $\gamma = 0.14$), the magnitude of the parameter η_1 practically does not affect the alignment. It testifies to that, in small fields of the substrate ($\eta_1 \approx 0$), the alignment in the considered chain (which is absolutely absent at $\gamma = 0$, see Fig. 1, b) is caused only

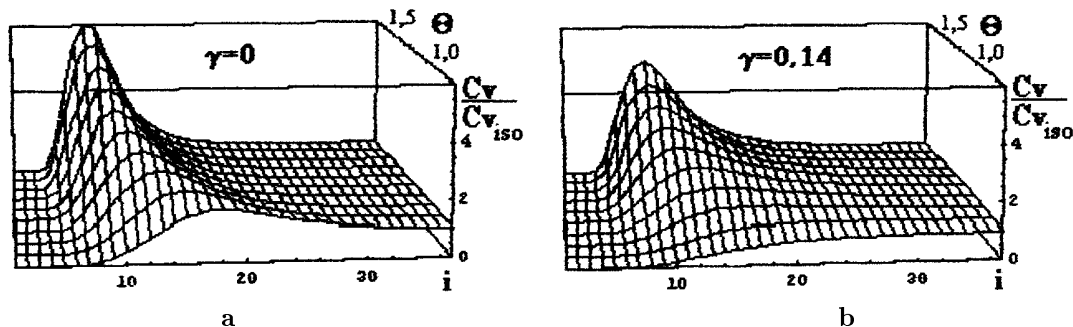


Fig. 2. 3D plots of the dependences of the relative isochoric heat capacity $C_v/C_{v_{iso}}$ of the chain on its number i and the temperature θ of the system at $\gamma = 0$ (a) and 0.14 (b). $C_{v_{iso}}$ is the heat capacity of the 500-th chain, $\eta_1 = 100$, $\xi = 1$

by the intermolecular interaction and the translation of the alignment from the highly aligned first layer.

For a system of noninteracting chains, their alignment near the surface is provided simultaneously by the interaction of molecules with one another and with the surface field (Fig. 1, b).

Since the field of the substrate has no effect at large distances, the alignment is governed only by intermolecular and interchain interactions [7]. The emergence of orientational liquid-crystal ordering in the bulk is typical of mesogens within the temperature range of their mesophase. Therefore, the revealed property of the model of interacting chains was interpreted as follows. Above a certain, rather high, “threshold” intensity of the “internal” field, which is characterized by the value of γ^* , the simulated object becomes “mesogen”, i.e. capable to manifest an orientational alignment in the bulk. In a near-surface layer of such a “nematic”, there is a region, where the alignment is higher in comparison with the bulk. In this case, the role of the substrate reveals itself in the experimentally found [13] enhancement of the alignment in the near-surface layer of the nematic and in a certain orientation of the director, which depends on the surface microstructure. This near-surface orientation is translated into the bulk by the anisotropic intermolecular and, in the model under consideration, interchain coupling. A more detailed study of the influence of the parameter γ on the basic properties of the model allowed us to establish that the smaller kT the smaller the threshold intensity of the internal field (the quantity γ^*).

For the spatial dependence of the heat capacity $C_v(i)$, a “splash”, i.e. the growth of this quantity, as the number i increases, up to a value that is greater than the heat capacity $C_{v_{iso}}$ of the bulk phase, followed by a decay to the value $C_{v_{iso}}$ (see Fig. 2, a), is typical of the simplified chain model. The higher the temperature

the greater the amplitude of the splash. The influence of interchain coupling on the local heat capacity of a chain manifests itself in a reduced value of the C_v “splash” and in the existence of this “splash” only at high temperatures. If the temperature is lower than θ^* (the temperature at which the value $\gamma^* = 0.14$ of interchain coupling is a threshold provided the chosen value, $\xi = 1$, of intermolecular one), only a monotonous increase of the “chain” heat capacity, if one moves away from the substrate, is observed. Within the range of such temperatures, the system is in a “mesophase” state and there is no interface between the ELC layer and a bulk “isotropic” liquid.

The described peculiarity of the heat capacity corresponds qualitatively (to a greater extent, in the model of interacting chains) to a jump of the isochoric heat capacity, which was observed experimentally in calorimetric researches [9] of ELC layers of a nonmesogenic liquid in thin gaps between hard lyophilic substrates (in the disperse system nitrobenzene—quartz powder).

3. The Model of the ELC Layer Making Allowance for the Polarization of Molecules

In order to develop the model with interchain coupling, we introduce an additional interaction between chain elements, supposing that it is caused by polarization properties of liquid molecules. Such an interaction is an analog of the field that polarizes each molecule of the i -th chain and is created by the molecules of the neighbor $(i - 1)$ -th and $(i + 1)$ -th (in the first approximation) chains.

Supposing the average value of the order parameter of the i -th chain $Q_i \simeq (Q_{i-1} + Q_{i+1})/2$, the intermolecular potential of interaction of adjacent

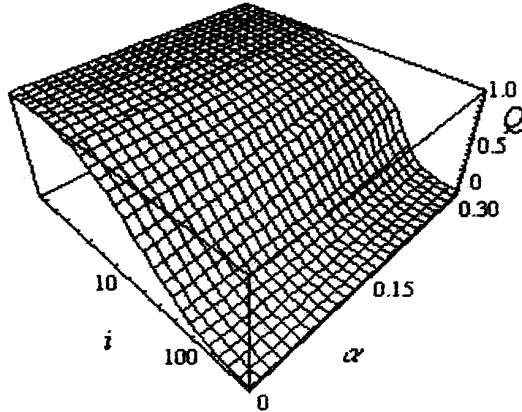


Fig. 3. Dependence of the alignment degree Q in the system on the chain number i ($i = 1$ to 245, logarithmic scale), which corresponds to a spatial distance from the substrate, and on the small parameter of polarization α . Other parameters of the system are $\eta_1 = 100$, $\zeta_0 = 1$, $\theta = 1$, and $\gamma = 0.1$

elements in the i -th chain, in the first approximation, looks like

$$\xi_i = \xi_0 + \alpha Q_i, \quad (4)$$

where α is the parameter of “polarization” of the intermolecular potential of the system, which determines the influence of neighbor chains on the degree of order of the t -th chain. In this work, this parameter is supposed small. We note that the analysis of the polarization properties of the medium in the framework of the Ising model was done in work [14], but real dipole-dipole interactions were considered there as the interchain coupling, and the model was built on the basis of two-dimensional Bravais lattices.

Mechanism (4) is caused by the emergence of a “mean field”. Potentials (2) and (4) bring about the variation of the system energy (1) and reflect the appearance of some additional “internal field” caused by polarization properties of the medium. Making potentials (2) and (4) dependent on the molecule ordering enables one to describe some two-dimensional properties of the ELC model with the help of the one-dimensional Ising model, because the coupling changes not only between chains but also inside them. Consider some of those properties.

Since the local value of the order parameter (3) for the i -th chain depends on the potential ξ (Fig. 2) and the value of ξ depends now on the value of Q , one may expect a significant variation of the order parameter in the range where the gradient of Q (the derivative $\partial Q/\partial i$) is the most variable. This assumption is reflected in Fig. 3.

Fig. 3 illustrates the results of our calculations for an ELC layer adjacent to an isotropic phase. Owing to

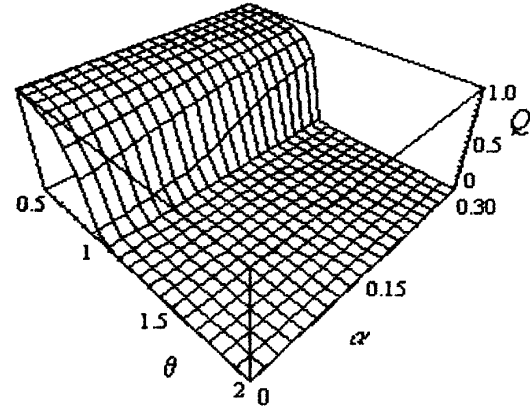


Fig. 4. Dependence of the alignment degree Q of a near-surface chain ($i = 40$) on the temperature θ and the polarization parameter α . Here, $\eta_1 = 100$, $\zeta_0 = 1$, and $\gamma = 0.135$

a strong internal field, which is determined by the value $\gamma = 0.1$, the thickness of the layer is significant. At the boundary of this transition region, the parameter ξ is reduced by 25% as compared with the value $\xi_0 = 1$. Therefore, as the parameter α grows, the transition from the state of aligned elements to the isotropic one becomes steeper in space. This is in agreement with the experimental results [15] which evidence for the “steepness” of the phase interface (within 3–5 molecular lengths) that separates the ELC layer from the isotropic liquid.

From the analysis of expression (4) and Fig. 3, one can see that the energy per volume unit of the ELC layer grows (the intermolecular potential ξ increases), while its value diminishes in the isotropic medium. The interface between the ELC phase and the isotropic liquid is defined as points, where, e.g., the second derivative of the order parameter with respect to i equals zero. The appearance of micelles in some polymer liquids may be regarded as an example of natural processes, where the model under consideration can be applied. For this purpose, it is enough to simulate the external field by a periodic function.

Since the order parameter Q depends on temperature, the derivative $\partial Q/\partial T$ allows the kinetics of the phase transition to be traced qualitatively. Melting, i.e. a variation of the order parameter Q of an aligned chain that belongs to the ELC layer, is illustrated in Fig. 4. One can see that the width of a temperature interval where the phase transition aligned–nonaligned chain takes place (the temperature interval of its melting) decreases as the parameter α grows. It is explained by an increase of the ratio between the intermolecular interaction energy ξ and kT . So, the

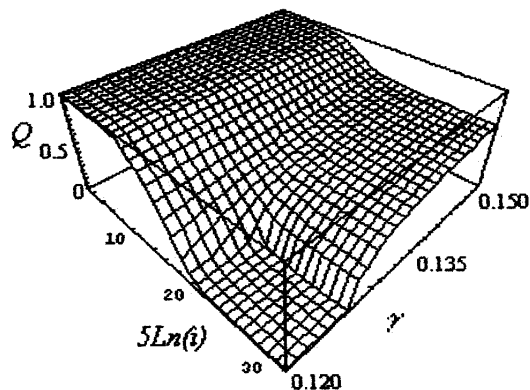


Fig. 5. Spatial dependence of the order parameter Q of a chain within the interval $i = 1 - 500$ on γ . The parameters of the system are $\theta = 1$, $\eta_1 = 100$, $\zeta_0 = 1$, and $\alpha = 0.3$

phase transformation of the medium, namely, the melting of a selected oriented chain in the ELC layer, becomes steeper.

It is of interest to observe the influence of the parameter α on the threshold value γ^* of the mesogeneity parameter of the system. As was shown in work [8], there exists a dependence $\gamma^*(T, \xi)$. According to work [7], the parameter of the internal field γ^* equals 0.135 at $\xi = 1$ and $\theta = 1$. Since the quantity α is a summand in the expression for ξ , it is possible to predict the existence of the dependence $\gamma^*(\alpha)$. Let us demonstrate it for the spatial dependence of the order parameter $Q(i, \gamma)$, assuming hereafter, for convenience of the analysis, that $\xi_0 = 1$.

Fig. 5 displays the surface $Q(i, \gamma)$ calculated using Eqs. (3) and (4). For the chosen parameters, the threshold value $\gamma^* = 0.126$, contrary to its value $\gamma^* = 0.135$ at $\alpha = 0$ [8]. With increase in both the coordinate i and the parameter γ , the character of the surface does not change, but the transition occurs at lower intensities of the interchain coupling.

The dependence $\gamma^*(\alpha)$ becomes more illustrative, if the order parameter Q is analyzed in the (γ, α) -coordinates. The dependences $Q(\alpha, \gamma)$ presented in Fig. 6 show that, as the parameter α increases, the system becomes mesogenic at lower intensity of the interchain coupling. It can be explained by the fact that the order parameter Q grows faster, when the parameter γ (Fig. 5), as well as the parameter ξ (Eq. (4)), grows. That is, the alignment of elements in the chains which are adjacent to an arbitrary i -th one promotes, through polarizing the latter, the ordering in the whole chain. Therefore, a lower intensity of the interchain coupling is required for the transition of a substance into the mesogenic state to occur. Moreover, a comparison of

Figs. 6, *a* and 6, *b* shows that the relative temperature θ does not affect the dependence $\gamma^*(\alpha)$. This result was to be expected, because the reciprocal temperature enters explicitly into the model Hamiltonian as a multiplier, affecting thus the statistical sum, and implicitly into expression (2) and (4) as a parameter.

Since the introduced parameter α influences the mesogeneity of the object, we can predict that, provided the field of surface forces disappears but the internal field is preserved, the alignment degree in the near-surface region should enhance. In so doing, the ordering, as was said (see also Fig. 5), should appear at the expense of the growth of α at $\gamma^* < 0.135$, although the very amplitude of the internal field at $\xi_0 = 1$ is not sufficient for the ELC phase to emerge (see Fig. 1). Such an influence of the magnitude of α on the alignment of chains that are in the near-surface region is illustrated by the surfaces $Q(\alpha, \eta_1)$ displayed in Fig. 7. One can see that, predictably, the average value of the order parameter of the 10-th chain which belongs to the ELC layer is not equal to zero, provided $\eta_1 > 0$. For $\gamma^* > 0.135$ (Fig. 7, *a*), the ELC system is ordered for any values of α and η_1 . But if $\gamma^* < 0.135$ and the field of the substrate is absent ($\eta_1 = 0$), there is no alignment in the near-surface region of the system considered in the framework of the model with weak polarization ($\alpha \approx 0$) (Fig. 7, *b*).

This result can be compared with those illustrated in Figs. 1 and 6. The dependence of the quantity γ^* on the parameter α results in the transition of the system into the mesogenic state at $\gamma^* < 0.135$ (Fig. 7, *a*). In this case, since the value of ξ in Eq. (4) becomes greater than a certain critical value (for the given values of γ^* and the temperature), the existing "threshold" (see Fig. 1, *a*), i.e. the lack of a potential for the mesophase to be organized in the near-surface region, is overcome by the quantity α (Fig. 7, *a*).

Thus, the conclusion can be made that a small parameter of the intermolecular potential α influences substantially the parameter of mesogeneity γ^* . At the same time, since the order parameter Q (at constant i and T) is connected (Eq. (4)) with the field ξ (Fig. 1), the variation of α induces the variation of the derivatives of Q with respect to both the spatial coordinate and the temperature, which has already been shown above.

The study of the influence of the parameter α on the heat capacity of the system is of special interest. It affects the system noticeably in the region where the variation of the derivative of Q is maximal. So, we may suppose that the behavior of the heat capacity should also change in this region. It was demonstrated above

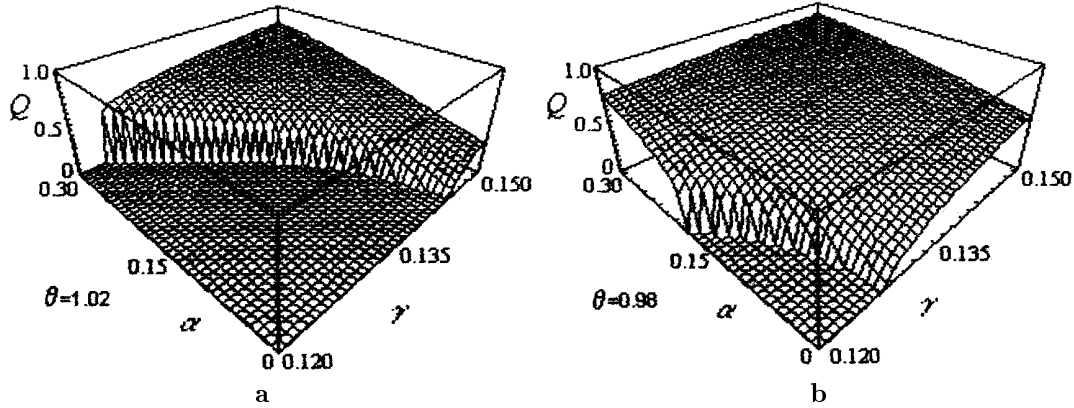


Fig. 6. Dependences of the order parameter Q of a chain of elements, which is far from the substrate ($i = 500$), on the polarization parameter α of the intermolecular potential and the internal field γ at $\theta = 1.02$ (a) and 0.98 (b). The parameters of the system are $\eta_1 = 100$ and $\zeta_0 = 1$

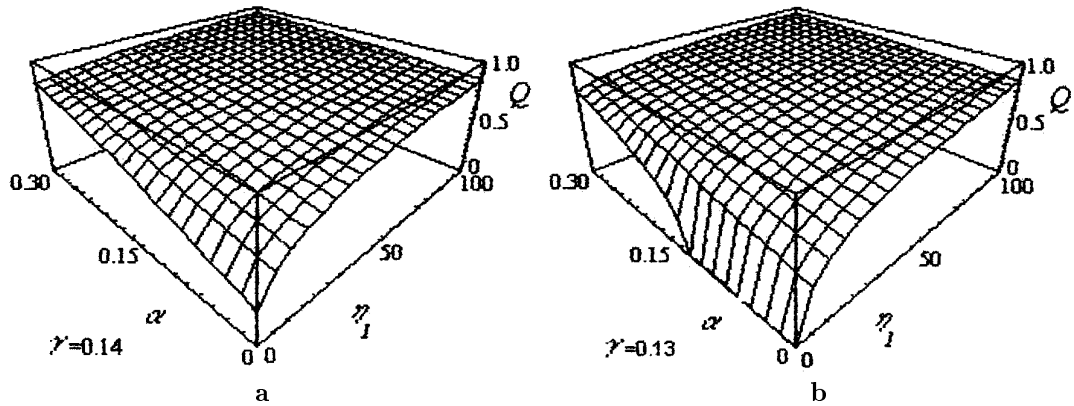


Fig. 7. Dependences of the alignment degree of a near-surface chain ($i = 10$) on the polarization, α , and the external field, η_1 , parameters for $\gamma = 0.14$ (a) and 0.13 (b). The parameters of the system are $\xi_0 = 1$ and $\theta = 1$

that the parameter of the internal field γ exerts a significant effect on the heat capacity (Fig. 2). It is evident that the dependence $\gamma^*(\alpha)$ will not supply new unusual properties to the system, which would make worth considering the influence of α in the same coordinates. The influence of the parameter α on the properties of the model can be considered in the most general manner by analyzing the ratio $C_v/C_{v_{iso}}$ in the coordinates (i, η_1) (Fig. 8), because the relative heat capacity depends monotonously on η_1 at $\gamma = 0.13$ [8]. Generally speaking, the form of the surface $C_v(i, \eta_1)/C_{v_{iso}}$ calculated in work [8] coincides with that obtained for $\alpha = 0$ and $\gamma = 0.135$ and shown in Fig. 8, a.

From Fig. 8, one can see that if $\alpha = 0$, then the maximal value of the heat capacity remains constant as η_1 increases, with a smooth displacement of the maximum in space caused by an enlargement of the

conventional width of the layer ($Q > 0.3$) by the oriented surface of the phase (the anisotropic ELC layer). But if $\alpha \neq 0$ (Fig. 8, b), a reduction of the maximum by 25% is observed, with the monotonicity being preserved. Such a character of the influence of the parameter α is explained by the emergence of a more abrupt interface ELC phase–isotropic liquid (with an insignificant reduction of the width of the ordered region, Fig. 3). In this connection, the heat of melting must decrease too.

4. Conclusion

A sharp phase interface between the ELC phase and an isotropic liquid, which was discovered experimentally in work [15], can be described within the frame of the model that takes into account polarization and the internal

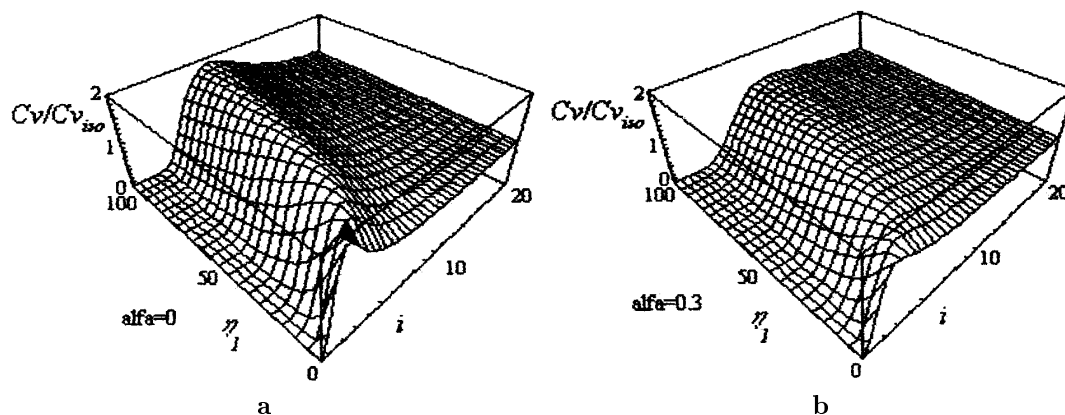


Fig. 8. Dependences of the relative heat capacity $C_v/C_{v_{iso}}$ on the number of the chain i and the parameter of the external field η_i for $\alpha = 0$ (a) and 0.3 (b). The parameters of the system are $\xi_0 = 1$, $i = 10$, $\theta = 1$, and $\gamma = 0.135$

field. The introduction of the small parameter of polarization α results in a variation of the derivative of Q with respect to each variable included. The adequacy between the presented model and the experiment will increase appreciably under condition that the parameter of polarization of the intermolecular potential α approaches the value of this potential in the zeroth-order approximation ξ_0 . The physical validity of such an approximation and the form of the intermolecular interaction potential (the additivity of the molecular polarization energy) will be discussed elsewhere.

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1. *Derjagin B.V., Altoiz B.A., Nikitenko I.I.* // J. Coll. Interface Sci. — 1991. — **145**, N 2. — P. 441 — 446.
2. *Baxter R.J.* Exactly Solvable Models in Statistical Mechanics. — London: Academic Press, 1982.
3. *Huang K.* Statistical Mechanics. — New York: Wiley, 1987.
4. *Dyson F., Montroll E., Katz M., Fisher M.* Stability and Phase Transitions. — Moscow: Mir, 1973 (in Russian).
5. *Altoiz B.A., Popovskii Yu.M., Lyakhova E.S.* // Kolloid. Zh. — 2000. — **62**, N 3. — P. 299 — 302.
6. *Lyakhova E.* // J. Mol. Liquids. — 2001. — **93**. — P. 203 — 206.
7. *Altoiz B.A., Naroditskaya T.V.* // Kolloid. Zh. — 2004. — **66**, N 3. — P. 1 — 6.
8. *Altoiz B.A., Nedyalkov D.D., Dadonova E.Yu.* // FAS. — 2003. — **40**. — P. 176 — 191.
9. *Derjagin B.V., Popovskii Yu.M.* // Dokl. AN SSSR. — 1967. — **175**, N 2. — P. 385 — 389.

10. *Altoiz B.A., Popovskii Yu.M.* Physics of Near-Surface Layers. — Odesa: Astroprint, 1995 (in Russian).
11. *Derjagin B.V., Popovskii Yu.M., Altoiz B.A.* // Otkryt. i Izobret. — 1991. — N 12. — P. 1.
12. *Scalapino D.J., Imry Y.* // Phys. Rev. B. — 1975. — **11**, N 5. — P. 2042 — 2048.
13. *Altoiz B.A., Popovskii Yu.M.* // Kolloid. Zh. — 1987. — **49**, N 3. — P. 419 — 423.
14. *Rozenbaum V.M.* // Zh. Eksp. Teor. Fiz. — 1991. — **99**. — P. 1836.
15. *Derjagin B.V., Popovskii Yu.M., Altoiz B.A.* // Dokl. AN SSSR. — 1982. — **262**, N 4. — P. 853 — 855.

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ПАРАМЕТР “ПОЛЯРИЗАЦІЇ” В МОДЕЛІ ІЗІНГА І ЙОГО ВПЛИВ НА ТЕРМОДИНАМІЧНІ ВЛАСТИВОСТІ ЕПІТРОПНОЇ РІДКОКРИСТАЛІЧНОЇ СИСТЕМИ

Д.Д. Недялков

Резюме

Розглянуто модифіковану (введенням параметра “поляризації” α в міжмолекулярний потенціал) одновимірну модель Ізінга, що описує орієнтаційно впорядкований стан у приповерхневому епітродному рідкокристалічному (ЕРК) шарі. Отримано просторовий розподіл впорядкованості в ньому та термодинамічні властивості такої моделі, зокрема теплоємність. Проведено порівняння цих властивостей з властивостями раніше розглянутої моделі, що враховує орієнтуючий вплив шарів один на одного за допомогою “внутрішнього” поля з характеристичною величиною γ^* .