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Investigation of the liquid crystalline phase transitions using the new modified Pople–Karasz model

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Abstract

Thermodynamics of solid–nematic and nematic–isotropic liquid transitions are studied by using a new modified model that combines the modified theories of Chandrasekhar et al. with those Keskin and Özgan which are based on the Pople–Karasz theory. The thermodynamic properties of the disordered system are evaluated relative to those of the perfectly ordered one within the lowest approximation of the cluster variation method which is identical to the mean-field approximation. The results are compared with the some available experimental data, the predictions of the original Pople–Karasz (PK) theory and its previous modified theories. For nematic–isotropic and s(nematic) at the transition temperatures, the agreement is very good and much better than the predictions of the PK theory and its previous modified theories. For the solid–nematic transition, all theories give very nearly the same results, but the values are significantly lower than the observed data. Moreover, one of the theoretical phase diagrams is also qualitatively similar to the experimental phase diagram for p-azoxyphenetole (PAA).

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Recently, we have studied the thermodynamics of melting (solid–liquid) and solid–solid transitions of the molecular crystals with a new modified model [1] that combines the modified theories of Chandrasekhar et al. [2] with those Keskin and Özgan [3] which are based on the Pople–Karasz (PK) theory [4]. The thermodynamic properties of the disordered system are evaluated relative to those of the perfectly ordered one within the lowest approximation of the cluster variation method (LACVM) [5] which is identical to the mean-field approximation (MFA) or the Bragg–Williams approximation. The good agreement is found

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between the new modified theory and with the some available experimental data. For melting transitions the agreement is very good and much better than with the calculations of the PK theory [4] and its previous modified theories [2,3]. Approximate agreement is obtained for the solid–solid transitions. Nevertheless, for these transitions the experimental agreement with the new modified theory is still better than the PK theory [4] and its previous modified theories [2,3], except at zero temperature and low pressures. Since the PK theory [4] and the modified theory of Chandrasekhar et al. [2] contain no adjustable parameter, the agreement is reasonable good only for certain kind of substances. On the other hand, since the new modified theory [1] and the modified theory of Keskin and Özgan [3] have an adjustable parameter, they give a agreement not only for certain kind of substances but also give reasonable satisfactory agreement for the different kind of substances if one changes the adjustable parameter.

In the present Letter, this new modified theory [1] is applied to study thermodynamics of the solid–nematic and nematic–isotropic liquid transitions. The thermodynamic properties of the disordered system are evaluated relative to those of the perfectly ordered one within the lowest approximation of the cluster variation method (LACVM) [5]. We also compare the predictions of the new modified theory with the available experimental data and as well as the PK [4] and its previous modified theories [2,3]. It is worthwhile the mention that the LACVM (or the MFA) in spite of its limitations, such as neglecting the correlation between molecules on different lattice sites, is an adequate starting point. Within this theoretical framework it is easy to determine the phase diagrams and find some outstanding features of the solid–nematic and nematic–isotropic liquid transitions.

Since the new modified model and its solution at equilibrium were described extensively in Ref. [1], therefore we shall only give a brief summary here. In the theory, molecules may occupy sites on one of two equivalent interpenetrating lattices of N-sites, referred to as A-sites and B-sites, in order to allow for possibility of increasing disorder in the positions of molecules in a crystal. It is also assumed that the molecule can take up one of two orientations on any site, so that now we have four possibilities A_1, A_2, B_1 and B_2. If all molecules occupy sites and orientations of the same type, say A_1-sites, the state is perfect order (or solid at the zero temperature), and the state of complete disorder (or the liquid phase) as one in which all four configurations are equally populated. It should be mentioned that there could also be states with a positional order and no orientational order and vice versa. It is assumed that each A-site is surrounded by z equivalent neighboring B-sites and each B-site by z A-sites. Also the number of A-sites closest to any given A-site or the number of B-sites closest any given B-site is z'. Moreover, there are three energies: the first one is W, the energy of the A_1B_1 or A_2B_2 interactions, the second one is W', the orientational energy of the A_1A_2 or B_1B_2 and the third one is W'' which is associated with positions and orientations together, hence W'' is the energy of the A_1B_2 or A_2B_1 interactions as in Ref. [3] but it was neglected in the other theories [2,4]. Thus zW is the energy needed to transfer the molecule from one site to the other sites with the same orientation, e.g., A_1 to B_1. $z'W'$ is the energy required to turn out the molecule from one orientation to the other orientation on the same site, e.g., from A_1 to A_2 when remainder of the orientation is A_1. Interactions between more distant neighbors are neglected. Since W'' is associated the positional and orientational energies, it should be combined with zW and $z'W'$. We used simply the arithmetic mean, including the adjustable parameter r. The reason including r factor is to obtain better agreement with experimental data. Hence,

$$W'' = r\left(\frac{zW + z'W'}{2}\right). \tag{1}$$

It is worthwhile to mention that this choice is arbitrary. Nevertheless, we have tried to use the geometric mean of W and W' in our previous modified works [3,6,7], but the better agreement with experimental data have been found by using the arithmetic mean of W and W'. Hence, we also use the arithmetic mean in Ref. [1] and also in this Letter. Up to this stage, the present theory is exactly the same with the modified PK theory introduced by Keskin and Özgan [3].

On the other hand, to evaluate the contribution of the disorder to the various thermodynamic quantities it is necessary to specify the dependence of W and W' on volume. Chandrasekhar et al. [8,9] found that the empirical trends in the properties, particularly for large orientational barriers which is the main region of interest in the present work, are reproduced well by the