

## Effect of intramolecular motions on melting

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1987 J. Phys. A: Math. Gen. 20 1557

(<http://iopscience.iop.org/0305-4470/20/6/037>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

### Download details:

IP Address: 129.252.86.83

The article was downloaded on 31/05/2010 at 15:21

Please note that [terms and conditions apply](#).

## Effect of intramolecular motions on melting

M S Giammarinaro and S Micciancio

Istituto di Fisica della Facoltà di Scienze, Università di Palermo, Via Archirafi 36, 90123 Palermo, Italy

Received 25 June 1985

**Abstract.** The coupling between lattice modes and intramolecular modes in a molecular crystal is described by a mean-field model. The effect of this coupling is investigated semi-quantitatively and it is found that in certain cases a molecular crystal becomes unstable against both an ordered crystal structure and a completely disordered structure. This instability can be eliminated if the system is allowed to take on either a mesomorphic structure or a structure characterised by space-inhomogeneous order parameters.

### 1. Introduction

Molecular crystals may exhibit several kinds of partially ordered (liquid or solid) phases between the low-temperature fully ordered crystal phase and the high-temperature isotropic liquid phase. The intermediate phases differ in their overall symmetry, i.e. the symmetry of the structure defined by positions and orientations of the molecules combined with the symmetry of the molecules themselves. Usually a phase is homogeneous in space, i.e. if defects are neglected, there is translational invariance over a scale length of a very few average intermolecular distances. However, phases exhibiting a domain structure or characterised by a spatial modulation over a much greater distance have been observed in molecular crystals: see, e.g., Luzzati and Tardieu (1974), Sigaud *et al* (1981) and Kistenmacher *et al* (1980).

Many dedicated theories, often providing good predictions, account for certain phase transitions. These theories, most of which are only phenomenological, cannot be extended to cover a wider temperature range, from the solid to the isotropic liquid phase. On the other hand, there are a few theories which, starting from the crystal phase, account for the main intermediate phases observed in molecular crystals, i.e. those exhibiting orientational disorder in crystal and/or orientational order in liquids (Pople and Karasz 1961, Kobayashi 1970). These theories assume rigid molecules and are not able to account for all kinds of phase transitions observed in molecular crystals. The purpose of this paper is to show in quite a general form that the interplay between internal and external modes should also be included in a theory of melting of molecular crystals in order to explain the occurrence of space-modulated structures as well as the fact that mesomorphic behaviour cannot be predicted only from the properties of the isolated molecule.

Throughout this paper the set of lattice modes (involving the centres of mass of the molecules) will also be designated as 'external modes', while the terms 'internal modes' or 'intramolecular motions' will be used to indicate all those motions (be they vibrational or rotational) of the single molecule which do not involve the centres of mass. The reason for treating all 'internal modes' (in the above sense) on the same

footing is that any kind of intramolecular motion qualitatively has the same effect on the intermolecular potential (i.e. yields a softening of the latter), as will be discussed in the next section.

Previous work (Micciancio and Vassallo 1982, Giammarinaro and Micciancio 1984) has shown that several 'strange effects' (including hysteresis and reentrant phase transitions) observed in many kinds of physical systems can be accounted for qualitatively by essentially the same model featuring two coupled order parameters: different effects arise for different ranges of values of the coupling between the two order parameters. In this paper we refine the model and adapt it to the melting of a molecular crystal. The latter is described as a composite system made up of two subsystems: the lattice subsystem (defined as the set of centre-of-mass degrees of freedom) and the subsystem of the intramolecular degrees of freedom (referred to as subsystem M). For each subsystem we define an order parameter and an equation of state (a phenomenological one for the lattice) which contains a control parameter whose value depends on the order parameter of the other subsystem. The properties of the coupling between the two subsystems are derived from general considerations of the intermolecular potential and the dynamics of the whole system. We show that for a suitable coupling between lattice modes and internal modes a molecular crystal exhibits a finite interval of temperature in which its structure must be different from both a fully ordered solid and an isotropic liquid. Our model cannot provide a direct indication about which structure the system must take on to cope with this instability against the two extreme kinds of structure. However, it is argued that, between the low-temperature fully ordered phase and the isotropic liquid phase, there must be an intermediate phase exhibiting orientational disorder in the crystal or orientational order in the liquid or else a space-modulated structure, depending on the overall symmetry of the system.

## 2. Theory

In order to build the model we assume that the two subsystems composing a molecular crystal can be kept in contact with two independent heat baths at the temperatures  $\theta_L$  for the lattice subsystem and  $\theta_M$  for the subsystem M of the internal degrees of freedom, respectively. We also assume that internal motions are faster than lattice motions.

Let us first consider a lattice of undeformable molecules (i.e.  $\theta_M = 0$ ), which is expected to melt at some well defined temperature  $T_L$ . On cooling the liquid we usually expect the occurrence of supercooling, a phenomenon related to the existence of metastable states of the liquid. In order to simplify our phenomenological picture of melting and freezing we neglect this kind of metastability and assume that in the lattice subsystem freezing occurs at the same temperature  $T_L$  as melting.

We know that the symmetry change occurring at the solid-liquid phase transition causes this transition to be first order. For simplicity we assume that our subsystem of undeformable molecules exhibits no mesophase and that a single scalar order parameter  $Q_L$  adequately describes the solid-liquid phase transition.  $Q_L$  might be related, e.g., to the amplitude of the density component with wavevector corresponding to a basic lattice periodicity. In a solid of rigid molecules,  $Q_L$  is expected to be a continuous and monotonically decreasing function of  $\theta_L$  which vanishes with a discontinuity at  $\theta_L = T_L$ . We write

$$Q_L = f(\theta_L)u(T_L/\theta_L - 1) \quad (1)$$

$$\partial f/\partial \theta_L \leq 0. \quad (2)$$

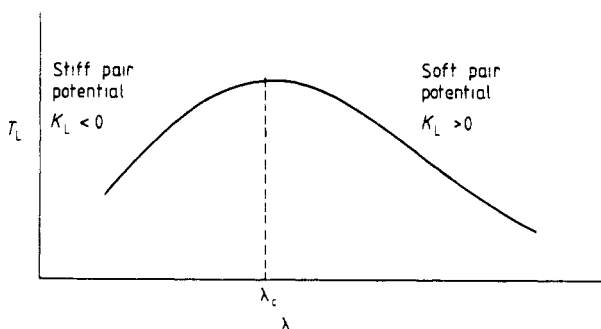
In equation (1)  $u(x)$  is the unit step function:

$$\begin{aligned} u(x) &= 0 & x \leq 0 \\ u(x) &= 1 & x > 0. \end{aligned} \quad (3)$$

The melting temperature of the lattice certainly depends on the intermolecular potential. The thermal excitation of internal modes introduces time-varying terms in the pair potential. However a time-independent effective potential is expected to yield qualitatively correct results because internal motions have been assumed faster than lattice motions. In any case the repulsive part of the pair potential is expected to become softer and softer as  $\theta_M$  increases, i.e. as the internal modes become excited. This softening is a second-order effect in the amplitude of the internal modes. However there may be skeletal modes whose amplitude can become an appreciable fraction of the molecular size. In the case of rotational motions of the whole molecule or a part of it a sizable softening of the potential is also expected to occur. In the following the term 'internal modes' will be especially referred to those modes, be they vibrational or rotational, which, when thermally excited, yield a sizable softening of the intermolecular potential.

The effects of the softening of a repulsive pair potential on the melting temperature of a lattice of point-like atoms has been investigated by Stillinger (1976) and Stillinger and Weber (1977, 1980), who adopted a Gaussian pair potential. Stillinger (1976) shows that the melting temperature of such a lattice,  $T_L$ , exhibits a maximum versus the crystal reduced density  $\rho^* = \rho\lambda^3$ , where  $\rho$  is the number density and  $\lambda$  is the halfwidth of the potential. A simple change of variables yields the curve of figure 1, which shows the melting temperature of the lattice plotted against  $\lambda$  for a fixed number density. The results of Stillinger rely on the fact that (a) for vanishing  $\lambda$  a system of Gaussian particles behaves like a hard-sphere system; (b) for diverging  $\lambda$  the disordered state is thermodynamically more stable than the crystal at all finite temperatures (this second result applies to a larger class of potentials). In both these extreme cases the melting temperature is 0 K. Hence  $T_L$  must exhibit a maximum at some finite value  $\lambda = \lambda_c$ .

The physical meaning of the arguments underlying this behaviour makes it plausible that the same also occurs in the case of more realistic pair potentials than those used by Stillinger. In this case  $\lambda$  will take on the meaning of a general parameter measuring the softness of the potential.



**Figure 1.** Qualitative plot of the melting temperature  $T_L$  of a lattice against the parameter  $\lambda$  measuring the softness of the repulsive part of the interparticles potential.  $T_L$  exhibits a maximum at  $\lambda = \lambda_c$ . The potentials can be roughly labelled as stiff or soft. See text for further details.

According to figure 1 the molecules can be roughly labelled as stiff ( $\lambda < \lambda_c$ ) or soft ( $\lambda > \lambda_c$ ), the terms 'stiff' and 'soft' being referred to the pair potential. It will be, respectively, either

$$\partial T_L / \partial \lambda > 0 \quad \text{or} \quad \partial T_L / \partial \lambda < 0. \quad (4)$$

Now let us look at the subsystem M of the intramolecular degrees of freedom. The frequencies of the internal modes of a molecule to some extent depend on the local potential generated by all the other molecules. In the absence of lattice vibrations all the molecules see the same local potential and exhibit the same spectrum of internal modes. (We neglect the coupling between modes of different molecules.) The subsystem M can thus be treated as  $n$  identical particles at the temperature  $\theta_M$ . From simple statistics we may get  $Q_M$ , the fraction of particles in the ground state.  $Q_M$ , which is a convenient parameter measuring the average internal disorder caused by the thermal excitation of the internal modes of the molecules, is a smooth continuous and monotonically decreasing function of  $\theta_M$ . The rate of decrease of  $Q_M$  as  $\theta_M$  increases is ruled, to quite a large extent, by the energy of the lowest internal mode  $T_M$ , while the detailed distribution of the energy levels higher than the first plays a minor role. In particular we may state that, for finite  $\theta_M$  a decrease of  $T_M$  always yields a decrease of  $Q_M$ . We write

$$Q_M = g(T_M / \theta_M) \quad (5)$$

$$\partial g / \partial \theta_M \leq 0 \quad (6)$$

$$\partial g / \partial T_M > 0. \quad (7)$$

The thermal excitation of lattice modes, corresponding to a decrease of  $Q_L$ , produces a modulation of the crystal potential and hence a similar modulation of the frequency of the internal modes. This is observed experimentally as a broadening of the far-infrared absorption bands as well as their shift to lower frequency as the temperature increases. The parameter  $T_M$  of equation (5) is thus coupled to the lattice order parameter:

$$\partial T_M / \partial Q_L = K_M < 0. \quad (8)$$

The excitation of internal modes, i.e. a decrease of  $Q_M$ , is expected to yield a softer effective pair potential:

$$\partial \lambda / \partial Q_M \leq 0. \quad (9)$$

This relationship allows us to link the melting temperature of the lattice to the intramolecular order. Using equations (4) and (9) we get

$$K_L = \partial T_L / \partial Q_M = (\partial T_L / \partial \lambda)(\partial \lambda / \partial Q_M) \leq 0 \quad (10a)$$

for stiff molecules and

$$K_L \geq 0 \quad (10b)$$

for the soft ones. For simplicity we assume that, at least in the temperature range of interest, a stiff pair potential does not become soft as the temperature increases. That is, we assume that  $K_L$  is a monotonic function of  $Q_M$ .

The quantities  $K_M$  and  $K_L$  defined in (8) and (10) will be referred to as coupling parameters.

If we let  $\theta_L = \theta_M = T$  in all equations (1)-(9) we get a qualitative description of the behaviour of the whole composite system as a function of temperature. From equations (1), (3) and (5) we obtain

$$Q_L = f(T_L/T) \quad T < T_L \tag{11a}$$

$$Q_L = 0 \quad T > T_L \tag{11b}$$

$$Q_M = g(T_M/T). \tag{12}$$

In equations (11a) and (11b) explicit use has been made of equation (3).

These two equations are coupled by two more equations linking  $T_L$  to  $Q_M$  and  $T_M$  to  $Q_L$ , respectively. For simplicity, and with no loss of generality as far as the qualitative features of the result are concerned, we expand  $T_L(Q_M)$  and  $T_M(Q_L)$  in Taylor series and drop second-order and higher terms. This is equivalent to taking the coupling parameters as constants. Using equations (8) and (10) we obtain

$$T_L = T_L^* + K_L Q_M \tag{13}$$

$$T_M = T_M^* + K_M Q_L. \tag{14}$$

The properties of the solutions  $Q_L(T)$  and  $Q_M(T)$  of the system of equations (11)-(14) can be easily derived by means of graphical methods from the properties of  $f$  and  $g$  stated in equations (2), (6) and (7). The task is even simpler if we put  $f(T_L/T) = 1$ : equation (2) is satisfied and the qualitative features of the result do not change.

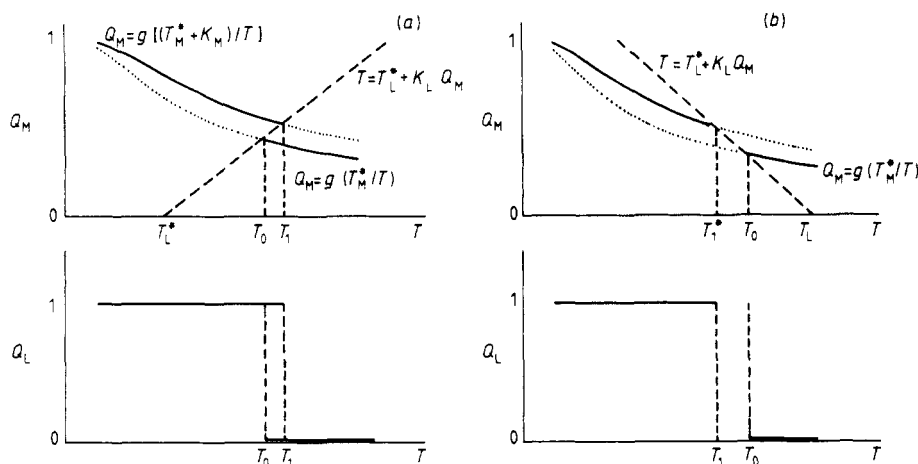
In this case if we take  $Q_L = 1$  equations (11a) and (13) yield

$$T < T_L^* + K_L Q_M \tag{15}$$

while equations (14) and (12) yield

$$Q_M = g[(T_M^* + K_M)/T]. \tag{16}$$

As shown in figure 2(a) for  $K_L > 0$  and in figure 2(b) for  $K_L < 0$  equations (15) and (16) define  $T_1$ , the upper bound of the range of validity of equations (11a) and (16).



**Figure 2.** Graphical solution (full curves) of equations (11)-(14). (a) When  $K_L > 0$  the solution is two-valued for  $T_0 < T < T_1$ . (b) When  $K_L < 0$  the equations have no solution for  $T_1 < T < T_0$ . In both cases  $|T_1 - T_0|$  vanishes if either  $K_L$  or  $K_M$  vanish. As discussed in the text the instability appearing in (a) may lead to the onset of mesophases or of space-modulated structures.

If we let  $Q_L = 0$  we obtain in a similar way (see figure 1)

$$T > T_L^* + K_L Q_M \quad (17)$$

$$Q_M = g(T_M^*/T) \quad (18)$$

which define  $T_0$ , the lower bound of the range in which equations (11b) and (18) hold.

As shown by figure 1(a), when equation (10b) holds,  $T_1 > T_0$  and the solutions  $Q_L(T)$  and  $Q_M(T)$  are two-valued in the range  $T_0 < T < T_1$ . In the opposite case, when equation (10a) holds,  $T_1 < T_0$  and the system of equations (11)–(14) has no solution in the range  $T_1 < T < T_0$ .

The amplitude of the intermediate range,  $\Delta T = |T_1 - T_0|$  is a monotonically increasing function of  $K_M$  and  $|K_L|$ . When either coupling parameter vanishes  $\Delta T$  also vanishes.

An inspection of the graphical solutions of figure 2 shows that using non-linear  $T_L(Q_M)$  and  $T_M(Q_L)$  relationships instead of equations (13) and (14) does not qualitatively affect the solutions, provided that the monotonicity of  $T_L(Q_M)$  and  $T_M(Q_L)$  is granted.

### 3. Discussion

Although the model of molecular crystal worked out in the last section is quite crude, the results obtained are based on the inequalities (2) and (6)–(9) which are certainly correct. Our results show that the interplay between internal and external modes can produce two kinds of synergetic effects, whose physical meaning will be discussed now.

When  $K_L > 0$  the interplay between the lattice order and the intramolecular order forces the latter to exhibit a discontinuity when the former does. The presence of the temperature range  $T_0 < T < T_1$  in which the solutions of equations (11)–(14) are two-valued was expected on the ground of previous work (Micciancio and Vassallo 1981, Giammarinaro and Micciancio 1984). This feature of the solutions leads us to expect that the composite system exhibits metastability in that range of temperature. Since in writing down equations (11)–(14) we neglected all metastability of the isolated subsystems, the metastability present in the range  $T_0 < T < T_1$  is to be ascribed to an effect of the coupling between the lattice modes and the intramolecular modes. This synergetic effect is an additional mechanism contributing to the onset of the metastable states of real molecular substances composed by soft deformable molecules. This matter needs to be investigated in more detail. Work is under way.

Another synergetic effect arises when  $K_L < 0$ . Equations (11)–(14) have no solutions in the range  $T_1 < T < T_0$  because they become overconstrained in that range. The constraints which make the equations unsolvable arise because we obtained the equations using the implicit assumption that the state of the composite system could be described by just the same parameters  $Q_L$  and  $Q_M$  defined in the isolated subsystems. In particular the composite system was left with no possibility to take on a structure different from either that of the lattice subsystem, described by  $Q_L$ , or that of an isotropic liquid.

As shown by several authors (Pople and Karasz 1961, Kobayashi 1970) the single scalar order parameter describing the lattice can be substituted by a set of several parameters in a theory predicting the existence of phases with an overall symmetry intermediate between that of the fully ordered solid and that of the isotropic liquid; these intermediate phases have been identified with liquid crystals or with plastic

crystals. These models are modifications of older theories of melting which are extended, through the addition of terms describing anisotropic interactions, to cover the cases of liquid and plastic crystals. In these models, letting the anisotropy vanish just causes the cancellation of the possibility of intermediate phases. Our model only considers the effects of the interplay between internal and external modes, i.e. a kind of interaction which is certainly present in all molecular crystals irrespective of the symmetry of the intermolecular interactions, and which yields a softening of the latter. When this softening occurs in stiff molecules ( $K_L < 0$ ), according to our model some intermediate phase must occur between the fully ordered solid and the isotropic liquid, although our model is unable to provide information about the symmetry of the intermediate phase.

Our model does not use explicitly the symmetries of the phases of the interacting subsystems, but only the fact that one of them is expected to undergo a first-order phase transition. It has been shown that, besides the solid-liquid transition, the transition between any liquid crystalline mesophase and the isotropic liquid also must be first order (de Gennes 1969, Goshen *et al* 1971). On the other hand first-order transitions may also occur between mesophases.

Arguments similar to those reported in § 2 can be applied to the interplay between internal and external modes near any phase transition which is expected to be first order. If a softening of the molecular potential causes the shift of this transition to higher temperature and no structure with an intermediate symmetry is allowed to exist between the two phases, the system should be forced to take on a spatially modulated structure, i.e. a superlattice or a domain structure. Such structure have been indeed observed in smectic liquid crystals both lyotropic (Luzzati and Tardieu 1974) and thermotropic (Sigaud *et al* 1981) and in systems with a quasi-one-dimensional structure (Kistenmacher *et al* 1980).

## Acknowledgments

Financial support has been provided by the Italian Ministero Pubblica Istruzione (Fondi 60% and Fondi 40%). The manuscript was typed by Mrs A La Franca.

## References

- de Gennes P G 1969 *Phys. Lett.* **30A** 454
- Giammarinaro M S and Micciancio S 1984 *J. Phys. A: Math. Gen.* **17** 1291
- Goshen S, Mukamel D and Shtrikman S 1971 *Solid State Commun.* **9** 694
- Kistenmacher T J, Destro R, Marsh R E and Samson S 1980 *Mol. Cryst. Liquid Cryst.* **62** 173
- Kobayashi K 1970 *J. Phys. Soc. Japan* **29** 101
- Luzzati V and Tardieu A 1974 *Ann. Rev. Chem. Phys.* **25** 79
- Micciancio S and Vassallo G 1982 *Nuovo Cimento D* **1** 627
- Pople J A and Karasz F E 1961 *J. Phys. Chem. Solids* **18** 28
- Sigaud G, Nguyen Huu Tinh, Hardouin F and Gasparoux H 1981 *Mol. Cryst. Liquid Cryst.* **69** 81
- Stillinger F H 1976 *J. Chem. Phys.* **65** 3968
- Stillinger F H and Weber T A 1977 *J. Chem. Phys.* **68** 3837
- 1980 *Phys. Rev. B* **22** 3790