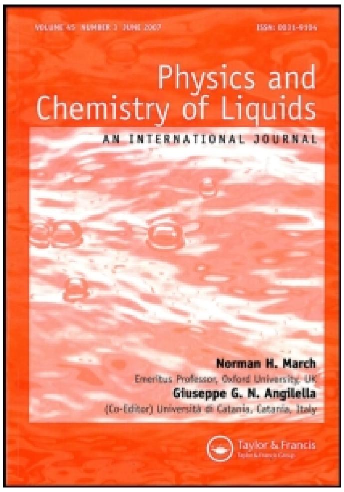

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Letter

ORIENTATIONAL DISORDER AND MELTING TRANSITION: PHENOMENOLOGY AND MODELLING WITH RELEVANCE TO SOLID HALOGENS AND H_2

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Experiment and computer simulation indicate that zig-zag I_2 (H_2) chains play a role in the behaviour of I_2 (H_2) solids under high pressure. Therefore, the phenomenological treatment of Pople and Karasz, which includes an energy barrier between different molecular orientations, is utilized to correlate a reduced melting temperature T_m with the inverse of T_c, the orientational disorder temperature. Contact is also made with a possibly relevant model, due to Longuet-Higgins, in which flexible molecules perform torsional oscillations under the influence of an intermolecular interaction energy. Further pressure experiments could provide an experimental test of the phenomenology and/or modelling.

Keywords: C. Zig-zag diatomic molecular chains; D. orientation disorder

The primitive phase diagram for hydrogen, as sketched, for example, by Leung *et al.* [1], has been greatly enriched by recent work: some of which is described in the review by Mao and Hemley [2]. For more recent work on a unified view of orientational ordering, and its relevance for understanding the evolution of the physical behavior of solid hydrogen with increasing pressure, the reader is referred to the

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study of Mazin *et al.* [3]. Work on the solid halogens is also highly relevant in the current context. In the molecular phases, I_2, and much more recently Br_2, have been studied by Fujihisa *et al.* [4] using X-ray diffraction, following early work of Drickamer *et al.* [5] both for thermodynamics and electrical transport [6]. In both solid halogens and solid hydrogen, there is evidence that over a limited pressure range, at least, zig-zag chains play an important role. Specifically, Pasternak *et al.* [7], employing Mössbauer techniques, identify zig-zag chains in solid I_2. Subsequent computer studies of solid H_2 by Hohl *et al.* [8] are interpreted in terms of zig-zag chains of diatomic molecules in solid hydrogen.

With this background, and stimulated especially by the very recent model of Siringo [9] in which he has proposed a *d*-dimensional lattice model, incorporating some degree of frustration and thereby capable of describing some properties of molecular orientation in appropriate molecular solids, we shall here utilize the early phenomenology laid down by Pople and Karasz [[10], see also [11] and [12]]. Below the predictions of their approach will then be briefly compared and contrasted with a possibly relevant model proposed earlier by Longuet-Higgins [13].

Starting with the Pople-Karasz (PK) phenomenology, we note first that it generalizes the Lennard-Jones and Devonshire [14] approach to positional disordering (melting), based on the Bragg-Williams approximation to include the possibility of orientational disordering. In the PK phenomenology only two possible orientations, separated by an energy barrier, are considered for simplicity, the case of n orientations with $n > 2$ being treated subsequently by Amzel and Becka [12].

Following the summary and notation used in the book by Ubbelohde [15], one can write simultaneous equations for the two order parameters Q and S, namely

$$\frac{1}{2Q-1}\log\left[\frac{Q}{1-Q}\right] = L[1-2S(1-S)y] \tag{1}$$

and

$$\frac{1}{2S-1}\log\left[\frac{S}{1-S}\right] = 2Ly[1-2Q+2Q^2]. \tag{2}$$

Here Q denotes specifically the fraction of molecules on site α, with S the corresponding fraction of orientation α. These Eqs. (1) and (2) are characterized by the quantities [15]

$$L = \frac{ZW}{2k_BT} \tag{3}$$

and

$$y = \frac{Z'W'}{ZW}. \tag{4}$$

If we put $y=0$ in Eq. (1) we recover the melting model of Lennard-Jones and Devonshire, with k_BT_m determined solely in terms of the energy ZW. The other energy $Z'W'$ constitutes a barrier height separating different orientational arrangements: this is, of course, the major new feature introduced by PK [10].

Figure 1 essentially reproduces the results of PK by plotting the melting temperature T_m and the orientational disordering temperature T_c, both measured in units of $(ZW/2)$, versus y defined in Eq. (4). The plot has been restricted to the range in which $T_c \leq T_m$ and we shall insist on this requirement throughout this work. For reasons which will be elaborated a little further later, we have chosen in Figure 2 to plot the ratio T_m/T_c over the range for 1 to 10 versus the inverse of the reduced orientational disordering temperature T_c. The corresponding range of this variable, denoted by $1/t_c$, is from $\sim 3-20$ as can be seen from Figure 2. Also shown in Figure 3 is the quantity $\log(T_m/T_c)$ vs $1/t_c$.

Though L^{-1} in Eq. (3) enters the plots in Figures 1–3, it is of course the parameter y that is the crucial variable in the PK phenomenology. In the present context of molecular solids under pressure, one can view y as a function of pressure p. Thus, if, for example, in one of the light halogens it should subsequently turn out that experiment can identify a 'plastic' crystal phase before melting, it should be of obvious interest to make the plot in Figure 2 from experiment. This predicts, of course, that T_m/T_c is a 'universal' function of the inverse of the reduced orientational disordering temperature. Roughly speaking, this is an inevitable consequence of the fact that once that temperature is scaled to L^{-1} through Eq. (3), then T_m and T_c are simply functions of y, as of course emphasized by PK and displayed in our Figure 1 above.

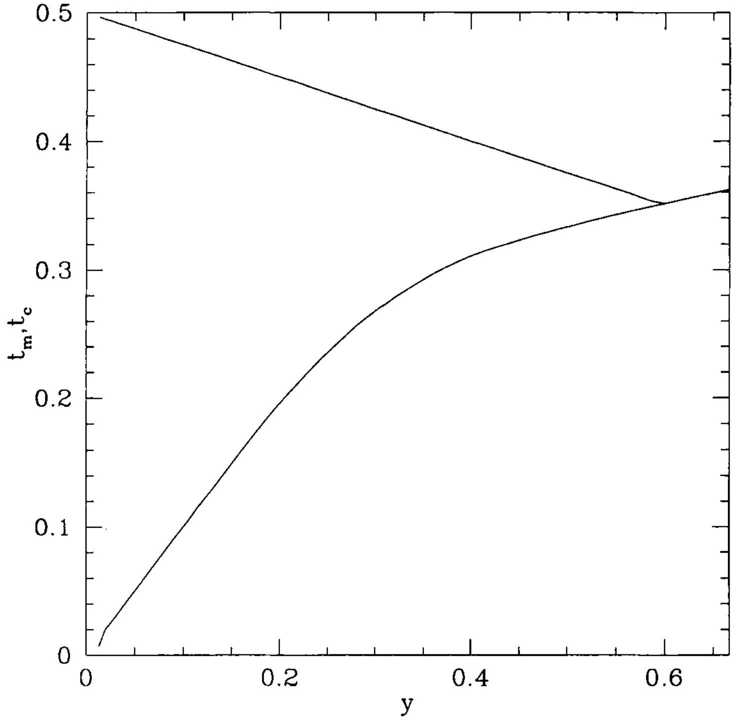

FIGURE 1 Reduced melting temperature $t_m = 2k_B T_m/ZW$ (upper line) and reduced orientational disordering temperature $t_c = 2k_B T_c/ZW$ (lower line) versus the parameter $y = Z'W'/ZW$. The two lines meet at $y_0 \simeq 0.595$ and coincide for $y > y_0$.

In this context, it is therefore relevant to return, before concluding, to the possibly relevant model of Longuet-Higgins [13]. He considers flexible molecules performing torsional vibrations. Again referring to the summary given in the book of Ubbelohde [15], we note that if ε measures the (short-range) interaction energy between flexible molecules, then one can write from the work of Longuet-Higgins [13]:

$$\frac{k_B T_m}{\varepsilon_1} = \left(\frac{\nu_0}{\nu}\right) \exp\left(\frac{\varepsilon}{k_B T_c}\right). \tag{5}$$

In Eq. (5), ε_1 is the quantity $h^2/8\pi^2 M l^2$ with M the mass and l the length of the flexible molecule, while ν_0 is the lowest torsional vibration frequency and ν is an appropriate average including higher

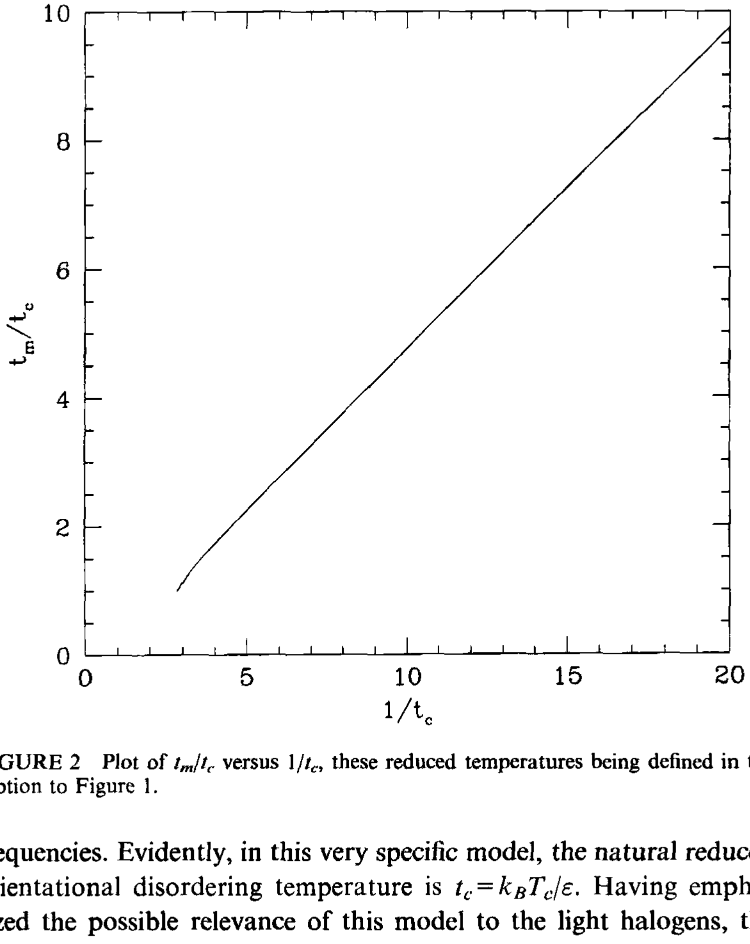

FIGURE 2 Plot of t_m/t_c versus $1/t_c$, these reduced temperatures being defined in the caption to Figure 1.

frequencies. Evidently, in this very specific model, the natural reduced orientational disordering temperature is $t_c = k_B T_c/\varepsilon$. Having emphasized the possible relevance of this model to the light halogens, the study of Pasternak *et al.* [7] suggests that ε should be a strong function of pressure p. Dividing both sides of Eq. (5) by t_c one readily finds, with $t_m = k_B T_m/\varepsilon$, the result

$$\frac{t_m}{t_c} = A(\varepsilon)\left[\frac{1}{t_c}\exp\left(\frac{1}{t_c}\right)\right] : A(\varepsilon) = \left(\frac{\varepsilon_1 \nu_0}{\varepsilon \nu}\right). \tag{6}$$

Thus again, with the scaling in terms of the intermolecular energy ε, the ratio T_m/T_c is a function of $1/t_c$, as in the plot of Figure 2 for the PK phenomenology. Of course, the square bracket in Eq. (6) is a very strongly varying function of $1/t_c$.

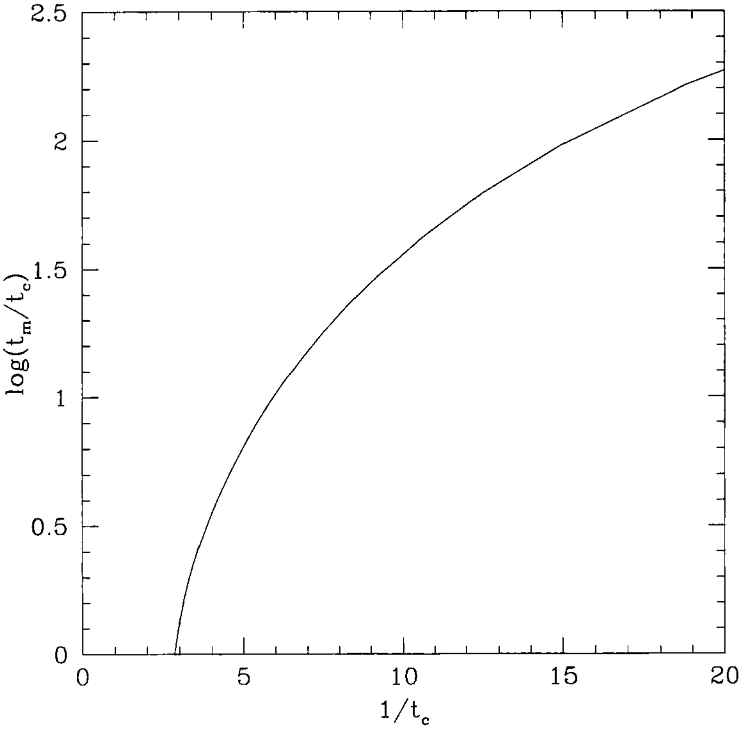

FIGURE 3 Similar to Figure 2, but now a logarithmic plot of t_m/t_c versus $1/t_c$.

In conclusion, should it prove possible in the future, for say a light halogen, to identify over some pressure range a 'plastic' crystal phase before melting, the present study points to the interest in plotting T_m/T_c from experiment versus $1/T_c$. The test of the 'universal' prediction of the PK phenomenology would be the first obvious step.

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