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THEORETICAL ASPECTS OF POLYMER MELTING

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Abstract - The Gibbs free energy of partially crystalline polymers of linear flexible chain molecules is intrinsically a non-linear function of the crystallinity. Owing to this fact the partially crystalline state may appear as stable equilibrium state. The equilibrium melting transition has no defined order and may be subject to hysteresis effects. Extended chain crystals are separated from the melt by a potential wall. That is why the polymer melt tends to metastable or stable partially crystalline states which can be attained more easily when the equilibrium crystallization is taking place.

INTRODUCTION

Homopolymers of linear flexible chain molecules generally melt continuously over a broad temperature range. The heat capacity as function of the temperature proceeds in a λ-shaped manner (Refs. 1 & 2). In the literature two controversial explanations are given :

(a) Some people (e.g. Refs. 2-4) suppose that in the ideal case the equilibrium melting of a polymer is an infinitely sharp phase transition of the first order as is with low molecular substances. In the ideal case the partially crystalline state is considered as a non-equilibrium state. The broadening of the melting range is thought to be due to mixing effects (impurities, molecular weight distribution, end groups and branches of the chain molecules), homophase pre-melting, caused by phonon interaction and crystal defects, the Thomson-Gibbs effect (crystal size distribution) and non-equilibrium effects.

(b) Other people (e.g. Refs. 5-8) lay stress upon the fact that owing to the lamellar structure of the partially crystalline state the individual chain molecule traverses the crystalline as well as the amorphous phase. In this case the conformational entropy of the chain segments remaining in the amorphous phase depend on the amount of the crystallized part. Thus the partially crystalline state is stabilized. Also in the ideal case the melting process is continuous as is in the case of a second-order order-disorder transition.

It is evident that the question whether the partially crystalline state can be or cannot be an equilibrium state and whether the equilibrium melting of high polymers of flexible chain molecules is a transition of the first or the second order can only refer to samples the melting curve of which is reversible below the crystallization temperature (Refs. 9 & 10). In my opinion this question is still unanswered. In the following some simple arguments shall be delivered from the merely phenomenological point of view.

THEORETICAL

In the simplest case (in which all deviations from the ideal case including the surface effects are neglected) we may describe a partially crystalline system by Gibbs' fundamental equation

$$g = g(T,p,\alpha) \quad . \tag{1}$$

g is the Gibbs free energy of the system per unity of mass, T the temperature and p the pressure (or pressure tensor). α can be considered as ordering parameter in the sense of the Landau theory of second-order transitions or as internal variable of order in the sense of the thermodynamics of irreversible processes. Eq. (1) is valid for one-phase as well as for two-phase systems, irrespective of the system being in an equilibrium or a non-equilibrium state with regard to α. Of course, the homogeneity of the system with respect to T and p involves the necessity of thermal and mechanical equilibrium. In the case of a two-phase system α can be called the degree of crystallinity.

The equilibrium states of the system which are stable or metastable with respect to the ordering parameter are characterized by

$$\partial g/\partial\alpha = 0 \quad ; \quad \partial^2 g/\partial\alpha^2 \geqq 0 \quad . \tag{2}$$

The equilibrium condition (2) fixes one of the independent variables T,p,α as function of the others, for instance

$$\alpha_{eq} = \alpha_{eq}(T,p) \quad . \tag{3}$$

That means that in the equilibrium state α may be eliminated as done in Ehrenfest's theory of the transition phenomena. For our arguments, however, it proves advantageous to maintain α as (in this case dependent) variable also in the equilibrium.

Like g the entropy of the system

$$s(T,p,\alpha) \equiv - \partial g/\partial T \tag{4}$$

depends on the variables T,p,α. For the specific heat capacity at constant pressure it follows that

$$c_p \equiv T\,(ds/dT)_p = T\,[\partial s/\partial T + (\partial s/\partial\alpha)(d\alpha/dT)_p] \quad . \tag{5}$$

In the non-equilibrium the independent variables have to be considered as explicit functions of the time t. Consequently the ratio $d\alpha/dT$ is generally represented by

$$(d\alpha/dT)_p = (d\alpha/dt)_p/(dT/dt)_p \quad . \tag{6}$$

The heat capacity depends on the ratio of the melting rate to the heating rate as is frequently found with partially crystalline polymers.

In the following we are only interested in the phenomenon of equilibrium melting. Therefore we take it for granted that the system is heated up so slowly that the equilibrium value of the ordering parameter can be balanced immediately after a change in temperature ($d\alpha/dt \gg dT/dt$; quasi-static process). The time rate of $\partial g/\partial\alpha$ at constant pressure is generally described by

$$\left[\frac{d}{dt} \left(\frac{\partial g}{\partial \alpha}\right) \right]_p = \frac{\partial}{\partial T} \left(\frac{\partial g}{\partial \alpha}\right)\left(\frac{dT}{dt}\right)_p + \frac{\partial}{\partial \alpha} \left(\frac{\partial g}{\partial \alpha}\right)\left(\frac{d\alpha}{dt}\right)_p$$

This equation entails that the change of the ordering parameter with the temperature during a quasi-static process is given by the equation

$$(d\alpha/dT)_p^{eq} = - (\partial^2 g/\partial T \partial \alpha)/(\partial^2 g/\partial \alpha^2) = (\partial s/\partial \alpha)/(\partial^2 g/\partial \alpha^2) \qquad (7)$$

In consequence, the equation (5) for the equilibrium heat capacity reads as follows :

$$c_p^{eq} = T\,[\partial s/\partial T + (\partial s/\partial \alpha)^2/(\partial^2 g/\partial \alpha^2)] \quad . \qquad (8)$$

Moreover we restrict ourselves to a two-phase system as proved, for instance, for linear polyethylene by electron micrographs (Refs. 11-13). In the case of a two-phase system the enthalpy h and the entropy s can be split into two additive parts

$$h(\alpha) = (1-\alpha)h_a + \alpha h_c \quad ; \quad s(\alpha) = (1-\alpha)s_a + \alpha s_c \qquad (9)$$

(h_a,s_a : enthalpy and entropy of the amorphous phase; h_c,s_c : enthalpy and entropy of the crystalline phase). Those equations, however, are real linear relations only if the two phases are independent of each other. If the chain molecules traverse the crystalline as well as the amorphous phase and if the entropy of the amorphous phase depends on the amount of the crystalline phase (Refs. 5-8), the second equation (9) is a non-linear equation in α. By contrast, the first equation (9) may be considered as a linear relation, at least in a first approximation (Ref. 14).

If h(α) is a linear and s(α) a non-linear function of α, (2) and (9) together with

$$g = h - Ts \qquad (10)$$

lead to the conditions

$$- \partial s/\partial \alpha = \Delta h/T \quad ; \quad - \partial^2 s/\partial \alpha^2 \geqq 0 \qquad (11)$$

($\Delta h \equiv h_a - h_c > 0$) for a stable or metastable equilibrium. The change of the equilibrium crystallinity with the temperature is described by

$$(d\alpha_{eq}/dT)_p = \Delta h/T^2(\partial^2 s/\partial \alpha^2) \leqq 0 \quad . \qquad (12)$$

The equilibrium heat capacity is given by

$$c_p^{eq} = T\,(\partial s/\partial T) - (\Delta h/T)^2/(\partial^2 s/\partial \alpha^2) \geqq 0 \quad . \qquad (13)$$

The equilibrium melting is governed by the dependence of $-\partial s/\partial \alpha$ on α, that means by the microstructure of the partially crystalline texture.

DISCUSSION

In order to give an idea of the contents of the Eqs. (10-13) some examples are treated in Fig. 1. They neglect the explicit dependence of the enthalpy and of the entropy on the temperature (see Note a).

A. In case $-\partial s/\partial\alpha$ is a constant, i.e. $s(\alpha)$ is a linear function of α, also $g(\alpha)$ becomes a linear function of α. The minimum values of $g(\alpha)$, that means the equilibrium states relative to α, are always at $\alpha=1$ for temperatures below a certain critical temperature

$$T_c \equiv \Delta h/\Delta s \qquad (14)$$

$[\Delta s \equiv s_a(0)-s_c]$ and at $\alpha=0$ for temperatures $T > T_c$. Only at T_c the partially crystalline state is an equilibrium state and it is worth mentioning that this equilibrium state is a neutral one. The equilibrium melting appears as an ideal first-order transition.

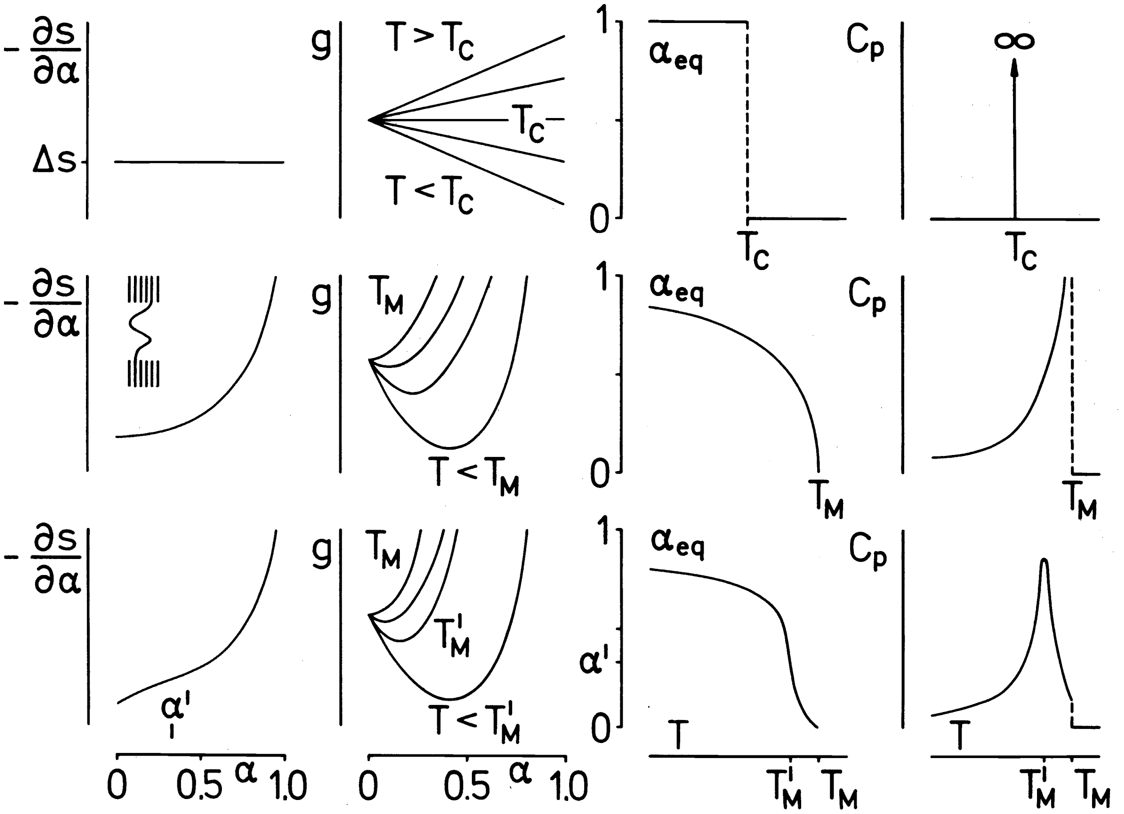

Fig. 1 A-C. Characteristic thermodynamic functions of polymers in various partially crystalline microstates (schematic representation) : the change $\partial s/\partial(1-\alpha) = -\partial s/\partial\alpha$ of the entropy s with the amorphous part $(1-\alpha)$ and the Gibbs free energy g as functions of the crystallinity α, g for different temperatures T. The equilibrium crystallinity α_{eq} and the equilibrium heat capacity C_p as functions of the temperature T. The rows from top to bottom correspond to the examples A-C mentioned in the text.

Note a. For an explicit analytic representation of $-\partial s/\partial\alpha$ special molecular models (Refs. 7 & 15) or a Landau expansion of $g(\alpha)$ (Refs. 16) may be taken as basis.

B. If $-\partial s/\partial\alpha$ is a positive function which increases monotonously with α [according to Zachmann (Refs. 7 & 15) this phenomenon is to be expected with surface melting of lamellae which are connected by tie-molecules] $g(\alpha)$ has a minimum for each temperature $T \leq T_M$. That means that for each temperature $T \leq T_M$ there exists a partially crystalline equilibrium state. With rising temperature the minimum moves continuously to $\alpha=0$. The equilibrium crystallinity decreases continuously with rising temperature until it disappears at

$$T_M = T_c \Delta s \,/\, \lim_{\alpha \to 0}(-\partial s/\partial\alpha) \gtreqless T_c \qquad (15)$$

(see Note b). If $-\lim(\alpha\to 0)\partial^2 s/\partial\alpha^2 = 0$ (as shown in the second row of Fig. 1) the equilibrium melting appears as anomalous second-order transition ($c_p^{eq} = \infty$ at T_M). If $-\lim(\alpha\to 0)\partial^2 s/\partial\alpha^2 > 0$ the equilibrium melting appears as normal second-order transition (c_p^{eq} = finite at T_M).

C. So far as the monotonously rising positive function $-\partial s/\partial\alpha$ has an inflection point at α', $\alpha_{eq}(T)$ traverses an inflection point, too. The heat capacity $c_p^{eq}(T)$ has a maximum. The equilibrium melting appears as a more or less marked diffuse transition.

D. The equilibrium melting resembles a transition of the Onsager type if the slope of $-\partial s/\partial\alpha$ vanishes at the inflection point α', i.e. $(\partial^2 s/\partial\alpha^2)_{\alpha'} = 0$.

E. If $-\partial s/\partial\alpha$ is sigmoid (as shown in the fifth row of Fig. 1) $g(\alpha)$ has two minima in the temperature range $T_u < T < T_s$. The minima reach the same level at $T_M' \leq T_M$. If the system persists in the absolute minimum $\alpha_{eq}(T)$ and $s_{eq}(T)$ suffer a jump at T_M'. The equilibrium melting appears as a transition of the first order at T_M' with a more or less significant two-phase pre- and post-melting range. Two minima in the free energy mean, however, that hysteresis effects are possible. Since the system has to overcome an energy barrier on melting at T_M' it may stay in the relative (metastable) minimum during the heating process. The sample may be superheated up to T_s. Of course, the homologous undercooling effect has a competition in the nucleation. A ($-\partial s/\partial\alpha$)-curve with a minimum and an inflection point with a negative slope (as in the fifth row of Fig. 1), however with the maximum at $\alpha=0$, was calculated by Zachmann (Refs. 7 & 15) for the surface melting of lamellae with pendent short loops. In this case we get from Eqs. (10-13) a transition of the first order with two-phase pre-melting, but without post-melting.

F. According to Zachmann (Refs. 7 & 15) for lamellae with chain ends hanging around $-\partial s/\partial\alpha$ is a function monotonously decreasing with rising α. From Eqs. (10-13) it follows that $g(\alpha)$ has a maximum in the temperature range $T_u < T < T_s$. The minimum values of $g(\alpha)$ are always at $\alpha=1$ or $\alpha=0$. At T_c the level of the minimum values becomes equal. That means that all partially crystalline states are unstable. Consequently extended chain lamellae melt, in the ideal case, at T_c with an infinitely sharp first-order transition without any pre- or post-melting. Since at T_c a barrier of free energy has to be overcome extended chain crystals may easily be superheated up to T_s and the melt may be undercooled down to T_u.

Note b. In practice T_M may always be equal to T_c. Theoretically, however, it is also possible that $T_M \neq T_c$, for instance in case of mere surface melting (Ref. 7). In Fig. 1 $T_M > T_c$ was only chosen by reason of an easy drawing.

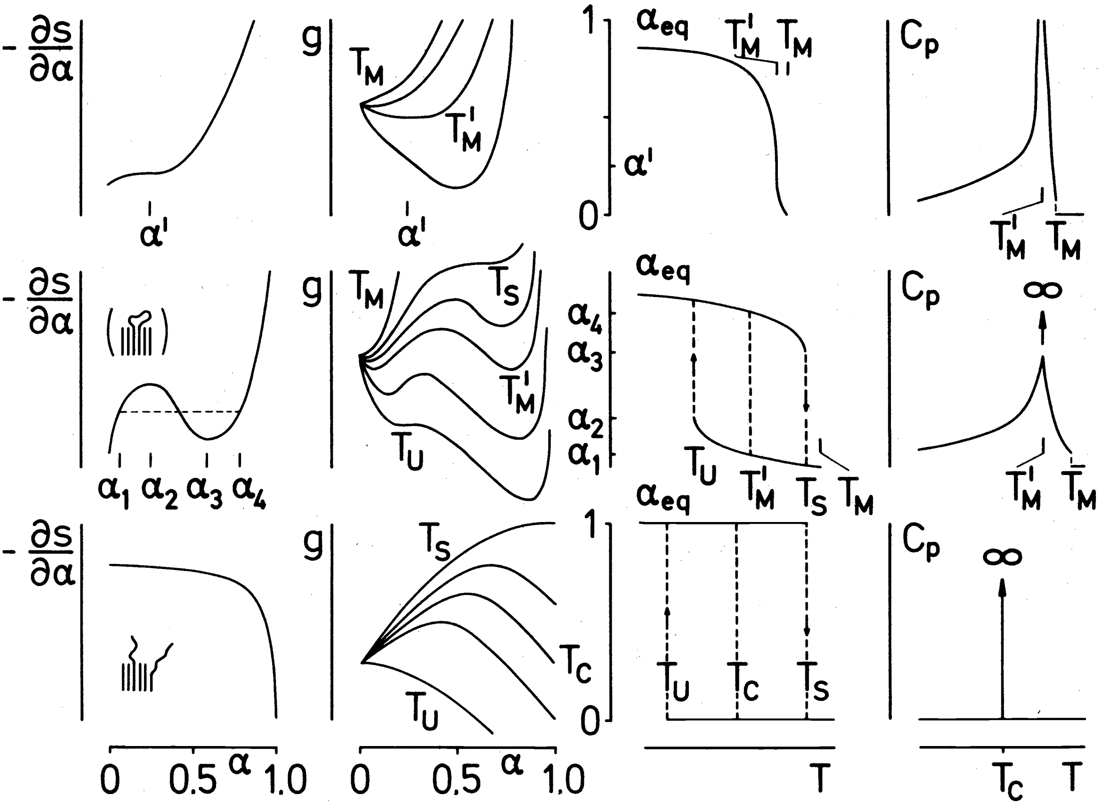

Fig. 1 D-F. Compare Fig. 1 A-C. The rows from top to bottom correspond to the examples D-F mentioned in the text.

CONCLUSIONS

Actually the effects mentioned in (a) of the introduction will more or less play a part. In the case of small lamellae mainly the surface effects cannot be neglected. However, in my opinion there is also a perspicuous indication that the entropic coupling of the phases is efficient : The superheating phenomena measured on etched extended chain crystals (Ref. 17) and the fact that during a crystallization under normal conditions no extended chain crystals develop.

If the amorphous and the crystalline phase were independent of each other and the free energy a linear function of α, there would be a neutral equilibrium at the melting point T_c (see the first row of Fig. 1). Owing to the mobility of the chain molecules there would be no motivation for superheating phenomena which are due to slow melting. The undercooling would only be a question of nucleation. The rather slow melting process of the extended chain crystals [which contrasts with the great mobility in the melting range of other microstructures (Ref. 12)] requires, on the contrary, a barrier between the melt and the crystal at T_c (as shown in the sixth row of Fig. 1). That indicates a free energy which is non-linear in α. On the other hand the existence of a potential wall between the melt and the extended chain crystal means that during the equilibrium crystallization under normal conditions metastable or stable partially crystalline states will develop which are more easily accessible. The formation of an extended chain crystal is only possible by a very long annealing at T_c.

Another indication of the efficiency of the entropic coupling can be concluded from the statement that the melting peak in the heat capacity of crystal lamellae of a defined thickness may be located at higher temperatures than predicted by the Thomson-Gibbs equation (Ref. 13). This phenomenon cannot be explained by mixing effects or homophase premelting etc. But this statement should be confirmed by additional investigations.

I think that further elucidation regarding the efficiency of the entropic effects could be gained by investigations of the fluctuation phenomena in the melting range and in the superheated state in dependence on the microstructure of the samples. The fluctuations ought to be especially great in those regions where $-\partial^2 s/\partial \alpha^2 \approx 0$.

If the entropic coupling of the two phases of a partially crystalline polymer is accepted as a matter of fact, it can be concluded that the equilibrium melting of polymers, like the non-equilibrium melting, depends, to a large extent, on the microstructure of the samples. The equilibrium melting can appear as transition of the first or the second order or just as well as a diffuse transition or a transition of the Onsager type.

A non-linear dependence of the free energy on the composition is also given in mixtures. However, the cause of the non-linearity of the free energy in mixtures, viz., the concentrations of the components in the melt which change during the melting process, can be varied at will by manipulations from outside. That is why it is reasonable to choose the pure substances as standard systems. The situation is different for a defined polymer. In this case the cause of the non-linearity, i.e. the flexibility of the chain molecules, cannot be manipulated from outside. On the contrary, it is an intrinsic property of the polymer. Therefore I do not think it reasonable to give preference to one of the possible microstructures, e.g. the extended chain crystals, as standard. Probably the extended chain crystals below the melting temperature are in the energetically preferred state. For the equilibrium melting at constant pressure, however, it is not the energy but the Gibbs free energy that is decisive. But at higher temperatures the Gibbs free energy strongly depends on the entropy of the system. With respect to the Gibbs free energy a partially crystalline state may be the preferred equilibrium state.

REFERENCES

1. B. Wunderlich, M. Dole, J. Polymer Sci. 24, 201 (1957).
2. L. Mandelkern, Crystallization of Polymers, McGraw-Hill, New York, 1964.
3. P. Flory, Ric. Sci. Suppl. 25, 636 (1955); J. Chem. Phys. 17, 223 (1949); J. Am. Chem. Soc. 84, 2857 (1962).
4. B. Wunderlich, Macromolecular Physics Vol. III, Academic Press, New York, to be published 1980.
5. A. Münster, Ric. Sci. Suppl. 25, 648 (1955); Z. physik. Chem. N. F. 1, 259 (1954).
6. R. J. Roe, K. J. Smith Jr., W. R. Krigbaum, J. Chem. Phys. 35, 1306 (1961).
7. H. G. Zachmann, Kolloid-Z. & Z. Polymere 216/217, 180 (1967).
8. E. W. Fischer, Kolloid-Z. & Z. Polymere 218, 97 (1967)
9. H. G. Zachmann, Adv. Polymer Sci. 3, 581 (1964).
10. E. W. Fischer, Kolloid-Z. & Z. Polymere 231, 458 (1969).
11. G. Kanig, Kolloid-Z. & Z. Polymere 251, 782 (1973).
12. G. Kanig, Progr. Colloid & Polymer Sci. 57, 176 (1975).
13. G. Kanig, Colloid & Polymer Sci. 255, 1005 (1977).
14. E. Schrader, H. G. Zachmann, Kolloid-Z. & Z. Polymere 241, 1015 (1970).
15. G. H. Zachmann, Kolloid-Z. & Z. Polymere 231, 504 (1969).
16. H. Baur, Progr. Colloid & Polymer Sci. 66, 1 (1979).
17. B. Wunderlich, Macromolecules 10, 906 (1977).