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# A classification of molecules, phases, and transitions as recognized by thermal analysis[☆]

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## Abstract

Chemistry has been fragmented into many separate disciplines during its modern development over the last 200 years. This subdivision has let us forget the common basis of classification of molecules, phases, and transitions. First, one finds that there are but three large classes of molecules (small molecules, large and flexible molecules, and large and rigid molecules). By taking into account the two roots of the properties of molecules, structure and motion, the numbers of types of phases is limited to 10, namely the four classical phases: gas, liquid, crystal, and glass; and six mesophases: liquid, plastic, and conformationally disordered crystals (condis crystals), and their three corresponding mesophase glasses. Adding the possible transitions between these phases and considering the phase-sizes (macro, micro, and nanophases) completes a simple, unifying frame for chemistry based on equilibrium and non-equilibrium thermal analysis. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Thermal analysis; Phase; Transition; Macromolecule; Equilibrium; Non-equilibrium

## 1. Introduction

In many lectures and discussions I have suggested that it was time to revisit our definitions and classifications of molecules, phases, and transitions. This special issue of *Thermochimica Acta* with the title "Reactivity of Solids," honoring the 70th birthday of Professor Dollimore, is perhaps a good forum to address these topics, especially after being encouraged by Prof. Dollimore to do so.

Chemistry is the basic natural science encompassing the description, understanding, and manipulating of matter as we recognize it. One may take the year 1808 when John Dalton published the book "A New System of Chemical Philosophy" as the beginning of chemistry as an experiment-based science [1]. At that time it became clear that atoms are the smallest particles of the chemical elements, and a given molecule contains a fixed combination of different atoms. One notices, however, when reading the early literature that at that time only compounds with rather small molecules were understood. This is quite in contrast to most objects of interest to man, and to the molecules of today's "macromolecular chemistry".

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As the knowledge of chemistry grew, a confusing array of sub-disciplines arose, obliterating the basic simplicity of the field. In the early days of chemistry it seemed reasonable to distinguish inorganic from organic molecules. Inorganic molecules were thought to be subject to reactions that could be affected in the laboratory, while "organic" molecules were not. When Wöhler in 1828 discovered that urea ($H_2N–CO–NH_2$), an organic, so-called "animal" substance, could be produced from inorganic ammonium cyanate $NH_4^+$ $^-O–C{\equiv}N$, this subdivision became unnecessary. Instead of abolishing "organic" chemistry, biochemistry was created as an additional discipline for the study of substances "really" connected to the chemistry of life.

Turning to nowadays numerous Divisions of the American Chemical Society, one finds that their fields of expertise have nothing to do with a classification of chemistry, but rather with the accidental importance of certain molecules to society. From the offerings at a recent Meeting of the American Chemical Society, one can deduce that in addition to inorganic, organic, and biological chemistry there exist divisions of (alphabetically): Agricultural and Food Chemistry, Agrochemicals, Analytical Chemistry, Carbohydrate Chemistry, Cellulose Paper and Textile Chemistry, Chemical Health and Safety, Colloid and Surface Chemistry, Environmental Chemistry, Fuel Chemistry, Geochemistry, Industrial and Engineering Chemistry, Medicinal Chemistry, Nuclear Chemistry and Technology, Petroleum Chemistry, Physical Chemistry, Polymer Chemistry, and finally, Polymeric Materials. In addition, there are many scientists and engineers who are concerned with subjects of chemistry in fields such as Metallurgy, Ceramics, Glass Science, and Solid State Physics. It is hard to see that all these areas of chemistry deal with the same molecules, but it will be shown in this paper that basically there are, indeed, only three types of molecules.

The next topic of this paper deals with phases. The phases are at the root of the macroscopic appearance of matter. Traditionally a phase is defined in thermodynamic terms as a state of matter that is uniform throughout, not only in chemical composition, but also in physical state. In other words, a phase consists of a homogeneous, macroscopic volume of matter, separated by well-defined surfaces of negligible influence on the phase properties. Domains in a sample that differ in composition or in their physical state are considered as different phases. These definitions of the molecules as the microscopic constituents of the macroscopic phase will be shown to be overlapping when going to macromolecules and nanophases.

The possible transitions between phases in equilibrium and non-equilibrium are the final topics of this paper, where again, the term transition is in dire need of quantification. The best definition is, perhaps, given in Webster's Dictionary as "a passing from one condition, form, stage, activity, place, etc. to another." For phase transitions one must thus say that "a transition is a passing from one phase to another." These transitions can occur under equilibrium or non-equilibrium conditions and lead to the basic subject of thermal analysis of materials [2].

It was the experience with what are now called phases that lead to the first theories of matter. After considerable discussion by many earlier Greek philosophers, Plato and Aristotle, in the fourth century BC, formulated the idea that there exists only one primeval matter and two pairs of "qualities": hot/cold and wetness/dryness. As these qualities are impressed on the primeval matter, four elements were thought to be produced, fire (hot + dry), air (hot + wet), earth (cold + dry), and water (cold + wet). All material things were then thought to be different combinations of these four elements. Today it is not difficult to extract the roots of this theory, namely that heat is equated with "fire" and the other three "elements" stand for gases, solids, and liquids, respectively. A self-consistent continuum theory of matter was thus created, based exclusively on macroscopic observations.

Modern science has since established the detailed atomic and molecular structure of matter. The microscopic length scale, the angstrom (0.1 nm), is based on the diameter of atoms and must be multiplied with a factor of 10 000 to reach the smallest, macroscopically recognizable length, the micrometer.

Quantitative experiments with heat, $Q$, the fourth "element" of antiquity began after the invention of reliable, closed-capillary, liquid-in-glass thermometers in the 17th century. Somewhat later, Richmann established in 1747 the calorimetric mixing formula that expresses how bodies that are initially at different temperatures come to equilibrium at some intermediate temperature, $T$. By following discrepancies between experimental values and results expected from Richmann's formula, Black and Wilcke, inde-

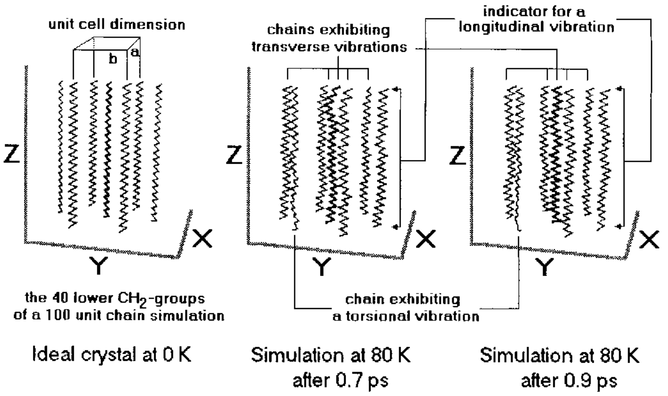


Fig. 1. Snapshots of molecular motion resulting from molecular dynamics simulation of polyethylene crystals [3].

pendently, discovered the concepts of latent heat and heat capacity. Latent heat is absorbed without change in temperature, and heat capacity is the heat needed to increase temperature by one unit (kelvin).

Today it is easy to visualize atomic motion by molecular dynamics simulation using supercomputers. Fig. 1 shows an example of a representation of the skeletal motion of a polyethylene crystal at low temperature [3]. This vibrational motion was linked by Einstein [4] and Debye [5] to heat capacity ($C_v = \partial Y/\partial T$ at constant volume, and composition). The total energy ($U = \int C_v \mathrm{d}T$) is represented by the Hamiltonian of the crystal, and the temperature can be extracted from the kinetic energy ($3NkT/2 = \sum mv^2/2$), where the sum goes over the kinetic energy of all atoms $N$ of the system; $m$ is the atomic mass, $v$, the atomic velocity and $k$, Boltzmann's constant). The time scale of atomic motion is the picosecond ($10^{-12}$ s), far removed from the fastest event macroscopically perceivable which may take a millisecond (factor of 1 000 000 000). The separation of nine orders of magnitude in time between human level experience and atomic level motion, compared to only four orders of magnitude between visible objects and atoms, may be the reason for the relatively slow development of knowledge about molecular motion and calorimetry when compared to molecular structure and gravimetry.

## 2. Classification of molecules

In order to understand molecules, there is a need for a brief review of atoms and bonding [6]. A characterization of the atomic structure is given by the configuration of its valence electrons and the electronegativity. The electronegativity, $X$, is a measure of the ability to attract an electron pair, needed for covalent bonding [7]. Numerically, $X$ is approximately the average between the electron affinity (energy gained or lost when adding an electron) and the ionization energy (energy needed to remove an electron), and is adjusted with data from bond energies. The electronegativity has a scale from zero to four and permits an estimation of covalent bond energy.

The joining of atoms to form molecules requires interactions that keep the atoms bound together, at least long enough for identification. This statement is an operational definition [8] of a bond. Obviously, there is some correlation between the life-time of a bond and its strength. Often one judges the strength of a bond by its bond energy. Checking a large number of experimentally measured bond energies, one finds that there are only two well-separated classes of bonds between atoms, ions, and molecules, strong bonds and weak bonds. Bond energies in the region of 50 kJ mol$^{-1}$, that would be called intermediate, are rarely observed. Different types of bonding involve different interactions and displacements of the electrons of the bonding partners.

Fig. 2 summarizes the possible bonding between atoms. The strong bonds are classified as covalent, ionic, or metallic. Covalent bonding is exemplified by fluorine, $F_2$, and methane, $CH_4$. The bonds involve sharing of electrons between the bonding partners with similar and large electronegativities ($X_A$ and $X_B > 2.0$). Important in the description of a covalent

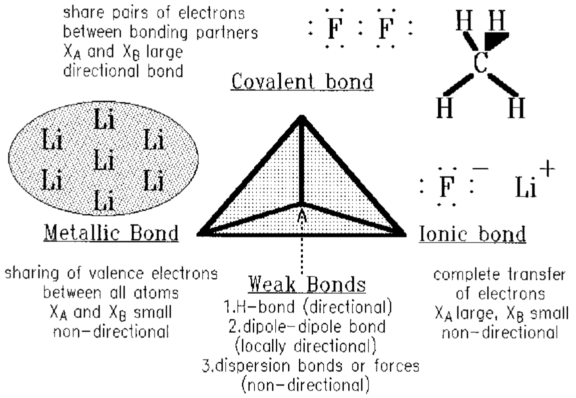


Fig. 2. Grimm's tetrahedron of bonding.

bond is its directionality, governed by the molecular orbital that contains the electron pair. Because of the close approach of the atoms needed in a covalent bond and the frequent involvement of only *s* and *p* orbitals, the coordination numbers one to four are most frequent.

Moving the (valence) electrons during bonding from one atom (of low electronegativity, $X_A$ 2.0) to another (of higher electronegativity, $X_B > 2.0$), leads to an ionic bond. The example given in Fig. 2 is lithium fluoride, LiF. The major bonding is in this case caused by Coulomb attraction between the positive ions and their negative counterparts. Important for the assembly of large aggregates of ions is the absence of any directionality. It must be recognized, however, that only negative ions in contact with positive ions lead to an attraction. There are, thus, strict rules of the alternation of charges that limit the coordination number between four and eight, depending on the size-ratio of the ions.

The metallic, strong bonds are shown for the example of lithium, Li. In this case the electrons are not concentrated in an identifiable bond, but are shared in a band structure between bonding partners of equally low electronegativity ($X < 2.0$). Such an arrangement makes the bonds again non-directional, and removes, in addition, all packing restrictions. Metals can thus pack most closely and the most dense materials are found among them (osmium. iridium, platinum, and gold have densities of 19–22 times that of water).

The three types of strong bonds just described make the corners of the base of Grimm's tetrahedron (Fig. 2). Bonds of intermediate character make up the area of the base. Weak bonds are collected at the top of the tetrahedron. The directionality is, as for strong bonds, important for the understanding of structures held together by weak bonds. Intermediate types of bonding are found within the volume of the tetrahedron.

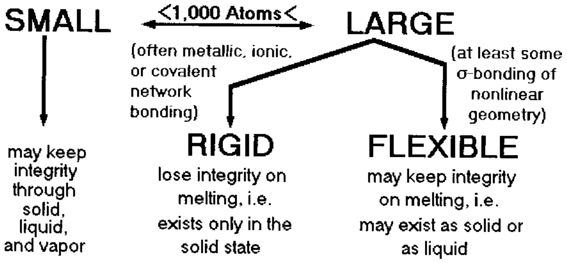
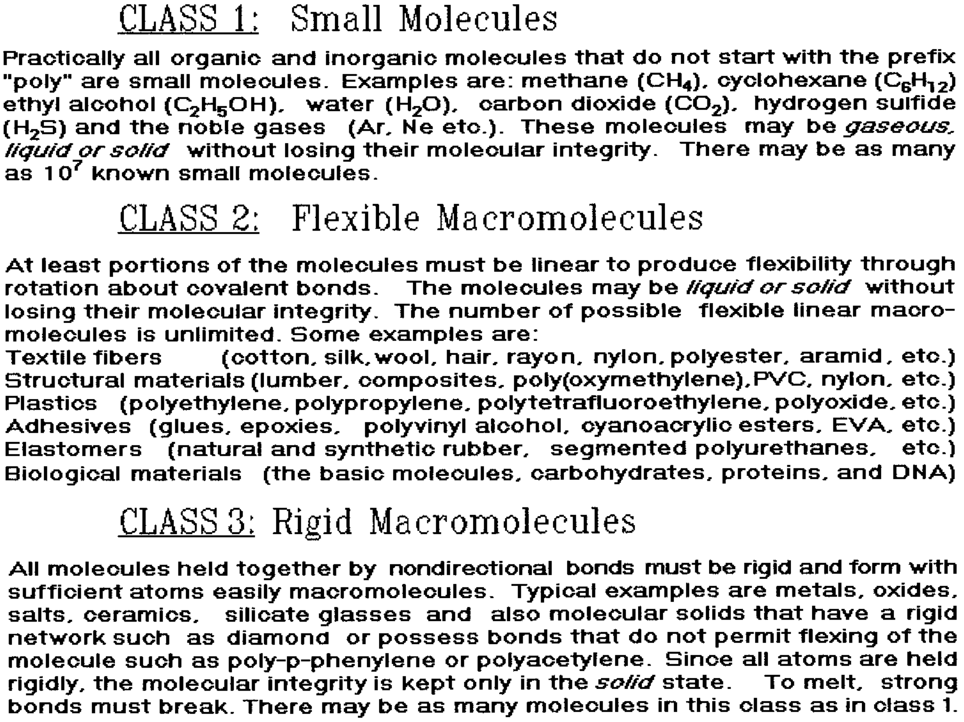


Fig. 3. Classification of molecules.

A classification of all molecules can now make use of the sizes of molecules, dividing all molecules into small molecules and macromolecules, as is indicated in the top line of Fig. 3. The importance of large molecules, or macromolecules was shown by Staudinger some 70 years ago. Following his suggestion, any molecule with more than 1 000 atoms, or a molar mass of more than 10 000 Da is called a macromolecule. This operational definition is quite useful since there are not many molecules that are made of about 1 000 atoms, and small changes in the number of atoms do not change most of the properties of molecules of such size.

To complete the classification of molecules, a further subdivision of the macromolecules into flexible and rigid molecules is advantageous, as is shown in the second row of Fig. 3. The flexible macromolecules are often (but less precise) just called "polymers". They also are the macromolecules Staudinger was introducing to chemistry as the last class of new molecules in 1920. The flexibility of a molecule is caused by internal rotation about at least some covalent sigma bonds of proper geometry. Missing such flexibility makes a macromolecule rigid, and places it into a class of molecules with very different properties. Rigid macromolecules easily reach the size of phases, making the distinction of separate molecules often superfluous and unwieldy (the molecule of a single crystal of 100 g has, for example, a molar mass of $6 \times 10^{19}$ metric tons (t), close to the mass of the moon).



**CLASS 1: Small Molecules**

Practically all organic and inorganic molecules that do not start with the prefix "poly" are small molecules. Examples are: methane ($CH_4$), cyclohexane ($C_6H_{12}$) ethyl alcohol ($C_2H_5OH$), water ($H_2O$), carbon dioxide ($CO_2$), hydrogen sulfide ($H_2S$) and the noble gases (Ar, Ne etc.). These molecules may be *gaseous, liquid or solid* without losing their molecular integrity. There may be as many as $10^7$ known small molecules.

**CLASS 2: Flexible Macromolecules**

At least portions of the molecules must be linear to produce flexibility through rotation about covalent bonds. The molecules may be *liquid or solid* without losing their molecular integrity. The number of possible flexible linear macromolecules is unlimited. Some examples are:

Textile fibers (cotton, silk, wool, hair, rayon, nylon, polyester, aramid, etc.)
Structural materials (lumber, composites, poly(oxymethylene), PVC, nylon, etc.)
Plastics (polyethylene, polypropylene, polytetrafluoroethylene, polyoxide, etc.)
Adhesives (glues, epoxies, polyvinyl alcohol, cyanoacrylic esters, EVA, etc.)
Elastomers (natural and synthetic rubber, segmented polyurethanes, etc.)
Biological materials (the basic molecules, carbohydrates, proteins, and DNA)

**CLASS 3: Rigid Macromolecules**

All molecules held together by nondirectional bonds must be rigid and form with sufficient atoms easily macromolecules. Typical examples are metals, oxides, salts, ceramics, silicate glasses and also molecular solids that have a rigid network such as diamond or possess bonds that do not permit flexing of the molecule such as poly-p-phenylene or polyacetylene. Since all atoms are held rigidly, the molecular integrity is kept only in the *solid* state. To melt, strong bonds must break. There may be as many molecules in this class as in class 1.

Fig. 4. Examples of molecules in the three classes.

Chemistry is the science dealing with the synthesis, reactions, and properties of all substances, still, traditionally small molecules have become the main focus of chemistry. Since the discovery of X-ray diffraction early in this century, rigid macromolecules have become the primary substances of interest to materials science and solid state physics. The "new", flexible macromolecules identified only 20 years later fell between these fields and have only slowly been accepted into the various academic disciplines. Presently polymer science, if it is not placed in a separate department, is most prominently taught in materials science, less in chemistry, and least in physics.

The key distinction between the three classes of molecules is summarized in the bottom portion of Fig. 3. Small molecules may appear as solid, liquid, and gaseous phases without decomposition, while rigid macromolecules keep their bonding to nearest neighbors (their molecular integrity) only in the solid state. Due to internal rotation, flexible macromolecules can attain sufficient intramolecular disorder to melt (or dissolve) without breaking strong bonds. This property is at the root of many of the useful properties of polymers (plastic and rubber–elastic behavior in addition to high strength, light weight, and low melting temperatures). The three classes of molecules are thus very distinct in their phase behavior. No macromolecule can be evaporated thermally without decomposition. If one tries to place flexible macromolecules into the gas phase by evaporation of small solvent molecules from a dispersion of droplets of a solution with only one macromolecule per droplet, the macromolecules become microphase particles and collect at the bottom of the container [9].

The top of Fig. 4 contains a listing of small molecules, the compounds of traditional chemistry. As pointed out above, they are often stable in all three phases, gas, liquid, and solid. One can see the importance of the different phases from terminology in use for hundreds of years. The molecules of $H_2O$, have three names linked to its phases (steam, water, and ice), a practice not carried to any other compound. Perhaps, the difference between molecules and phases was understood by the time other important molecules were identified in different phases.

A series of flexible macromolecules is listed together with their applications in the center of Fig. 4. At sufficiently high temperatures they form mobile, random coils in a liquid state. On cooling, they become solid, either by crystallization (although they usually crystallize only partially) or by formation of a glass. If the flexible macromolecules are cross-linked, they show rubber elasticity, another unique polymer property. Both small molecules and flexible macromolecules must contain directional strong bonds, as was illustrated by Grimm's tetrahedron in Fig. 2. Non-directional bonds would lead to three-dimensional aggregates and, thus, rigid macromolecules.

Rigid macromolecules are, finally, summarized at the bottom of Fig. 4. They are often not recognized as separate molecules because of their enormous size. The molecule determines the size of the phase or vice versa. A single crystal of NaCl is naturally a single molecule. It is thus more important to know the structure, shape, and defects of its crystal than the mass of the macromolecule which can easily be gained by weighing the macroscopic crystal. The chemical composition is sufficiently identified by its basic formula. On fusion or sublimation, rigid macromolecules lose their integrity, as discussed above, and break into smaller units. A sodium chloride melt is, thus, not a liquid of small NaCl molecules, but rather a dynamic aggregate of positive sodium and chloride ions that constantly changes their neighbors. In the gas phase, however, strongly polar, small NaCl molecules are found.

## 3. Classification of phases

To summarize the different states of matter, a schematic summary is given in Fig. 5. The four classical phases are listed in the shaded boxes — gas (the dilute phase), melt (or liquid), crystal and glass (the two solid phases). The main differences between the mobile (fluid) and solid phases are the presence or absence of the three types of large-amplitude motion (translation, rotation, and internal rotation or conformational motion). In special circumstances not all the large-amplitude motion is frozen. The resulting phases are then intermediate, they are mesophases (from Gk. με′σος, in the middle), as indicated in Fig. 5. The possible mesophases are: liquid crystals (LC, orientationally ordered and mobile liquids), plastic crystals (PC, positionally ordered crystal with local rotational disorder and mobility), and condis crystals (CD, fully or partially conformationally disordered and mobile crystals with positional and orientational order). These mesophases are, thus, characterized by an increase of disorder relative to a crystal and by the presence of distinct amounts of large-amplitude, molecular motion.

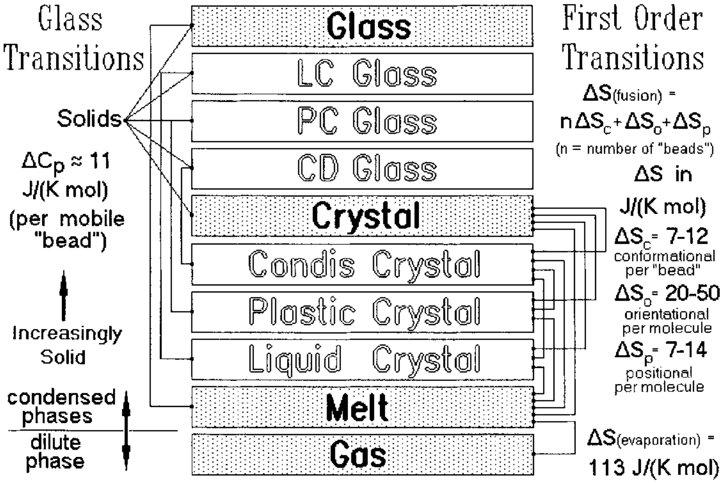
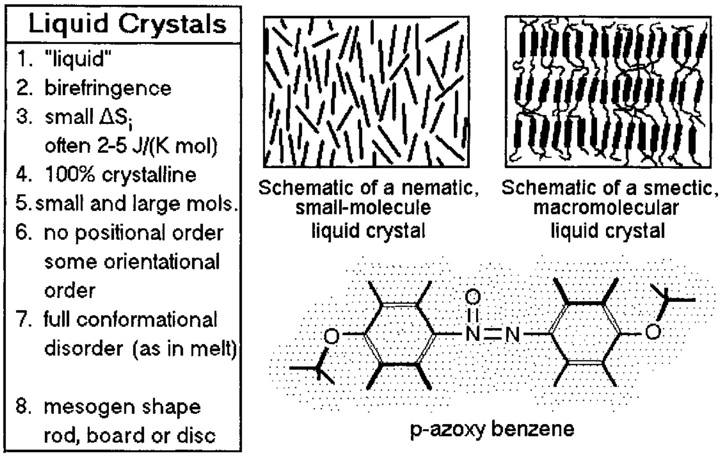


Fig. 5. Schematic of the classical phases (shaded boxes) and the mesophases. Transitions are indicated by the connections between the boxes. Orientational and positional entropy contributions refer to the whole molecule and are negligible for macromolecules. Conformational contributions depend on the number of rotatable parts of the molecule *n* ("beads").



**Liquid Crystals**
1. "liquid"
2. birefringence
3. small $\Delta S_i$ often 2-5 J/(K mol)
4. 100% crystalline
5. small and large mols.
6. no positional order some orientational order
7. full conformational disorder (as in melt)
8. mesogen shape rod, board or disc

Fig. 6. Properties and structure of liquid crystals.

The term mesophase was first coined in 1922 by Friedel [10] to describe mainly liquid crystals which are known since 1888 [11,12]. They are related to liquids, but maintain a certain, small degree of orientational order, as shown schematically in Fig. 6, together with a list of characteristic properties of liquid crystals [13]. In the examples shown in the figure, the liquid crystalline order is due to an elongated, rod-like or flat, board- or disk-like segment of the molecules, the mesogen. The left example is a two-dimensional representation of a nematic liquid crystal of a small molecule (Gk. νημα, thread, from the thread-like interference patterns of nematic liquid crystals under the polarizing microscope). The nematic phase shows orientation of the mesogens in only one direction. The right example is a smectic liquid crystal (Gk. σμεγμα, soap). In this case the limited orientational order is in two dimensions. The example is of a macromolecule that has a mesogen included in the otherwise flexible chain. For example $CH_2$-sequences can link the mesogens and provide the mobility needed to give a liquid–crystalline character. A typical example of a mesogen is shown at the bottom of Fig. 6. The orientation in the liquid crystals gives rise to the birefringence and their high mobility allows the use of liquid crystals in display devices. On crystallization, the molecules of the liquid crystals have to pack closely, which is not always possible for more complicated structures, so that glasses and condis crystals are common low-temperature phases for such molecules.

Plastic crystals are more closely related to the classical crystals. They have full positional order. The plastic crystals consist, however, of molecules that are almost spherical and can start to rotate within the crystal at a given transition temperature. Fig. 7 contains a list of typical properties of plastic crystals and allows a comparison to liquid crystals [14]. The plastic crystalline state was first recognized in the 1930s. Most plastic crystals have a cubic crystal structure. Due to the rotation of the molecules in the crystal, their actual symmetry is averaged to a sphere. This averaged spherical shape eliminates the birefringence by packing in cubic crystals and causes an entropy of fusion similar to that of metals and noble gases which have spherical motifs. Cubic crystals have also many slip planes, and with rotating, weakly bound molecules, the crystals deform easily, they are plastic. Metals with similar crystal structures and spherical motifs, but stronger bonding, still show ductility, but no plastic–crystal-like behavior. Both liquid and plastic crystals show conformational mobility and disorder if the basic molecule is flexible.

Conformationally disordered crystals were suggested to exist in 1975 [15], and were documented with many examples in 1985 [16]. They show positional and orientational order of the molecule as a whole but are partially or fully conformationally disordered and mobile. Fig. 8 lists a comparison between the three types of mesophases. Especially linear, flexible macromolecules can show chain mobility that leaves the position and orientation of the

| Liquid Crystals | Plastic Crystals |
|---|---|
| 1. "liquid" | 1. "plastic" |
| 2. birefringence | 2. no birefringence |
| 3. small $\Delta S_i$ often 2-5 J/(K mol) | 3. fixed $\Delta S_i$ 7-14 J/(K mol) |
| 4. 100% crystalline | 4. 100% crystalline |
| 5. small and large mols. | 5. small molecules only |
| 6. no positional order some orientational order | 6. positional order no orientational order |
| 7. full conformational disorder (as in melt) | 7. full conformational disorder (similar to melt) |
| 8. mesogen shape rod, board or disc | 8. mesogen shape close to spherical |

Some typical plastic crystals:

$CO$ $HBr$ $HI$
$N_2$ $P_4$ $SiH_4$
$H_2$ $HCl$ $CH_4$
$O_2$ $PH_3$ $CH_3OH$

Neopentane $C(CH_3)_4$
Pseudocumene
cis-1,2-Dimethyl-cyclohexane
Cyclohexane
Camphor $C_{10}H_{16}O$

Fig. 7. Comparison of liquid and plastic crystals.

| Liquid Crystals | Plastic Crystals | Condis Crystals |
|---|---|---|
| 1. "liquid" | 1. "plastic" | 1. "solid" |
| 2. birefringence | 2. no birefringence | 2. birefringence |
| 3. small $\Delta S_i$ often 2-5 J/(K mol) | 3. fixed $\Delta S_i$ 7-14 J/(K mol) | 3. large $\Delta S_i$ n x [7-12 J/(K mol)] |
| 4. 100% crystalline | 4. 100% crystalline | 4. limited crystallinity for macromolecules |
| 5. small and large mols. | 5. small molecules only | 5. small and large mols. |
| 6. no positional order, some orientational order | 6. positional order, no orientational order | 6. positional order and orientational order |
| 7. full conformational disorder (as in melt) | 7. full conformational disorder (similar to melt) | 7. partial or full conformational disorder |
| 8. mesogen shape rod, board or disc | 8. mesogen shape close to spherical | 8. rotational isomers that keep the chains largely parallel |

Fig. 8. Summary of mesophase properties.

molecule unchanged but introduces large-amplitude conformational motion about the chain axis [17]. Again, the symmetry of the molecule is in this case increased. Condis crystals are often hexagonal. Typical examples of condis crystals are the high-temperature crystal phases of polyethylene, polytetrafluoroethylene, *trans*-1,4-polybutadiene, and often the low-temperature phases of soaps, lipids and other liquid crystal forming molecules with long, flexible ends.

Fig. 9 illustrates the chemical structure and a thermal analysis curve of a typical small molecule which can exist in several liquid crystalline and condis–crystalline phases [18]. The mesogen is the rigid bis-oxybenzalphenylenediamine group. Two flexible octyl groups enable conformational disorder by rotation about the C–C and O–C bonds. The letter N represents the nematic phase, letters C, I, G', and H' the increasingly better ordered smectic phases, and K designates condis phases.

Fullerene, $C_{60}$, is an example of a molecule with a plastic–crystal phase. Fig. 10 is a thermal analysis trace [19]. The transition starts rather broad and becomes sharp as full rotation becomes possible. More details about this transition are available through $^{13}C$ nuclear magnetic resonance experiments [20]. The first large-amplitude motion is a jump-rotation about the five-fold symmetry axis of the molecule which is possible below 190 K. Because of the strict symmetry and indistinguishable atoms, there is no change in entropy (or heat capacity) for this motion. The next mechanism is an additional jump-rotation about the

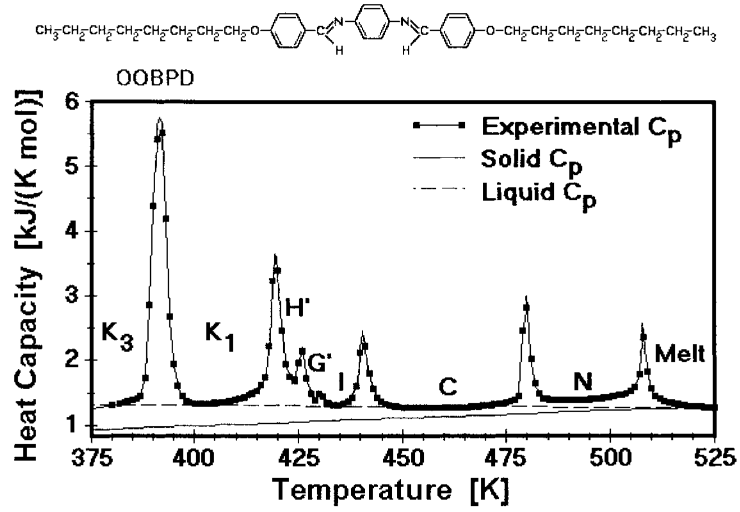


Fig. 9. Thermal analysis (DSC) of an example of a liquid crystal: N,N'-bis(4-n-octylbenzal)-1,4-phenylenediamine (OOBPD).

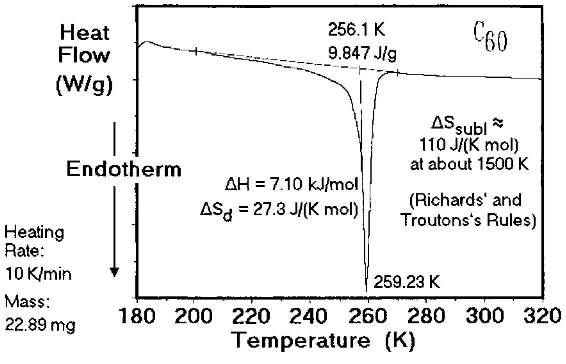


Fig. 10. Thermal analysis of a plastic crystal (fullerene, $C_{60}$).

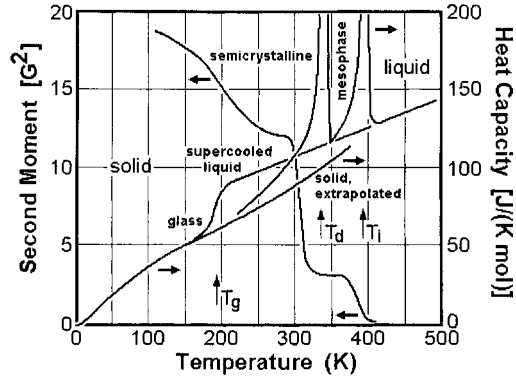


Fig. 11. Thermal analysis and solid-state NMR of the condis–crystal-forming *trans-poly*-1,4-(butadiene-1).

six-fold axis. It is energetically only slightly more difficult. It starts at about 190 K, coinciding with the beginning of the transition peak. The symmetry for this rotation or jump is incomplete and produces the observed disorder, i.e., the entropy increases. The third stage leads then to full rotation at 256 K (orientational disorder).

An example of a condis crystal is shown in Fig. 11 ([21], see also [17]). The polymer is *trans*-1,4-polybutadiene. Polymers of this type have at least two endothermic transitions in going from the crystal to the melt. First they disorder at the disordering temperature, $T_d$, to the condis phase, then they melt completely at the isotropization temperature $T_i$. In Fig. 11 motion is characterized with $^1H$ solid state NMR, using the line width of the signal as a measure of mobility. The line width can be modeled quantitatively in terms of its second moment ($G^2$). The first narrowing indicates the glass transition of the uncrystallized fraction of the semicrystalline polymer, the second, the conformational mobility gained at $T_d$, and the third, the final isotropization at $T_i$. More will be said below about the transitions.

## 4. Phase and molecular sizes

It was noted over 100 years ago, after the discovery of colloids [22], that the properties of phases change

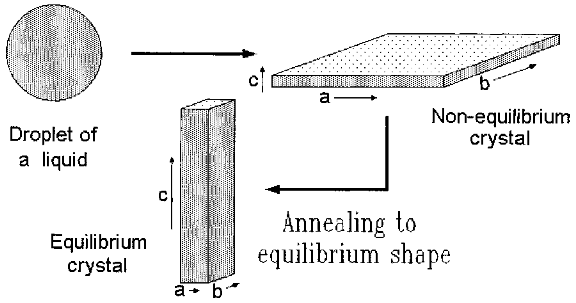


Fig. 12. Schematic of the crystallization of a small droplet of liquid to a metastable microphase, followed by annealing to an equilibrium microphase.

when their dimensions decrease to the micrometer scale. The small phases encountered in colloids are today identified as microphases. In microphases the effect of the surfaces can not be neglected. Surface free energies and charges (surface potentials) govern the properties and stability (or metastability) of the microphases.

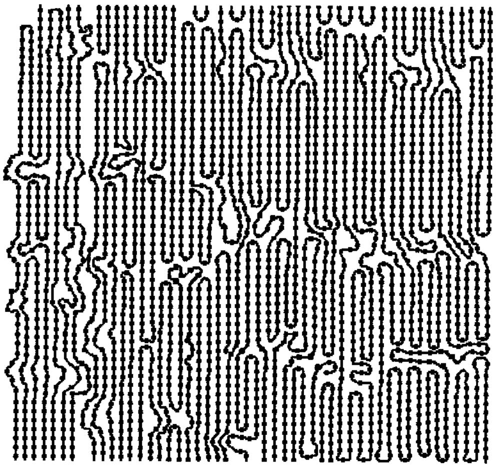
When forming a crystal via nucleation and growth, the linear growth rates in the various crystallographic directions determine the initial, usually metastable, crystal shape, as shown schematically in Fig. 12. Linear, flexible macromolecules chain-fold to lamellar crystals for entropic reasons with much faster growth in the crystallographic *a* and *b* directions than in direction *c*, the chain direction. The folds accumulate in the *ab*-surface. By limiting the available material to a few macromolecules, the initial liquid takes the shape of a small droplet with a micrometer diameter, and the crystal is also a microphase [9]. On annealing, the initial, kinetically-determined morphology (shape) may approach equilibrium. The major rearrangement of the molecules within the crystal requires sufficient mobility, as has been observed, for example, in the condis mesophase of polyethylene. The equilibrium crystal must have a minimum in the (positive) surface free energy. Based on this principle, Wulff devised in 1901 [23] a construction to establish the equilibrium shape. The equilibrium polymer crystal should thus have, as shown in Fig. 12, its large dimension at right angles to the high-energy fold-surface *ab*.

New properties arise when the molecular sizes increase to the dimensions of the phase, as for example in the case of a typical polyethylene of 500 000 Da. It has a contour length of 28 μm and can easily cross microphase boundaries. This traversing of the surface makes neighboring phases interact strongly, in contrast to the weak interactions by intermolecular forces. Another change in the interaction between neighboring phases arises when the microphases decrease in diameter below 10 nm. In this case the surfaces on opposite sides of a phase–domain interact and result in new properties. It has become fashionable to call such small phases nanophases. Fig. 13 is a representation of a model for a melt crystallized polymer, developed by Hosemann [24]. It shows the nanophase structure of a typical flexible macromolecule.

The non-crystalline material surrounding the macromolecular crystals, containing folds, chain ends, non-crystallizable repeating units and tie molecules, has similarly small phase dimensions. The macromolecule traversing a nanophase will strongly link the two surfaces; but even weaker forces, such as are caused by the change in polarity at the interface, or by charges residing in the surface, may bridge nanophase dimension and may give rise to special properties of the nanophases. For characterization, nanophases need a more detailed study of composition, physical state, molecular structure, and molecular motion. The macromolecules can now traverse not only one, but several or many phase domains and will strongly influence the macroscopic properties of the nanophase-separated substance.

Soaps and lipids, mentioned above as examples of smectic liquid crystals, consist of two parts that, if not connected by strong bonds, would phase-separate. In the pure state these molecules arrange themselves such that the junction between their two incompatible segments forms an interface (|) between two phase areas, as for example in sodium stearate, a soap: $Na^+$ $^-OOC$ (|) $(CH_2)_{16}$–$CH_3$, and in lipids as seen in Fig. 14. The domain size of these phases is about one nanometer in the direction of the molecule, i.e., they are nanophases. For the soaps and lipids, the nanophase-separation remains within the overall crystals. Sometimes the two nanophases may even undergo separate phase transitions.

The limit of nanophase structures towards smaller sizes occurs at perhaps one nanometer. Two causes exist for this limit: The increasing loss in homogeneity due to the inherent molecular structure makes the recognition of a homogeneous phase impossible,



The sketch includes: amorphous areas (defects), drawn fibrils, bulk crystals, chain ends, rotated crystals, loose folds, sharp folds, para-crystalline areas, extended chains, voids, sheared regions, kinks, single fibrils, migrating folds, and single-crystal regions.

Scale: 2.0 nm

Fig. 13. Hosemann's model of a melt–crystallized polymer [24].

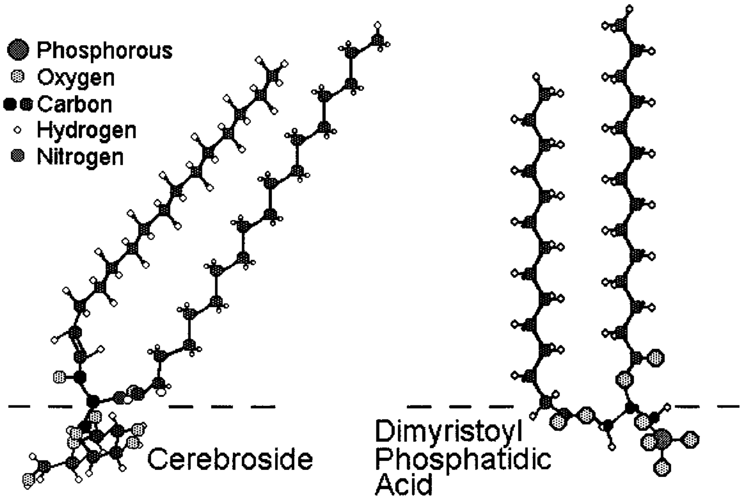


Fig. 14. Examples of two lipids. The dashed lines indicate the nanophase boundary in the crystal.

and the decreasing gain in enthalpy on mixing (due to the larger surface contribution) relative to the entropy loss on phase separation makes the nanophase unstable.

This short summary of phase sizes suggests that, for each type of phase, three size-ranges must be considered: macrophases, microphases, and nanophases. In addition, the phase structure may be different for each of the three types of molecules. This leads to a total of nine possible situations for each of the nine condensed phases shown in Fig. 5. Of these 81 combinations, 57 have been suggested to be possible [25].

## 5. Phase transitions

On the right-hand side of Fig. 5 the possible first-order transitions are marked by the connections between the boxes representing the states. A first-order transition is coupled with a latent heat of transition, and as a result has an entropy of transition. This thermodynamic classification of transitions was first established by Ehrenfest [26]. Some details for the interpretation of first-order transitions can be derived from calorimetry. Empirical observations relate materials with the same type of transition to similar changes in disorder — in other words, the entropies of transition are similar for structurally related materials.

Richards's rule [27], for example, which applies to solids that melt by producing spherical, mobile motifs, such as noble gases and metals, says that the entropy of melting, $\Delta S$ (fusion), is somewhere between 7 and 14 J $K^{-1}$ $mol^{-1}$ [28]. A similar empirical rule exists for the boiling point, known as Trouton's rule [29]. Normal boiling materials have an entropy of boiling, $\Delta S_b$, of approximately 90 J $K^{-1}$ $mol^{-1}$, or more precisely, 113 J $K^{-1}$ $mol^{-1}$ when evaporated to a common state of a fixed vapor concentration of 0.005 mol $l^{-1}$, $\Delta S$(evaporation) [30].

More detailed empirical rules for the entropy of melting can be derived when recognizing the three types of disorder that make up the changes on fusion: positional (p), orientational (o), and conformational disorder (c). The approximate contributions to $\Delta S$ are listed on the right-hand side of Fig. 5. The last term in the equation for $\Delta S$(fusion) represents Richards' rule. It is the only contribution for spherical motifs. Irregular motifs can, in addition, show orientational disorder, and thus gain an extra 20–50 J $K^{-1}$ $mol^{-1}$ on fusion (Walden's rule [31], the middle term in the equation). Flexible molecules have a third contribution to the entropy of fusion of 7–12 J $K^{-1}$ $mol^{-1}$ for each flexible bead, *n*, within the molecule [28] (see also [16] and [17]). Fig. 8 compares the corresponding $\Delta S$ for the mesophases, and Figs. 9–11 illustrate the thermal analyses of first-order transitions of mesophases.

The boiling transition is simpler to describe because the vapor is close to an ideal gas without interaction between the molecules. No additional disorder due to the excitation of different motion is added since the liquid state is already fully mobile. The increase of entropy is caused by the increase in volume and explains Trouton's rule when considering that the volume of the liquid phase is negligible when compared to the gas. The heat of evaporation is also called the cohesive energy density, a quantity that can also be related to other properties of liquids as well as solids.

All mesophases, when kept for structural or kinetic reasons from crystallization on cooling, display, in addition to the first-order transitions, a glass transition, as is indicated on the left-hand side of Fig. 5. The glass transition leads to a glass with mesophase order but without the large-amplitude motion. The recognition of mesophases and mesophase glasses as states of intermediate order and their study by thermal analysis has become of great importance for the understanding of the multitude of materials. Liquid-crystal glasses were already observed in the 1930s [32]. Liquid crystals are quite similar to the liquids in their mobility, their glass transition is similar to the glass transition of an amorphous liquid, i.e., they show an increase in heat capacity of about 11 J $K^{-1}$ $mol^{-1}$, an empirical rule that is often obeyed [33]. The number of "beads" that can be evaluated from the glass transition of the fully amorphous material agrees with the beads evaluated from the evaluation of *n* for complete conformational disordering. Fig. 15 shows a special example for a thermal analysis of the glass transition of a macromolecule that can form a liquid crystal. The monomer of the chosen polymer, acryloyloxybenzoic acid, does not have a liquid crystalline phase. On polymerization, an amorphous liquid results that changes to a liquid crystal on dimerization of the oxybenzoic acid side-group via hydrogen bonds. The thermal analysis of Fig. 15 shows in its upper trace a sample quenched to the amorphous glass before ordering [34]. A normal glass transition occurs on heating, followed by ordering to the liquid crystal. On subsequent cooling an LC glass is formed which, on reheating (bottom trace) shows a glass transition of similar magnitude, but of higher temperature because of the

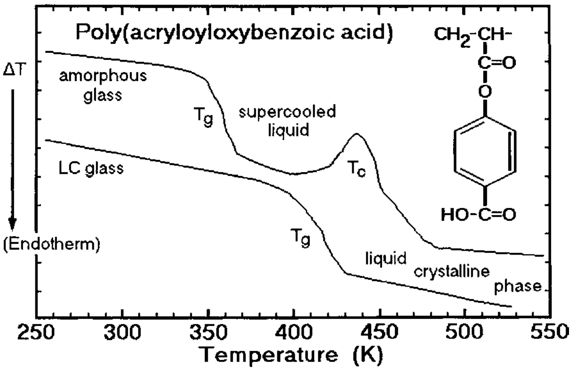


Fig. 15. Phase transitions in poly(p-acryloyloxybenzoic acid) [34].

dimerization. Glass transitions have also been observed for plastic crystals and condis crystals. Depending on the degree of cooperation necessary between neighboring molecules, narrow or broad glass transition regions result on heating and cooling.

Based on the present discussion, knowledge about the macroscopic thermodynamics and the microscopic molecular motion can be used as a base for an operational definition of the solid state. A solid is a phase below its glass- or melting-transition temperature where the molecular motion is almost completely restricted to small-amplitude vibrations. Both transitions are easily determined by thermal analysis (the operation). Note that such definition is more precise than any based on mechanical criteria. There exist crystals that are softer than high-molar-mass liquid polymers. Fig. 16 summarizes once more the discussion of phases and their transitions and the link to molecular mobility, packing density, and physical behavior.

## 6. Non-equilibrium transitions

Assuming that a one-component polymeric system is limited to one crystal polymorph and one mesophase, in addition to the liquid and glassy phases, the 15 phase structures of Fig. 17 become possible [35].

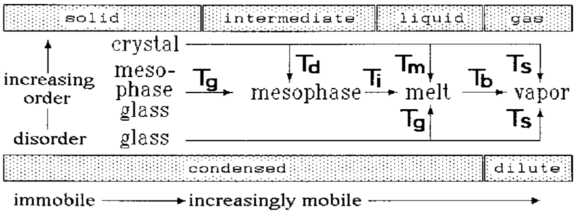


Fig. 16. Schematics of the transitions in a one-component system.

Only the structures on the left-hand-side are in equilibrium. All others are metastable. The corresponding free enthalpy diagram for the first-order transitions is shown in Fig. 18. The importance of these diagrams lies in the illustration of the large variety of phase structures that may be possible when equilibrium is not attained. Increasing the number of possible components, polymorphs of crystals and mesophases increase the number of combinations so much that analysis becomes rather complicated. The discussion in this paper provides, however, a map of how to place the observed sample behavior and, in particular, how to interpret thermal analysis results.

Examples of polymer systems for the scheme of Fig. 17 have been found for all the 15 combinations of phases. In principle, every macromolecule may be brought into all phase areas when given the proper

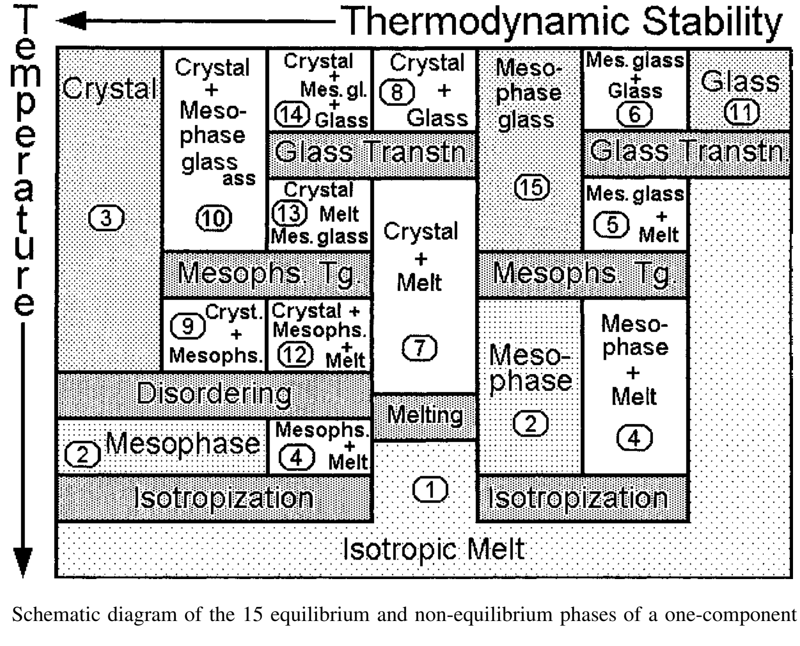


Fig. 17. Schematic diagram of the 15 equilibrium and non-equilibrium phases of a one-component system.

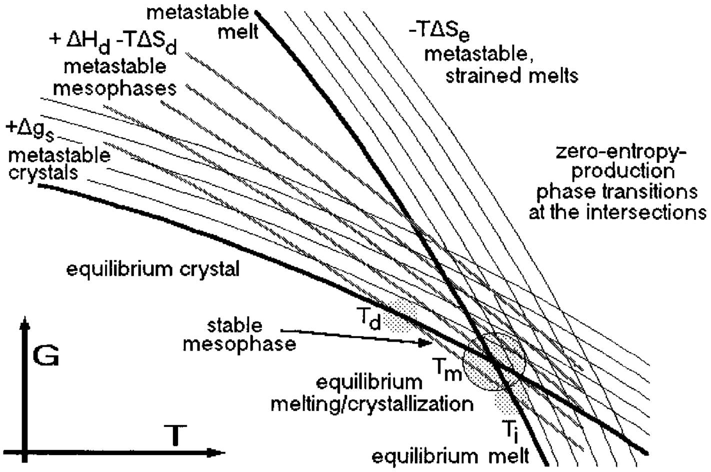


Fig. 18. Free enthalpy diagram of a crystal/mesophase/liquid system. The dotted circles indicate the equilibrium transitions. At any temperature the lowest-free-enthalpy state represents equilibrium. All higher states may become metastable if the path to equilibrium is arrested.

conditions of ordering and freezing of the large-amplitude motion. For polyethylene, the most studied polymer, most of these phase areas have, indeed, been realized. The equilibrium sequence on cooling of melt (phase area #1), to mesophase (#2), and to crystal (#3) is seen in the crystallization of linear polyethylene under high hydrostatic pressure [36]. The hexagonal condis crystal phase is sufficiently mobile to permit chain extension after initial folding, as required by the chain-folding principle [37,38]. Other examples of crystallization to equilibrium via a condis phase are found for polytetrafluoroethylene, *trans*-1,4-polybutadiene, and polydiethylsiloxane [17].

The metastable phase area #4 may result on partial crystallization of polyethylene at elevated pressure above the triple point. On sufficiently quick cooling, areas #5and #6 may be produced. It must be observed, however, that the glass-transition temperatures of mesophase and melt are not necessarily fixed in sequence as given in Fig. 17. If the mesophase permits easier large-amplitude motion (as observed in some liquid crystals), the mesophase $T_g$ may be lower in temperature than the glass transition of the melt. An existence of a metastable mesophase together with melt or glass is also observed, for example, in quenched polypropylene (areas #5and #6) [16]. The mesophase of polypropylene has been known for many years but has not been observed in a stable form. The conformational disorder consists mainly of helix reversals. When the condis glass reaches its glass-transition temperature at about 350 K, the metastable condis crystal orders to the monoclinic crystal with an exotherm of about 600 J $mol^{-1}$. It was shown recently that the semicrystalline condis phase of polyethylene (area #4) is also produced as a metastable intermediate below the triple point [39,40]. On lamellar thickening the condis crystals convert to the more stable, orthorhombic crystal phase, switching, thus, to phase areas #7 and #8. The phase area #4 is less likely for liquid crystals than for condis crystals since the small increase in order that is needed to change a mobile melt into a mobile liquid crystal occurs quickly and is usually complete.

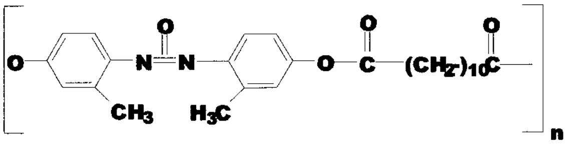
On crystallization of polyethylene at atmospheric pressure, the typical semicrystalline structures result, consisting of nanophase-separated crystalline/amorphous phase structures, as described above (phase areas #7 and #8, Fig. 13). The glass transition of the amorphous phase can be used to estimate the strain introduced in the metastable, amorphous nanophases. The local strains manifest themselves in an increase in the glass-transition temperature and the possible presence of a "rigid amorphous fraction" that does not show a contribution to the increase in heat capacity at the glass transition [41]. Most bulk–crystallized macromolecule without intervening mesophases are similarly described by phase areas #7 and #8 [28].

A hexagonal condis phase of polyethylene was also found at atmospheric pressure when heating fibrillar crystals under constraint so that the crystals superheat [42]. More recently, the discrepancy between the high crystallinity suggested by X-ray diffraction, and the lower crystallinity observed by calorimetry of gel–spun, ultra-high-molar-mass polyethylene could be resolved by proving that the metastable phase structure of the fibers is represented by areas #9 and #10 [43].

Fully amorphous polyethylene is rather difficult to make because of its fast crystallization. By super-fast quenching it was, however, possible to make small amounts of polyethylene glass (phase area #11) [44]. Glassy polymers are much more easily available for macromolecules that crystallize more slowly, such as poly(ethylene terephthalate) (PET) and poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarboxy-1,4-phenylene) (PEEK), or macromolecules that have structural irregularities that prohibit crystallization completely, such as atactic polystyrene and poly(methyl methacrylate). With polyethylene alone one has, thus, produced 11 of the 15 different phase structures, most of them metastable, and several of them mesophases. The remaining four phase areas #12–15 may well also be possible for polyethylene by proper quenching of phase areas #2 and #4.

The three-phase structures #12, #13, and #14 are of particular interest because of the severe violation of the phase rule. Only one phase should be stable at varying temperature and pressure. A typical example of a polymer that shows such metastable phases is drawn PET [45]. As in polyethylene, the drawing to fibers or films orients the amorphous nanophase and achieves mesophase order. Since the drawing of PET is much less efficient than for gel–spun polyethylene, there remains a sizeable portion of the amorphous phase. On quick cooling of PET from the melt (area #1) the glass results (area #11). On heating the glass beyond the glass transition, or on slower cooling, semicrystalline PET can be produced (area #7). On renewed cooling, area #8 is reached. Calorimetry showed that semicrystalline PET has a much smaller increase of heat capacity at the glass transition than expected from the amorphous PET, i.e. it contains a sizeable rigid–amorphous fraction. In PET one can, thus, find seven of the 15 phase areas in Fig. 17. The mesophase of PET has not been observed as a stable phase, as in polyethylene, but only as an intermediate on cold crystallization in drawn samples [46].

The final phase area #15 is quite common for macromolecular mesophases that do not crystallize well. It is for example easily possible to quench poly(oxy-2,2’-dimethylazoxy-benzene-4,4’-dioxydodecanedioyl) (PDAD):



from the liquid state (#1) to the LC glass (#15) [47,48]. On heating, however, the mesophase (liquid crystalline, area #2) crystallizes partially, i.e. it shifts to area #9. Further heating produces the stable liquid crystalline state (#2) and on isotropization, the melt (#1). This example shows the rather complicated paths that are possible on heating the low-temperature structures.

The poly(p-acryloyloxybenzoic acid) shown in Fig. 15 quenched after polymerization represents area #11 in Fig. 17. On heating above the glass transition, it orders to a liquid crystal (area #2) and behaves now as a standard liquid–crystalline polymer with a higher glass-transition temperature (area #15). In addition, PABA can form other types of structures involving semicrystalline or smectic phases. Eleven different phase areas have been identified [34].

## 7. Conclusions

This brief excursion into the classification of molecules, phases, and transitions as recognized by thermal analysis has shown that one can develop a description that unifies all the divisions of chemistry. One can start with the four types of bonding that connect the about 100 different atoms that are of importance to chemistry. The resulting compounds yield only three types of molecules and 10 types of phases. The properties of the phases change, however, when their sizes reach micro- or nanometer-dimensions. Allowing non-equilibrium states, extends this already large number of combinations to an enormous multiplicity, which is, however, easily correlated with the simple sequence of diagrams of Figs. 2,3,5, and 17.

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