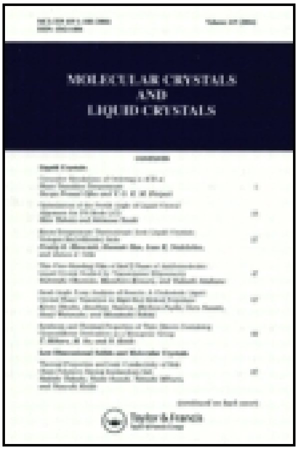

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Principle of Maximum Flow Energy, a Useful Working Hypothesis to Approach Ordering Phenomena in Fluids

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Principle of Maximum Flow Energy, a Useful Working Hypothesis to Approach Ordering Phenomena in Fluids

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The hypothesis that the variation of energy with time and volume for real and/or imaginary exchange processes leads to a maximum is applied to various phenomena found with fluids, especially with liquid crystals. Reference is made to some qualitative regularities in the correlation of chemical structure and the thermodynamic stability of the thermotropic nematic phase, the enthalpy of the phase transition between fluid phases, the heuristically important finding of an exothermic transition from the nematic to the isotropic phase, a very distinct deuterium isotopic effect on the optical nonlinearity of a dye-doped nematic phase, and the additional hydrodynamic lifting force observed in technical slide bearings lubricated with isotropic oils containing mesogenic compounds. The relation of the suggested variation to the universally valid principle of least action and its applicability to irreversible processes are discussed.

Keywords: irreversible processes; Jánossy effect; liquid crystals; lubrication; phase transition; variation principles

INTRODUCTION

Decades-long pursuit and refinement of a working hypothesis, while neglecting a basic assumption behind established theories, is scarcely typical of modern science. To proceed in this manner would be justified only if practically exploitable results are found that otherwise could not be obtained easily, if at all. Some 30 years ago, an approximate extension of Poynting's theorem to the exchange of any kind of energy was used to overcome the then-prevalent concept that the transition temperature from nematic liquid crystal to isotropic phase transition, T_{NI}, was proportional to the polarization anisotropy [1]. The underlying idea of the new approach was to transform the universally valid

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variation principle of least action in such a way that all real and/or imaginary processes within a system lead to a maximum of exchanged energy (flow energy) for any interval of time. This can be expressed classically by

$$\int_V \int_t \Pi \, dVdt = \max \tag{1}$$

where V stands for the volume in which a process takes place and Π for any energy changing quantum description or/and location within V per unit time. In the following, some experimental results are treated under this concept showing that Eq. (1) is of general validity.

CHEMICAL STRUCTURE AND T_{NI}

The correlation of chemical structure with T_{NI} is still a challenge at present. The basis is the molecular statistical theory of Maier and Saupe [2], which is regarded as valid only if all the intermolecular interactions (repulsive, dispersive, inductive, and electrostatic) are considered. However, demanding computer work is needed to make allowance for these interactions plus the conformational dynamics. All of them can be regarded as being determined by the variation principle of least action, which also governs reversible thermodynamic processes. From the beginning of industrial exploitation of nematic liquid-crystalline materials for display techniques, it has become increasingly necessary for synthetic chemists to have rules enabling the selection of those classes of compounds with high T_{NI} out of the manifold of structural possibilities. The rule of the greatest continuity of bond order [1] was behind the synthesis of a number of technically important nematogenic compounds. Although this more practical tool can only support Eq. (1) imperfectly, the following qualitative comparison may help to make this concept familiar.

In Fig. 1, four compounds of almost identical molecular length are shown whereby one or two 1,4-phenylen groups of the cyano biphenyl 1 [3] are replaced by a trans-1,4-cyclohexylen group. In the conformational equilibrium of the compounds containing the hydrogenated rings, the equatorial–equatorial forms can be regarded as sufficiently predominant because of their substitution by an aromatic ring or a secondary alkyl group [4]. It came as a surprise to the liquid crystal community that the T_{NI} raised from 1 to 2 to 3 with polarization anisotropy (PA) decreasing in this sequence [5]. The fact that 4 has a PA somewhere between 1 and 3 did not find a conclusive explanation

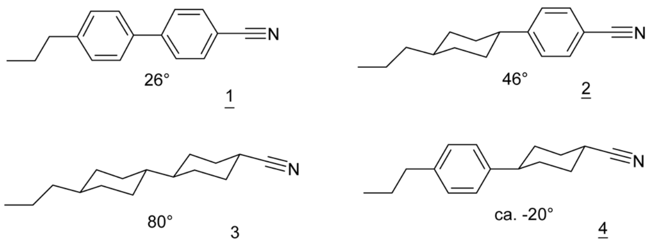


FIGURE 1 Transition temperatures (°C) from the nematic to the isotropic phase of some historically interesting carbonitriles.

either. Similar anomalies have been found, *e.g.*, with combinations of 1,4-phenylen and 1,4-bicyclo[2.2.2]octylen groups [6].

The finding that compounds 2 and 3 have higher T_{NI} than 1 can be explained within the frame of the hypothesis by a higher contribution of vibrational energy from the cyclohexylen group compared to that from the aromatic ring. Thus the energy being exchanged steadily in unit volume can be expected to increase in the sequence $1 < 2 < 3$. The exchange of energy by inelastic collisions between long-shaped molecules can be regarded as especially fast if the energy can travel within the molecules easily and if the molecules are *aligned parallel*. At first glance the very low T_{NI} of 4 does not fit into this scheme. However, this can be explained by the assumption that the flow energy depends also on the ease by which excited vibrational modes can be redistributed along the whole length of the molecule. In the case of 1, 2, and 3, we see a better "continuity of bond order" than in case 4. This view can be supported by the investigation of intramolecular vibrational and rotational redistribution by subpicosecond laser spectroscopy. It was found that the energy of a CH stretching excitation is redistributed far more slowly over a polyatomic molecule if its σ-bonds are interrupted by a π-system [7].

THE ENTHALPY OF THE NEMATIC–ISOTROPIC TRANSITION

The working hypothesis presented here offers a simple formulation of the molar enthalpy ΔH_{NI} of the phase transition from the nematic to the isotropic state. It depends on the change of molar volume ΔV and the energy content expressed by $(H_T - H_0)$, which is accessible via the heat capacities measured between a temperature close to the absolute zero point and T [1]. For any transfer of energy E_i from one quantum assignment and/or location in a bulk of molecules a partial "exchange pressure," $p_{\mathrm{e,i}} = 2E_{\mathrm{i}}/V$ was postulated. The total pressure can be taken as

$$p_{\mathrm{e}} = \Sigma p_{\mathrm{e,i}} = \frac{2(H_{\mathrm{T}} - H_0)}{V} \tag{2}$$

whereby $(H_{\mathrm{T}} - H_0)$ is seen as energy per mole being exchanged steadily within the molecular volume V with quite different exchange rates for the individual kinds of energy. The factor of 2 expresses the fact that any intake of energy is accompanied by a release. This view is unconventional because transfers of energy also are included, which are defined as imaginary in physics and physical chemistry. This becomes evident in the case of an elastic collision between two individual molecules in the bulk whereby kinetic energy is transferred from one species to another. In a center of mass system normally used in physical chemistry, this can be neglected and only a linear momentum given to a wall is relevant for the real pressure.

A phase change from nematic to isotropic occurs upon raising the temperature so that there is more energy exchanged in the disordered but less dense state than in the ordered state; the molar volume is expanded reversibly against p_{e} by ΔV. Assuming that the exchange processes are not affected markedly during the minor dilatation, one can approximate the enthalpy by

$$\Delta H_{\mathrm{NI}} = 2(H_{\mathrm{T}} - H_0)\frac{\Delta V}{V} \tag{3}$$

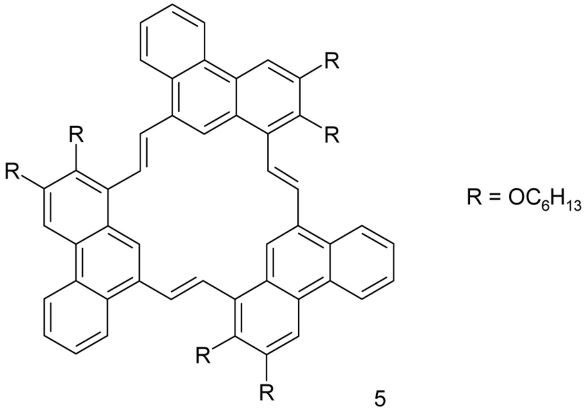
There are only a few measured data sets for ΔH_{NI}, $(H_{\mathrm{T}} - H_0)$, ΔV. For the four examples known, the agreement with Eq. (3) is surprisingly good [1,8].

It is interesting to note that this unconventional approach also holds for the transition between the liquid and the gaseous state [9]. Enthalpies of evaporation ΔH_{vap} can be obtained via a reversible expansion from the liquid to the gaseous volume against p_{e} at boiling temperature, whereby only the exchange of energy by collisions is taken into account, neglecting specific differences of intermolecular interactions between both phases. The resulting formula for ΔH_{vap} is identical with that of MacDougall derived from van der Waal's equation giving values that have better agreement with practice than Trouton's rule [10].

The application of Eq. (1) to transitions between a crystal phase or other highly ordered phases and the isotropic state needs a correct description of the individual exchange processes between all kinds of energy within the two states. Moreover, it is not at all clear in which part of a crystal volume an exchange takes place. This becomes obvious with solids that melt with an increase of density. Nevertheless, it is believed that Eq. (1) controls these transitions also.

THE EXOTHERMIC NEMATIC–ISOTROPIC TRANSITION

In 1994, H. Kretzschmann *et al.* [11] found that the [18] annulen 5, which exists in a conformational equilibrium, has a discoid–nematic phase between 115 and 187°C. The surprise was that the transition between the liquid crystal and the isotropic phase was exothermic.



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This unprecedented and not readily explainable finding can be regarded as being clarified by Eq. (1) if the phase transition is accompanied by an increase of flow energy. Other than in the previous case, where a reversible expansion against p_e leads to uptake of heat from the surrounding, we now can think of heat given to the surrounding by a reversible compression against p_e. This may stem from a higher speed of the conformal inversion [11] in the disordered phase, yielding a higher flow energy than in the case of the ordered phase. The negative sign for ΔV to be inserted in Eq. (3) has not yet been confirmed experimentally.

DEUTERIUM ISOTOPIC EFFECT ON THE OPTICAL NONLINEARITY OF DYE-DOPED NEMATICS

The Jánossy effect permits the threshold intensity of laser light for the optical Fredericks transition to be reduced considerably by the addition of small amounts of certain dyes to the nematic host [12]. Thus an optical nonlinear enhancement by two orders of magnitude was observed in a nematic solution of an anthraquinone dye in a 4-alkyl-4′-cyano-biphenyl when exposed to polarized light of a He-Ne

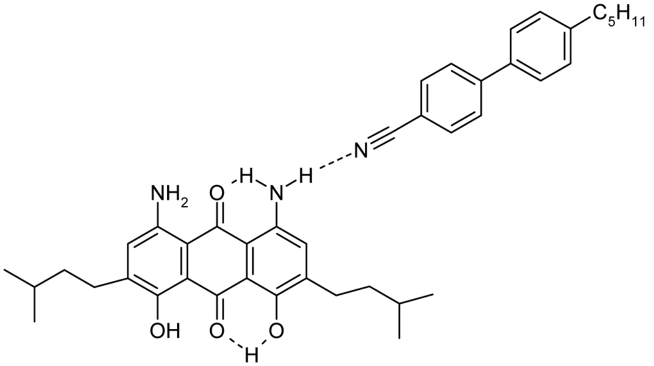


FIGURE 2 Hydrogen bond association of a cyano-biphenyl molecule with the 1-amino-anthraquinone 6.

laser. The most agreed-upon explanation for this effect is the stabilization of the excited state of the dye by the liquid-crystalline matrix [13].

Figure 2 shows how the well-known blue 1,8-diamino-4,5-dihydroxy-3,6-diisopentyl-anthraquinone (6) can be moored to a molecule of the nematic host via a hydrogen bond [14].

Within the hypothesis presented here, the flow energy within the system is greater the faster the absorbed energy can be passed on to the matrix of the nematic phase, where it can be distributed rapidly within the thermal pool. This is the case when the director of the nematic phase **n** can be arranged close to parallel to the transition moment of the dye. This can be effected by a hydrogen bond that also speeds up the transfer of the absorbed laser energy into the nematic matrix. Apparently, such advantageous transfers can also be brought about by other strong interactions between dye molecules and the nematic host [15].

To support this interpretation of the Jánossy effect, it was proposed to substitute all hydrogen atoms of 6 fixed to nitrogen and/or oxygen by deuterium atoms, thus forming a stronger association with the cyano-compound. This could easily be done by treating the nematic solution with deuterium oxide. A surprisingly large additional enhancement of the effect by a factor of 2.1 was found [16]. However, conventional explanations are possible [17].

HYDRODYNAMIC LIFT IN SLIDE BEARINGS BY CREATION OF INNER SURFACES

Based on Reynold's work, the effect of fluids on friction of technical slide bearings is well understood. Taking into account load, shearing

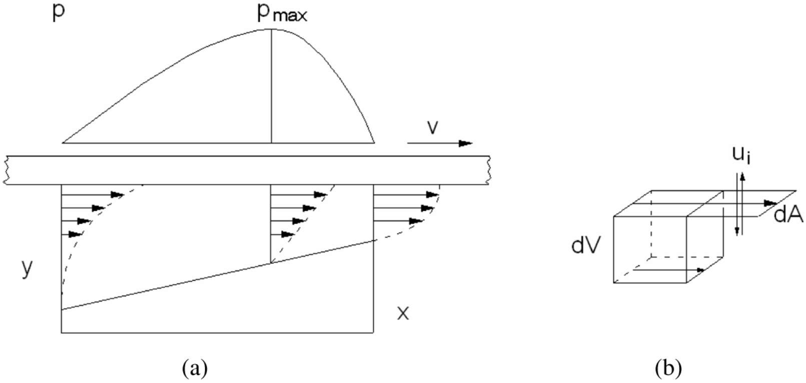


FIGURE 3 a) Generation of a pressure in a fluid under shear along distance x over slit y in the hydrodynamic regime of a slide bearing between a fixed plate and a plate of velocity v; b) creation of an inner surface dA normal to the velocity of energy exchange u_{i} on top of volume dV.

rate, dynamic viscosity and bearing clearance, practical understanding of the hydrodynamic regime as well as the transition to the regime of mixed friction was supplied a century ago by Sommerfeld [18].

Surprisingly, in industrial slide bearings lubricated with isotropic oils consisting of mesogenic compounds, an additional hydrodynamic lift could be generated [19]. Distinct characteristics of hydrodynamic friction were found, whereas for conventional oils of the same bulk viscosity, the system enters the regime of mixed friction with friction coefficients up to two orders of magnitude higher. Equation (1) can be proposed as the cause of the shear-induced isotropic–liquid-crystalline phase change. Conventional explanations for the additional lift in the high-loaded bearings are not available.

The following is an attempt to find an explanation within the frame of the present hypothesis. Figure 3a shows the textbook picture of velocity in a fluid layer between a fixed plate and one moving with velocity v. The narrowing of the friction slit y builds up a pressure p along the x-axis. From the average p, the hydrodynamic lift results as a force compensating the load. The creation of an infinitesimal inner surface dA known to depend on the shear rate dv/dy (Fig. 3b) is crucial for the view proposed here.

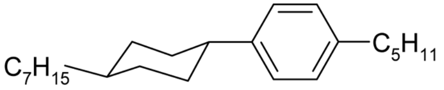
By means of Gauss' theorem, Eq. (1) is transformed to Eq. (4):

$$\int_A \int_t \frac{E_{\mathrm{i}}}{V} u_{\mathrm{i}}\, dA\, dt = \max \tag{4}$$

where E_i is the individual energy being steadily exchanged in volume V and u_i the velocity by which this exchange process proceeds within the bulk. As done with Eq. (3), one can interpret $2E_i/V$ as a pressure. Because dA is created on the top of every infinitesimal dV, this pressure must be directed from the fixed to the moved plate. This seems to be a very approximate interpretation of hydrodynamics with no chance of verification because all the E_i and u_i are not available. However, we can approximate the impact of an additional amount of steadily exchanged energy as in the case of an isotropic–liquid-crystalline transition that contributes $\Delta H_{\text{I-LC}}$. If u is the effective velocity (at first approximation not changed during the transition) over all individual u_i by which this additional energy is steadily exchanged within V, and if one realises that only 1/3 of this energy is exchanged through dA with u, the hydrodynamic lifting pressure can be expressed by

$$P_L = -\frac{2\Delta H_{\text{I-LC}}}{3V}. \qquad (5)$$

As a support for this, the measurements of friction coefficients in slide bearings lubricated with 4-(trans-4-heptyl-cyclohexyl)-4-pentyl-benzene (7) may be seen at elevated temperatures.



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This compound has a I-S_B transition at 18°C at normal pressure with an enthalpy of -4400 J/mol and a density of 0.89. P_L rated by (V) is at 8 MPa. This magnitude fits well into the results obtained [19].

PLAUSIBILITY OF THE CONCEPT

The ability to select the course of a physical process out of an infinite number of virtual possibilities makes variation principles of great value in subsuming physical processes. The invariant principle of least action, initially formulated for classical mechanics, has become the most inclusive principle of physics [20], which, for example, also contains the principle of conservation of energy. Its connection to the hypothesis presented can be understood if one varies a power instead of energy with time. The form of Hamilton

$$\int_t (K - P)dt = \min \qquad (6)$$

in which K means kinetic and P potential energy is transformed into

$$\int_t (\dot{K} - \dot{P})dt = \max. \tag{7}$$

To illustrate this concept, the elementary case of an undamped oscillation in a circuit consisting of capacitance C and a inductance L will be used. The solution of the Euler–Lagrange equation for Eq. (6) gives a sinusoid of charge Q and current I versus the product of angular velocity ω and time t. The electric and magnetic field energies being steadily in transition are

$$E_{el} = \frac{1}{2C} Q^2_{\max} \sin^2(\omega t) \tag{8a}$$

$$E_{mag} = \frac{L}{2} I^2_{\max} \sin^2\left(\omega t + \frac{\pi}{2}\right). \tag{8b}$$

The area between the two curves constitutes the action. To apply this formalism to Eq. (7) does not give a meaningful solution. This is because the power to be formulated for the exchange between both kinds of energy is imaginary (idle power). Equation (7) only makes sense if one is ready to separate the time the energy needs to change its description and the time appearing on the abscissae of the sinusoids. This can be regarded as the decisive step for a notionally equal treatment of imaginary and real exchanges of energy not usual in conventional theory. Differentiation of Eqs. (8a,b) gives

$$\dot{E}_{el} = \frac{\omega}{2C} Q^2_{\max} \sin(2\omega t) \tag{9a}$$

$$\dot{E}_{mag} = \frac{\omega}{2} L I^2_{\max} \sin(2\omega t + \pi). \tag{9b}$$

Under this aspect, the areas enclosed by both curves constitute an energy and are similar to those obtained previously. Comparing the signs of the slopes of both pairs of curves, it can be concluded that if integral (6) is a minimum integral, (7) must be a maximum. In the absence of a formal deduction that also would have to account for the total volume V that is involved, Eq. (1) must be regarded as empirical thus far. It can be supposed that Eq. (1) also presents the possibility of including reversible and irreversible processes, which is a long-cherished wish in thermodynamics [21]. This is validated by considering an irreversible adiabatic expansion of an ideal gas: for any infinitesimal time interval the gain of flow energy due to the transition of molecules into the additional volume is greater than the loss due to lower collision frequency. To be of general relevance in physical chemistry, all the exchange processes of energy need to be known in detail. This seems not yet to be possible.

CONCLUSION AND OUTLOOK

The principle of maximum flow energy can be supported by a successful rule for the sequence of molecular building elements advantageous for a high T_{NI}. A quantitative expression of the enthalpy of transition between the nematic and the isotropic phase can be given. The phenomenon of an exothermic nematic–isotropic transition can be explained. A huge deuterium isotopic effect on the optical nonlinearity measured with a dye-doped nematic phase could be predicted. The technically relevant hydrodynamic lift observed in slide bearings lubricated with mesogenic oils can be seen as a consequence of the principle. The principle is thought to be able to include reversible and irreversible processes if all the details of the change of energy within the volume of a system are known.

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