

Elastic moduli and instability in molecular crystals

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

1997 J. Phys.: Condens. Matter 9 5853

(<http://iopscience.iop.org/0953-8984/9/27/015>)

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

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 09:06

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

Elastic moduli and instability in molecular crystals

V P Shpakov[†], J S Tse[‡], V R Belosludov[†] and R V Belosludov[†]

[†] Institute of Inorganic Chemistry, 630090, Novosibirsk, Russia

[‡] Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

Received 3 October 1996

Abstract. The phenomenon of instability in pressurized molecular crystals is studied using the lattice-dynamics approach. General expressions for the elastic moduli are obtained taking into account both short-range and long-range (electrostatic) interactions within the framework of the quasi-harmonic approximation. The behaviour of a system under changing pressure and temperature conditions and the Born stability criteria are investigated. Two types of instabilities, dynamical and thermodynamical, associated with the elastic moduli are presented. The dynamical instability occurs when the instability of acoustic modes of the phonon Hamiltonian occurs in the $q = 0$ region. The nature of thermodynamical stability implies that the equilibrium state of the crystal becomes thermodynamically unstable with respect to a small homogeneous deformation of the crystal lattice when the Born stability criteria are violated for isothermal or adiabatic moduli. These types of instabilities are illustrated in a series of calculations for ice Ic using the SPC potential for water's interactions. The results show that one of the stability conditions for the isothermal (adiabatic) moduli ($C_{11} - |C_{12}| > 0$) is violated at $P \simeq 3\text{--}7$ kbar and, as a consequence, thermodynamical instability occurs. In contrast, the dynamical instability of the phonon spectrum occurs at a significantly higher pressure, about 20 kbar.

1. Introduction

The novel phenomenon of a pressure-driven crystalline \rightarrow amorphous transformation has been observed in ice Ic [1], α -quartz [2] and other materials [3–6]. The nature of this process is not well understood despite a number of theoretical and experimental studies having been performed. The initial proposal for the mechanism for the transformation in Ic was that it is due to a ‘melting’ effect [1]. This postulate was based largely on the empirical observation that the transition is very sharp with respect to the change in pressure and occurs at a pressure very close to that of the solid–liquid phase boundary extrapolated to lower temperature. Thermodynamically, the melting pressure is that at which both the crystalline and the amorphous phase can coexist and at which the Gibbs free energies of the two phases are equal. However a recent re-examination [7] of the melting curve of ice Ic showed that thermodynamic ‘melting’ should occur at a pressure much lower than that at which it is experimentally observed. On the other hand, it has been shown that the decrease in melting point with pressure is not a necessary condition for an order–disorder transformation. The most significant observation was made concerning ice clathrates [8]. It was found that ice clathrates collapse into high-density phases at high enough pressure, regardless of their melting behaviours.

In an earlier theoretical MD calculation [9], it was suggested that the mechanism for pressure-induced amorphization in ice Ih is due to a mechanical instability in the

water framework. The adiabatic elastic moduli calculated by the MD technique at the transition point show that there is a violation of the Born criteria for these moduli. Similar mechanical instabilities were also found in α -quartz (SiO_2) and α -berlinite (AlPO_4) [10–12] by employing the lattice-dynamics method developed for calculation of the elastic moduli of ionic crystals [13]. The lattice-dynamics approach can give a more detailed picture of the phenomenon insofar as it permits the investigation of the behaviour of selected vibrational modes at any point of the Brillouin zone. In fact, it was found for SiO_2 [10–12] that a softening of the lowest acoustic branch at the Brillouin zone-edge K point occurs at a lower pressure than does the mechanical instability.

The primary objective of this paper is to extend the lattice-dynamics method to the investigation of the phenomenon of instability in pressurized molecular systems. The ‘rigid’-molecule approximation is often used in the simulation of molecular crystals. Therefore, the dynamical matrix of the system includes the translation, rotational and mixed terms [14]. The well-known expressions for the calculation of the elastic moduli of ionic crystals are not suitable for molecular crystals since rotational degrees of freedom need not be considered. In this paper, analytical expressions appropriate for the elastic moduli of molecular solids are derived.

The second goal of this paper is the refinement of the concept of ‘mechanical instability’. This term has often been used to describe the violation of the Born stability conditions for the isothermal [15], adiabatic [9] and elastic moduli (dynamical moduli) determining the behaviour of the acoustic modes of the phonon Hamiltonian in the $\mathbf{q} = 0$ region [10–12]. However, in the strict theory these moduli are not the same and do not coincide. It will be shown here that the instability of a crystal associated with isothermal or adiabatic moduli has an origin different from that of the instability associated with the dynamical moduli.

The expressions for the elastic moduli of a molecular crystal derived in this paper may be used for the investigation of the stability problem for ice and clathrate hydrates under pressure. As a first example of applications of this kind, we chose ice Ic because of the simplicity of the cubic crystal structure. The calculation for other, more complex, crystal structures will be the subject of further investigations.

The organization of this paper is as follows. In the next section, the analytical theory for the derivation of elastic moduli under pressure will be given. The results of the calculations on ice Ic using the SPC potential for water’s interactions [16] will be presented and discussed in section 3. The paper concludes with a brief summary of the main results.

2. Theoretical details

The quasi-harmonic approximation is used in this paper for calculation of the isothermal and adiabatic moduli. It is well known [17] that this approximation is adequate for calculations of the thermal equation of state and the elastic moduli. The thermal magnitudes are determined here by the first and second derivatives of the free energy $F_{qh} = U + F_s$ with respect to the strain, where U is the potential energy of the crystal and F_s is the vibrational part of the free energy. The expressions for the elastic moduli [17], for example for the isothermal moduli, $C_{\alpha\beta\sigma\tau}^{is}$, can be divided into two parts in the quasi-harmonic approximation:

$$C_{\alpha\beta\sigma\tau}^{is} = C_{\alpha\beta\sigma\tau}^0 + C_{\alpha\beta\sigma\tau}^{is(1)} \quad (1)$$

where

$$C_{\alpha\beta\sigma\tau}^0 = \frac{1}{V_0} \left(\frac{\partial^2 U}{\partial \eta_{\alpha\beta} \partial \eta_{\sigma\tau}} \right)_0 \quad (2)$$

and, in the case of isotropic compression, $C_{\alpha\beta\sigma\tau}^{is(1)}$ takes the form

$$C_{\alpha\beta\sigma\tau}^{is(1)} = \frac{1}{V_0} \left(\frac{\partial^2 F_s}{\partial \eta_{\alpha\beta} \partial \eta_{\sigma\tau}} \right)_0 - P(\delta_{\alpha\sigma} \delta_{\beta\tau} + \delta_{\alpha\tau} \delta_{\beta\sigma} - \delta_{\alpha\beta} \delta_{\sigma\tau}) \quad (3)$$

where the Lagrangian strain tensor $\eta_{\alpha\beta}$ is determined through $u_{\alpha,\beta}$ magnitudes describing the general homogeneous deformation of any point of the crystal:

$$x'_\alpha = \sum_\beta (\delta_{\alpha\beta} + u_{\alpha,\beta}) x_\beta \quad (4)$$

$$\eta_{\alpha\beta} = \frac{1}{2} \left(u_{\alpha,\beta} + u_{\beta,\alpha} + \sum_\gamma u_{\gamma,\alpha} u_{\gamma,\beta} \right) = \eta_{\beta\alpha}. \quad (5)$$

$C_{\alpha\beta\sigma\tau}^0$ has the same form as it does with the harmonic approximation but here it is dependent on the temperature T and the pressure P to account for the change in the equilibrium configuration of the system. The equilibrium configuration is determined by the equation

$$\frac{1}{V_0} \left(\frac{\partial F_{qh}}{\partial \eta_{\alpha\beta}} \right)_0 = -P \delta_{\alpha\beta}. \quad (6)$$

The derivatives in (2), (3) and (6) with respect to $\eta_{\alpha\beta}$ are calculated for the equilibrium configuration and V_0 is the appropriate equilibrium volume. The second term in (1) is defined by the derivatives of the eigenfrequencies of the phonon Hamiltonian with respect to $\eta_{\alpha\beta}$ and depends explicitly both on T and on P .

To derive an expression for $C_{\alpha\beta\sigma\tau}^0$ we shall consider both the equation of motion for the elastic wave appropriate for a crystal with potential energy U [18], namely

$$\rho \omega^2 \bar{u}_\alpha = \sum_\beta \left(\sum_{\gamma\lambda} S_{\alpha\gamma\beta\lambda} q_\gamma q_\lambda \right) \bar{u}_\beta \quad (7)$$

and the solutions of lattice-dynamics equations for molecular crystals [19]:

$$\begin{aligned} m_k \omega^2(\mathbf{q}) U_\alpha^t(k, \mathbf{q}) &= \sum_{k', \beta} (\tilde{D}_{\alpha\beta}^{tt}(\mathbf{q}, kk') U_\beta^t(k', \mathbf{q}) + \tilde{D}_{\alpha\beta}^{tr}(\mathbf{q}, kk') U_\beta^r(k', \mathbf{q})) \\ I_{\alpha\alpha}(k) \omega^2(\mathbf{q}) U_\alpha^t(k, \mathbf{q}) &= \sum_{k', \beta} (\tilde{D}_{\alpha\beta}^{rt}(\mathbf{q}, kk') U_\beta^t(k', \mathbf{q}) + \tilde{D}_{\alpha\beta}^{rr}(\mathbf{q}, kk') U_\beta^r(k', \mathbf{q})) \\ &\quad - \omega^2(\mathbf{q}) \sum_{\beta \neq \alpha} I_{\alpha\beta}(k) U_\beta^t(k, \mathbf{q}) \end{aligned} \quad (8)$$

for the acoustic branch in the long-wavelength limit ($\mathbf{q} \rightarrow 0$), obtained by the perturbation-theory technique. The terms associated with the macroscopic Coulomb field were omitted from (7) and (8) because our concern is only with the expressions for the elastic moduli and the piezoelectric effects will not be considered here. In (8) $\tilde{D}_{\alpha\beta}^{ii'}(\mathbf{q}, kk')$ are the translational ($i, i' = t$), rotational ($i, i' = r$) and mixed ($i = t, i' = r$ or $i = r, i' = t$) terms of the dynamical matrix of the crystal. The tilde means that the part associated with the macroscopic field is excluded from the matrix. $\omega(\mathbf{q})$ and $U^i(k, \mathbf{q})$ are the phonon frequency and the associated eigenvector m_k and $I_{\alpha\beta}(k)$ are the mass and the moment of inertia tensor of the k th molecule. We restrict the discussion here to the case in which the total dipole moment of the unit cell and the net charge of molecules are equal to zero. In (7) ρ and \bar{u}_α are the mass density and the amplitude of the displacement vector. The $S_{\alpha\beta\sigma\tau}$ tensor is related to the $C_{\alpha\beta\sigma\tau}^0$ tensor in the following manner [20]:

$$S_{\alpha\beta\sigma\tau} = C_{\alpha\beta\sigma\tau}^0 + \delta_{\alpha\sigma} S_{\beta\tau} \quad (9)$$

From (6), we obtain for $S_{\beta\tau}$

$$S_{\beta\tau} = \frac{1}{V_0} \left(\frac{\partial U}{\partial \eta_{\beta\tau}} \right)_0 = -P\delta_{\beta\tau} - \frac{1}{2V_0} \sum_j \frac{\partial \ln \omega_j^2}{\partial \eta_{\beta\tau}} \varepsilon(\omega_j, T) \quad (10)$$

where the summation on j is over all phonon modes of the crystal and

$$\varepsilon(\omega_j, T) = \frac{1}{2} \hbar \omega_j + \frac{\hbar \omega_j}{\exp[\hbar \omega_j / (kT)] - 1} \quad (11)$$

is the vibrational energy corresponding to the j th mode. Now we consider the one-dimensional set of solutions appropriate to a fixed \mathbf{q} direction, for which we replace \mathbf{q} by $\epsilon \mathbf{q}$ and expand all quantities in a series of ϵ :

$$\tilde{D}_{\alpha\beta}^{ii'}(\epsilon \mathbf{q}, kk') = \tilde{D}_{\alpha\beta}^{ii'(0)}(k, k') + i\epsilon \sum_{\gamma} \tilde{D}_{\alpha\beta, \gamma}^{ii'(1)}(k, k') q_{\gamma} + \frac{1}{2} \epsilon^2 \sum_{\gamma\lambda} \tilde{D}_{\alpha\beta, \gamma\lambda}^{ii'(2)}(k, k') q_{\gamma} q_{\lambda} + \dots \quad (12)$$

$$\omega(\epsilon \mathbf{q}) = \epsilon \omega^{(1)}(\mathbf{q}) + \frac{1}{2} \epsilon^2 \omega^{(2)}(\mathbf{q}) + \dots \quad (13)$$

$$U_{\alpha}^i(k, \epsilon \mathbf{q}) = U_{\alpha}^{i(0)}(k, \mathbf{q}) + i\epsilon U_{\alpha}^{i(1)}(k, \mathbf{q}) + \frac{1}{2} \epsilon^2 U_{\alpha}^{i(2)}(k, \mathbf{q}) + \dots \quad (14)$$

Details of the coefficients of expansion $\tilde{D}_{\alpha\beta}^{ii'(0)}(k, k')$, $\tilde{D}_{\alpha\beta, \gamma}^{ii'(1)}(k, k')$ and $\tilde{D}_{\alpha\beta, \gamma\lambda}^{ii'(2)}(k, k')$ are presented in the appendix.

Using perturbation theory and the expansions (12)–(14) the solution of (8) gives for the polarization vector of zeroth order

$$\left(\frac{\sum_k m_k}{v_a} \right) [\omega^{(1)}(\mathbf{q})]^2 \bar{u}_{\alpha} = \sum_{\beta} \left\{ \sum_{\gamma\lambda} \{[\alpha\beta, \gamma\lambda] + (\alpha\gamma, \beta\lambda)\} q_{\gamma} q_{\lambda} \right\} \bar{u}_{\beta} \quad (15)$$

where v_a is the volume of the cell. A more detailed discussion of the analogous procedure was presented in [13] for the case of ionic crystals. The expressions for square and round brackets

$$[\beta\alpha, \gamma\lambda] = \frac{1}{2v_a} \sum_{kk'} \tilde{D}_{\alpha\beta, \gamma\lambda}^{tt(2)}(k, k') \quad (16)$$

$$(\alpha\beta, \gamma\lambda) = -\frac{1}{v_a} \sum_{kk', \mu\nu} \Gamma_{\mu\nu}(kk') \sum_{k''} B_{v\alpha, \beta}(k, k'') \sum_{k'''} B_{\mu\gamma, \lambda}(k', k''') \quad (17)$$

are closely related to the analogous expressions for the ionic crystals. However, the matrix $\Gamma_{\mu\nu}(kk')$ has the size $6n \times 6n$ in our case (n is the number of molecules in the cell) and is defined by the following relationships:

$$\begin{aligned} \Gamma_{\mu\nu}(kk') &= 0 && \text{if } k = 1, \mu \leq 3 \text{ or } k' = 1, \nu \leq 3 \\ \sum_{k', \gamma} \Gamma_{\mu\gamma}(kk') A_{\gamma\nu}(k', k'') &= \delta_{\mu\nu} \delta_{k, k''} && \text{otherwise.} \end{aligned} \quad (18)$$

The indices k, k', k'' and k''' range from 1 to n and the indices μ, ν and γ run from 1 to 6 in the formulae (16)–(18). The matrix $\hat{A}(k, k')$ is made for each k, k' from four 3×3 matrices:

$$\hat{A}(k, k') = \begin{pmatrix} \tilde{D}_{\alpha\beta}^{tt(0)}(kk') & \tilde{D}_{\alpha\beta}^{tr(0)}(kk') \\ \tilde{D}_{\alpha\beta}^{rt(0)}(kk') & \tilde{D}_{\alpha\beta}^{rr(0)}(kk') \end{pmatrix} \quad (19)$$

and the matrix $\hat{B}_{\gamma}(k, k')$ for each k, k', j from two 3×3 matrices:

$$\hat{B}_{\gamma}(k, k') = \begin{pmatrix} \tilde{D}_{\alpha\beta, \gamma}^{tt(1)}(kk') \\ \tilde{D}_{\alpha\beta, \gamma}^{tr(1)}(kk') \end{pmatrix}. \quad (20)$$

The expressions (16)–(20) and the one presented in the appendix are distinct from the analogous expressions in [13] since a different representation of the dynamical matrix and the definition of reciprocal-lattice vectors was used here [19].

By comparing (7) and (15) and using (9) one obtains

$$C_{\alpha\gamma\beta\lambda}^0 + C_{\alpha\lambda\beta\gamma}^0 + 2\delta_{\alpha\beta}S_{\gamma\lambda} = 2[\alpha\beta, \gamma\lambda] + (\alpha\gamma, \beta\lambda) + (\alpha\lambda, \beta\gamma) \quad (21)$$

or

$$C_{\alpha\gamma\beta\lambda}^0 + C_{\alpha\lambda\beta\gamma}^0 = 2\{\alpha\beta, \gamma\lambda\}. \quad (22)$$

Here a new symbol, the curly bracket, is introduced:

$$\{\alpha\beta, \gamma\lambda\} = [\alpha\beta, \gamma\lambda] - \delta_{\alpha\beta}S_{\gamma\lambda} + \frac{1}{2}((\alpha\gamma, \beta\lambda) + (\alpha\lambda, \beta\gamma)). \quad (23)$$

From (23) and the following symmetry properties of square and round brackets:

$$[\alpha\beta, \gamma\lambda] = [\beta\alpha, \gamma\lambda] = [\alpha\beta, \lambda\gamma] \quad (24)$$

$$(\alpha\beta, \gamma\lambda) = (\gamma\lambda, \alpha\beta) \quad (25)$$

it follows that the shaped brackets have the symmetry of the square brackets. On this basis equation (22) reduces to the case already familiar in ionic crystals (see [13] section 27). The unique solution of (22) that is symmetrical with respect to the first pair of indices is as follows [13]:

$$C_{\alpha\gamma\beta\lambda}^0 = \{\alpha\beta, \gamma\lambda\} + \{\beta\gamma, \alpha\lambda\} - \{\beta\lambda, \alpha\gamma\}. \quad (26)$$

The fulfilment of 15 additional conditions (see [13] section 27) is necessary in order that $C_{\alpha\gamma\beta\lambda}^0$ will be symmetrical with respect to the permutation of the first and second pairs of indices. For molecular crystals it takes the form

$$\{\beta\gamma, \alpha\lambda\} = \{\alpha\lambda, \beta\gamma\}. \quad (27)$$

In the case of multiple lattices ($n \neq 1$), the expression (26) takes into account the internal strain of the cell (round brackets) which is impossible to compute in the $C_{\alpha\gamma\beta\lambda}^0$ components via numerical differentiation of the potential energy U with respect to the strain $\eta_{\alpha\beta}$. The stability of the acoustic modes of the phonon Hamiltonian at $\mathbf{q} \rightarrow 0$ is determined by the values of the components of the $S_{\alpha\beta\sigma\tau}$ tensor (expressions (7) and (9)). However, it is more convenient to use another tensor:

$$C_{\alpha\beta\sigma\tau}^{dyn} = C_{\alpha\beta\sigma\tau}^0 - \frac{1}{2}(2S_{\alpha\beta}\delta_{\sigma\tau} - S_{\alpha\sigma}\delta_{\beta\tau} - S_{\alpha\tau}\delta_{\beta\sigma} - S_{\beta\tau}\delta_{\alpha\sigma} - S_{\beta\sigma}\delta_{\alpha\tau}) \quad (28)$$

which was derived from the stress–strain relations in [20]. This tensor is symmetrical with respect to the interchanges α, β and σ, τ and, in the isotropic case ($S_{\alpha\beta} = -S_0\delta_{\alpha\beta}$), it has the full symmetry of the elastic constants. In the isotropic case [20]

$$C_{\alpha\beta\sigma\tau}^{dyn} = C_{\alpha\beta\sigma\tau}^0 - S_0(\delta_{\alpha\sigma}\delta_{\beta\tau} + \delta_{\alpha\tau}\delta_{\beta\sigma} - \delta_{\alpha\beta}\delta_{\sigma\tau}) \quad (29)$$

and it may replace the $S_{\alpha\beta\sigma\tau}$ tensor in equation (7). From (29) it follows that

$$C_{\alpha\beta\sigma\tau}^{dyn} - C_{\alpha\beta\sigma\tau}^{is} = (P - S_0)(\delta_{\alpha\sigma}\delta_{\beta\tau} + \delta_{\alpha\tau}\delta_{\beta\sigma} - \delta_{\alpha\beta}\delta_{\sigma\tau}) - \frac{1}{V_0} \left(\frac{\partial^2 F_s}{\partial \eta_{\alpha\beta} \partial \eta_{\sigma\tau}} \right)_0. \quad (30)$$

From (10) and (30) the difference between the components of the dynamical ($C_{\alpha\beta\sigma\tau}^{dyn}$) and isothermal tensors is determined by the magnitudes of the first and second derivatives of the vibrational part of the free energy. For ices this difference is very significant, as will be demonstrated in the next section.

The violation of the Born stability conditions for the $C_{\alpha\beta\sigma\tau}^{dyn}$ tensor (in the isotropic case) reflects the instability of acoustic modes of the phonon Hamiltonian, or in other

words, the dynamical instability of the crystal. This instability is associated with the imaginary frequencies near the Γ point in the phonon spectrum above the critical pressure or temperature.

We prove now that the violation of the stability conditions for the isothermal or adiabatic tensors indicates a thermodynamical instability of the crystal. A thermodynamical instability is perceived here in the traditional meaning [21] as a macroscopic instability of the equilibrium state of the system with respect to small deviations from this equilibrium state. With the familiar approach (see [21] section 21) we consider the deviation from the equilibrium state at the temperature T_0 and the pressure P_0 of the closed macro-system part. In this equilibrium state $P_{cryst} = P_0$ and $T_{cryst} = T_0$, the crystal under stress has energy E , entropy S and volume V , as was shown in [21], the magnitude

$$\tilde{\Phi}_0 = E - T_0S + P_0V \quad (31)$$

decreases on the return of this closed macro-system to the equilibrium state and $\tilde{\Phi}$ has its minimum in the equilibrium state. This property is evident from the law of increasing entropy for a closed macro-system (see [21]). Hence it follows that the change in $\tilde{\Phi}$ is positive relative to the equilibrium configuration

$$\Delta\tilde{\Phi} > 0. \quad (32)$$

Consider two different types of deviation whereby the deviation of the crystal's configuration from the initial equilibrium configuration is by small homogeneous deformations of the crystal lattice at a constant temperature or with constant entropy. In the first case, when $T_{cryst} = T_0$, we have for the free energy of the crystal

$$F = E - T_0S \quad (33)$$

and

$$\Delta\tilde{\Phi} = (\Delta F)_{T_{cryst}=T_0} + P_0\Delta V. \quad (34)$$

By using (6) and the relationship between the volume V in the deformed state and the volume V_0 in the initial state [17]

$$V = [|\det(1 + 2\eta_{\alpha\beta})|]^{1/2}V_0 \quad (35)$$

it is possible to account for the change in $\Delta\tilde{\Phi}$ relative to equilibrium to within terms of the second order on the strain:

$$\Delta\tilde{\Phi} = \frac{1}{2}V_0 \sum_{\alpha\beta\sigma\tau} C_{\alpha\beta\sigma\tau}^{is} \eta_{\alpha\beta} \eta_{\sigma\tau} > 0. \quad (36)$$

In the second case, when $S = S_0$, we have

$$\Delta\tilde{\Phi} = (\Delta E)_{S=S_0} + P_0\Delta V. \quad (37)$$

By using the relationship

$$\frac{1}{V_0} \left(\frac{\partial E}{\partial \eta_{\alpha\beta}} \right)_{S=S_0} = -P_0\delta_{\alpha\beta} \quad (38)$$

we derive in a similar way

$$\Delta\tilde{\Phi} = \frac{1}{2}V_0 \sum_{\alpha\beta\sigma\tau} C_{\alpha\beta\sigma\tau}^{ad} \eta_{\alpha\beta} \eta_{\sigma\tau} > 0 \quad (39)$$

where

$$C_{\alpha\beta\sigma\tau}^{ad} = \frac{1}{V_0} \left(\frac{\partial^2 E}{\partial \eta_{\alpha\beta} \partial \eta_{\sigma\tau}} \right)_{S=S_0} - P_0(\delta_{\alpha\sigma} \delta_{\beta\tau} + \delta_{\alpha\tau} \delta_{\beta\sigma} - \delta_{\alpha\beta} \delta_{\sigma\tau}) \quad (40)$$

is the adiabatic tensor [17].

So the positive definiteness of the adiabatic and isothermal tensors (the Born stability criteria) are necessary for the stable equilibrium of a crystal. The failure of either of the two conditions brings into existence a small deformation of the crystal for which $\tilde{\Phi}$ decreases relative to that of the initial equilibrium configuration. This would mean that this configuration is unstable. In this case the crystal structure deviates from the initial equilibrium configuration to a deformed structure which is the true stable equilibrium configuration, resulting in a structural phase transition. $\tilde{\Phi}$ coincides with the Gibbs free energy for the initial and transformed phases. Hence, from (36) and (39), the Gibbs free energy of the initial phase is always larger than that of the transformed phase since $\tilde{\Phi}$ decreases on the return to the equilibrium state. This type of phase transition takes place only if the usual transition, in which the Gibbs free energies of the two phases are equal, does not occur. This is evidently true for ice Ic, taking into account the results of [7, 9], in which the thermodynamic ‘melting’ occurs at a pressure much lower than that which would be implied by the violation of the Born stability conditions for adiabatic moduli. The results of [15] are also a good illustration of the general considerations given above. The elastic stiffness coefficients B_{ij} in [15] are really the isothermal moduli for the case of a non-isotropic applied stress if one adheres to the definition used in our paper (see [17]). It has been shown in [15] that the actual instability observed by direct molecular dynamics simulation occurs at a point where the stability criteria are violated for B_{ij} . According to our analysis this means that the system becomes thermodynamically unstable above this point.

From knowledge of the isothermal moduli, the change in equilibrium state for a small change in pressure and temperature can be obtained:

$$\Delta\eta_{\alpha\beta}^{eq} = -\frac{1}{V_0} \sum_{\sigma\tau} C_{\alpha\beta\sigma\tau}^{(is)-1} F_{T,\sigma\tau}^s \Delta T - \sum_{\sigma} C_{\alpha\beta\sigma\sigma}^{(is)-1} \Delta P \quad (41)$$

where

$$F_{T,\sigma\tau}^s = \left(\frac{\partial^2 F^s}{\partial T \partial \eta_{\sigma\tau}} \right)_0$$

and $C_{\alpha\beta\sigma\tau}^{(is)-1}$ is the inverse of $C_{\alpha\beta\sigma\tau}^{(is)}$. This formula is a direct generalization of the expression given in [17]. Equation (41) permits the study of the gradual evolution of a system from any known thermodynamic starting point. Its use is illustrated in the ice Ic calculation presented in the next section.

3. The calculation for ice Ic

As a first application of the analytical expressions derived above, in this section we investigate the stability of ice Ic under compression. Ice Ic has a simple diamond structure for the oxygen atom arrangement. The interactions between the water molecules are described by the SPC potential. It had previously been shown that the SPC model gives very reasonable structural and vibrational properties for different polymorphic forms of ice [22]. In the SPC model, the Coulomb interaction is described by setting charges $q_O = -0.82|e|$ on the oxygen atom and $q_H = 0.41|e|$ on hydrogen atoms (e is the electron charge). The short-range interaction is considered between the oxygen atoms only and it is described by the formula

$$V_{O-O} = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \quad (42)$$

where $\sigma = 3.16 \text{ \AA}$, $4\epsilon = 2.60 \text{ kJ mol}^{-1}$. The water molecule is assumed to be rigid with O–H distances equal to 1.0 \AA and the valence H–O–H angle $109^\circ 28'$. The extended elementary cell used in the calculations contains 64 water molecules. The oxygen atoms of water molecules were arranged initially in the cubic ice Ic structure with the hydrogen atoms placed in an *ad hoc* manner according to the Bernal–Fowler rules [23]. A zero-dipole-moment cell was then prepared by permutating the positions of the hydrogen atoms until the net dipole vanished. For a larger cell size, the arrangement of hydrogen atoms chosen in this manner comes closer to the cubic symmetry. The calculation of the free energy F at $T = 0$ and $P = 0$ for various values of the cell parameter showed that F has a minimum for the SPC potential when $a = 12.82 \text{ \AA}$, which is comparable to the experimental value of $a = 12.70 \text{ \AA}$. It should be noted that the vibrational part of the free energy F_s gives a considerable contribution to F_{qh} , amounting to about 25% of the potential energy contribution (U).

The thermal expansion and isothermal compression values at $T = 0, 130$ and 250 K of ice Ic were computed from the theoretical equilibrium configuration at $T, P = 0$ ($a = 12.82 \text{ \AA}$) using the formulae presented in section 2. The expressions for the dynamical ($C_{\alpha\beta\gamma\sigma}^{dyn}$), isothermal and adiabatic moduli included also the derivatives of the frequencies of the phonon spectrum with respect to the strain. These derivatives were calculated numerically with the help of the algorithms [24] which give a guaranteed precision for the frequencies for any configuration. The calculated adiabatic moduli at $P = 0$ (in kbar) were $C_{11} = 129$, $C_{12} = 114$ and $C_{44} = 51$ at $T = 0 \text{ K}$; $C_{11} = 116$, $C_{12} = 104$ and $C_{44} = 37$ at $T = 130 \text{ K}$; and $C_{11} = 92$, $C_{12} = 86$ and $C_{44} = 23$ at $T = 250 \text{ K}$. These values are of the same order of magnitude as the moduli calculated [9] or measured [25] for ice Ih. It is noteworthy that the difference $C_{11} - |C_{12}|$ coincides for the isothermal and adiabatic moduli in the case of cubic symmetry at any P and T [17].

In figure 1, $C_{11} - |C_{12}|$ is plotted as a function of P for the adiabatic (isothermal) moduli at $T = 0$ (bottom curve). The upper curve corresponds to the same stability condition for dynamical moduli. Under an external pressure, at $T = 0$ the calculation shows that one of the Born stability conditions, $C_{11} > |C_{12}|$, is violated for the adiabatic and isothermal moduli at $P \simeq 3\text{--}7$ kbar. The dynamical instability occurs at a higher pressure ($P \simeq 20$ kbar). The reason for such a large difference can be rationalized by a qualitative analysis of equation (30). This formula is valid as long as $S_{\alpha\beta}$ (formula (10)) is isotropic (because of cubic symmetry) and

$$\Delta = P - S_0 = -\frac{1}{2V_0} \sum_j \frac{\partial \ln \omega_j^2}{\partial \eta_{ii}} \varepsilon(\omega_j, T) \quad (43)$$

for any i . On defining the average phonon spectrum as

$$\bar{\omega}^2 = \frac{1}{6nN} \sum_j \omega_j^2$$

where N is the number of elementary cells, Δ is approximately [17]

$$\Delta = \gamma U^{av} \quad (44)$$

where

$$\gamma = -\frac{1}{2} \frac{\partial \ln \bar{\omega}^2}{\partial \eta_{ii}}$$

is the averaged Gruneisen constant and

$$U^{av} = \frac{1}{V_0} \sum_j \varepsilon(\omega_j, T)$$

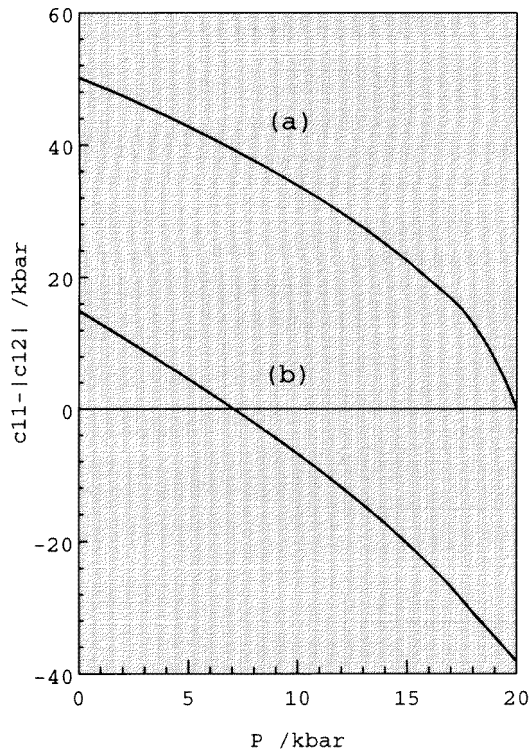


Figure 1. The evolution of the dynamical (curve (a)) and thermodynamical (curve (b)) stability conditions $C_{11} - |C_{12}|$ at $T = 0$ versus P .

is the vibrational energy calculated per unit volume. γ is calculated to be a positive value close to unity. For U^{av} at $T = 0$, taking into account the phonon spectrum of ice Ic within the energy interval 0–1000 cm^{-1} , one obtains

$$U^{av} \cong \frac{6n\hbar\sqrt{\bar{\omega}^2}}{2\nu_a} \approx 10 \text{ kbar.} \quad (45)$$

Only the first term in expression (30) gives the difference between the two curves in figure 1, about 20 kbar taking into consideration that Δ enters with opposite signs in the differences $C_{11}^{dyn} - C_{11}^{is}$ and $C_{12}^{dyn} - C_{12}^{is}$. The second term in (30) is approximately proportional to U^{av} at $T = 0$ and it gives essentially the same contribution to the difference between two curves in figure 1. Thus the large pressure difference between the dynamical and thermodynamical instabilities is associated with the features of the phonon spectrum of ice Ic. The existence of such features may be peculiar to all ices and ice clathrates in view of the similarity in their phonon spectra.

The dispersion curves at $T = 0$ for the lowest acoustic mode are depicted in figure 2 calculated at various values of P in the direction from the zone centre to the $K - (2\pi/a)(\frac{3}{4}, \frac{3}{4}, 0)$ point for small values of q . This mode is softened at the point corresponding to the thermodynamical instability ($P = 7$ kbar) but the full-scale proximity of dynamical instability emerges at a higher pressure ($P = 19$ kbar). The calculations at $T \neq 0$ show that, in this case, the thermodynamical instability occurs at a higher temperature for a lower pressure, for $T = 130$ K at $P = 6$ kbar and for $T = 250$ K at $P = 3$ kbar.

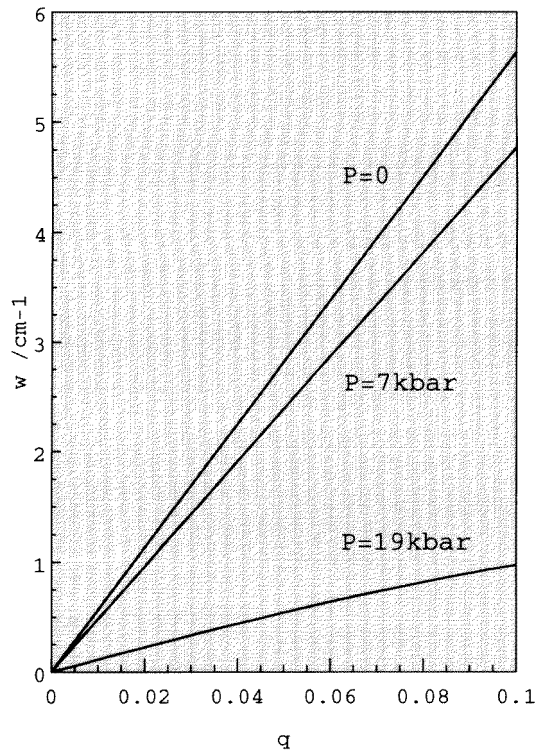


Figure 2. The dispersion curves for the lowest acoustic mode at various P values calculated in the direction from the centre of zone to the K point for small values of q .

The dependence of the difference $C_{11} - |C_{12}|$ on P for these temperatures is presented in figure 3 for the adiabatic (isothermal) moduli.

4. Conclusion

The general expressions for the elastic moduli of a molecular crystal have been obtained within the framework of the quasi-harmonic approximation, taking into account both short-range and long-range (electrostatic) interactions. These expressions permit the investigation of the stability of a crystalline molecular system under variable pressure and temperature conditions through the monitoring of the Born stability conditions. The dynamical and thermodynamical instabilities associated with the elastic moduli have been presented. The dynamical type is associated with the instability of acoustic modes of the phonon Hamiltonian in the $q = 0$ region. The thermodynamical instability is related to the fact that the equilibrium state of a crystal becomes thermodynamically unstable with respect to a small homogeneous deformation of the crystal lattice when the stability conditions are violated for the isothermal or adiabatic moduli. In this case, the Gibbs free energy of the initial phase is always larger than that of the transformed phase at the point of the structural phase transition.

The calculations on ice Ic, using the SPC potential for water interactions, show that one of the conditions for the modulus ($C_{11} - |C_{12}| > 0$) violated at $P \simeq 3\text{--}7$ kbar and, as a consequence, thermodynamical (mechanical) instability occurs. The dynamical instability

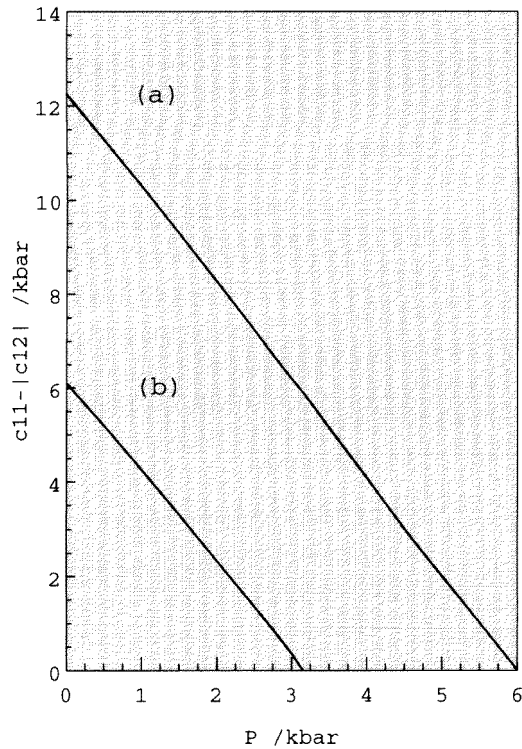


Figure 3. The evolution of the stability condition $C_{11} - |C_{12}|$ (a) at $T = 130$ K and (b) at $T = 250$ K versus P obtained for the adiabatic (isothermal) moduli.

or the instability of the phonon spectrum occurs at a much higher pressure. The qualitative analysis indicates that similar behaviour may be peculiar to the ices and ice clathrates as a whole. It will be interesting to examine this assumption further and in more detail by using the lattice-dynamics approach.

Acknowledgment

This work in Russia was supported by the Russian Fund for Basis Research through grant 96-03-32928.

Appendix

A1. The zeroth-order case

Matrices $\tilde{D}_{\alpha\beta}^{rr(0)}(k, k')$, $\tilde{D}_{\alpha\beta}^{ri(0)}(k, k')$, $\tilde{D}_{\alpha\beta}^{tr(0)}(k, k')$ and $\tilde{D}_{\alpha\beta}^{rr(0)}(k, k')$ are the same as the matrices forming the dynamical matrix of the crystal (see [19]) at $\mathbf{q} = 0$. The term in the Coulomb part of the dynamical matrix appropriate to the macroscopic field should be eliminated.

A2. The first-order case

Here

$$\tilde{D}_{\alpha\beta,\gamma}^{tt(1)}(k, k') = \sum_{l'} \Phi_{\alpha\beta}^{tt(N)}(0k, k'l') A_\gamma(l') + \sum_{m,m'} Z(k, m) Z(k', m') \Pi_{\alpha\beta,\gamma} \quad (\text{A1})$$

$$\tilde{D}_{\alpha\beta,\gamma}^{tr(1)}(k, k') = \sum_{l'} \Phi_{\alpha\beta}^{tr(N)}(0k, k'l') A_\gamma(l') + \sum_{m,m'} Z(k, m) Z(k', m') \sum_{\mu\nu} \epsilon_{\mu\alpha\nu} x_\nu(km) \Pi_{\mu\beta,\gamma} \quad (\text{A2})$$

where $\Phi_{\alpha\beta}^{ii'(N)}$ are non-coulombic force constants, A_γ are the translational vectors of the cell, $Z(k, m)$ is the charge of the atom (km), $x_\nu(km)$ is the position vector of the m th atom in the k th molecule relative to the centre of mass of this molecule and $\epsilon_{\mu\alpha\nu}$ is the full antisymmetrical tensor ($\epsilon_{123} = 1$). Furthermore:

$$\begin{aligned} \Pi_{\alpha\beta,\gamma} = \frac{4\pi}{v_a} \sum_{G \neq 0} \left\{ \left[\frac{1}{4\eta^2} (\delta_{\alpha\gamma} G_\beta + \delta_{\beta\gamma} G_\alpha) H\left(\frac{G^2}{4\eta^2}\right) + G_\alpha G_\beta G_\gamma \frac{1}{8\eta^4} H'\left(\frac{G^2}{4\eta^2}\right) \right] \right. \\ \left. \times \sin(\mathbf{G} \cdot \mathbf{x}) + \frac{1}{4\eta^2} G_\alpha G_\beta x_\gamma H\left(\frac{G^2}{4\eta^2}\right) \cos(\mathbf{G} \cdot \mathbf{x}) \right\} \\ - \sum_{l'} \Phi_{\alpha\beta}^c(0k, k'l') A_\gamma(l') \end{aligned} \quad (\text{A3})$$

where

$$\begin{aligned} \Phi_{\alpha\beta}^c(0k, k'l') = \frac{(A(l') - x)_\alpha (A(l') - x)_\beta}{|\mathbf{A}(l') - \mathbf{x}|^5} \left(3\text{erfc}(y) + \frac{e^{-y^2}}{\pi^{1/2}} (4y^3 + 6y) \right) \\ - \frac{\delta_{\alpha\beta}}{|\mathbf{A}(l') - \mathbf{x}|^3} \left(\text{erfc}(y) + \frac{2y e^{-y^2}}{\pi^{1/2}} \right) \end{aligned} \quad (\text{A4})$$

here $\mathbf{x} = \mathbf{x}(0km) - \mathbf{x}(0k'l')$, \mathbf{G} are the reciprocal-lattice vectors, $y = \eta|\mathbf{A}(l') - \mathbf{x}|$, $H(x) = e^{-x}/x$,

$$\text{erfc}(y) = 1 - \frac{2}{\pi^{1/2}} \int_0^y e^{-x^2} dx \quad (\text{A5})$$

and η is an arbitrary constant, the value of which is chosen so the fast convergence was provided for the direct and reciprocal lattices.

A3. The second-order case

Here

$$\begin{aligned} \tilde{D}_{\alpha\beta,\gamma\lambda}^{tt(2)}(kk') = - \sum_{l'} \Phi_{\alpha\beta}^{tt(N)}(0k, k'l') A_\gamma(l') A_\lambda(l') + \sum_{mm'} Z(km) Z(k'm') \\ \times \left\{ \sum_{l'} \Phi_{\alpha\beta}^c(0k, k'l') A_\gamma(l') A_\lambda(l') + \frac{\pi}{\eta^2 v_a} \right. \\ \times \sum_{G \neq 0} \left[(\delta_{\alpha\lambda} \delta_{\beta\gamma} + \delta_{\beta\lambda} \delta_{\alpha\gamma} - G_\alpha G_\beta x_\lambda x_\gamma) H\left(\frac{G^2}{4\eta^2}\right) \cos(\mathbf{G} \cdot \mathbf{x}) \right. \\ \left. - (\delta_{\alpha\lambda} G_\beta x_\gamma + \delta_{\beta\lambda} G_\alpha x_\gamma + \delta_{\beta\gamma} G_\alpha x_\lambda + \delta_{\alpha\gamma} G_\beta x_\lambda) H\left(\frac{G^2}{4\eta^2}\right) \sin(\mathbf{G} \cdot \mathbf{x}) \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2\eta^2} (\delta_{\alpha\lambda} G_\beta G_\gamma + \delta_{\beta\lambda} G_\alpha G_\gamma + \delta_{\beta\gamma} G_\alpha G_\lambda + \delta_{\alpha\gamma} G_\beta G_\lambda + \delta_{\gamma\lambda} G_\alpha G_\beta) H' \\
& \times \left(\frac{G^2}{4\eta^2} \right) \cos(\mathbf{G} \cdot \mathbf{x}) - \frac{1}{2\eta^2} (G_\lambda x_\gamma + G_\gamma x_\lambda) G_\alpha G_\beta H' \\
& \times \left(\frac{G^2}{4\eta^2} \right) \sin(\mathbf{G} \cdot \mathbf{x}) + \frac{G_\alpha G_\beta G_\gamma G_\lambda}{4\eta^4} H'' \left(\frac{G^2}{4\eta^2} \right) \cos(\mathbf{G} \cdot \mathbf{x}) \Bigg\}. \quad (\text{A6})
\end{aligned}$$

References

- [1] Mishima O, Calvert L D and Whalley E 1984 *Nature* **310** 393
- [2] Hemley R J, Jephcoat A P, Mao H K, Ming L C and Manghnami N H 1988 *Nature* **334** 52
- [3] Kruger M B and Jeanloz R 1990 *Science* **249** 647
- [4] Kruger M B, Williams Q and Jeanloz R 1989 *J. Chem. Phys.* **91** 5910
- [5] Fuji Y, Kowaka M and Onodera A 1985 *J. Phys. C: Solid State Phys.* **18** 789
Sugai S 1985 *J. Phys. C: Solid State Phys.* **18** 799
- [6] Melo F E A, Lemos V, Cerdiera F and Mendes Filho J 1987 *Phys. Rev. B* **35** 3633
- [7] Handa Y P, Tse J S, Klug D D and Whalley E 1991 *J. Chem. Phys.* **94** 623
- [8] Whalley E, Klug D D and Handa Y P 1989 *Nature* **342** 782
- [9] Tse J S 1992 *J. Chem. Phys.* **96** 5482
- [10] Binggeli N and Chelikowsky J R 1992 *Phys. Rev. Lett.* **69** 2220
- [11] Binggeli N, Keskar N R and Chelikowsky J R 1994 *Phys. Rev. B* **49** 3075
- [12] Keskar N R, Chelikowsky J R and Wentzcovitch R M 1994 *Phys. Rev. B* **50** 9072
- [13] Born M and Huang H 1954 *Dynamical Theory of Crystal Lattices* (Oxford: Clarendon)
- [14] Venkataraman G and Sahni V C 1970 *Rev. Mod. Phys.* **42** 409
- [15] Wang J, Yip S, Phillpot S R and Wolf D 1993 *Phys. Rev. Lett.* **71** 4182
- [16] Berendsen H J C, Postma J P M, van Gunsteren W F and Hermans J 1981 *Intermolecular Forces* (Amsterdam: North Holland) p 331
- [17] Leibfried G and Ludwig W 1961 *Theory of Anharmonic Effects in Crystals* (New York: Academic)
- [18] Huang K 1950 *Proc. R. Soc. A* **203** 178
- [19] Belosludov R V, Igumenov I K, Belosludov V R and Shpakov V P 1994 *Mol. Phys.* **82** 51
- [20] Barron T H K and Klein M L 1965 *Proc. Phys. Soc.* **85** 523
- [21] Landau L D and Lifshitz E M 1958 *Statistical Physics* (Oxford: Pergamon)
- [22] Tse J S, Klein M L and McDonald I R 1984 *J. Chem. Phys.* **81** 6124
- [23] Bernal J D and Fowler R H 1933 *J. Chem. Phys.* **1** 515
- [24] Godunov S K 1980 *Solution of Sets of Linear Equations* (Novosibirsk: Nauka) (in Russian)
- [25] Cagnon R E, Kiefte H F, Clouter M J and Whalley E 1988 *J. Chem. Phys.* **89** 4522