Nonlinear rotational waves in a molecular chain

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Abstract
A molecular chain with rotational degrees of freedom and quadrupolar interaction between
linear molecules is investigated theoretically. Rotation of the molecules is in the plane of an
adsorbing surface only and their centres of gravity are pinned. Continual nonlinear wave
equations are derived for the rotational excitations of the molecules from the discrete ones. The
oscillations of the molecules near the equilibrium positions are investigated. The interactions
are expanded in powers of angles and nonlinear terms are accounted for. Dispersion is
considered to be small. The normal modes are found to split the initial entangled nonlinear
system into two independent equations. A Linear equation describes waves of the stiffer normal
mode. A nonlinear equation describes waves of the softer normal mode. A nonlinear
Schrödinger equation is derived for waves of the softer normal mode, and a solution for
nonlinear waves is obtained.

1. Introduction

Molecular crystals have been investigated extensively because
of their unusual electric and thermal conductivity and structural
properties [1, 2]. Molecular cryocrystals [2] are interesting
for applications in low temperature techniques, and they
have the simplest molecules with well known interactions.
A considerable number the properties of molecular crystals
are connected with rotation of their molecules or molecular
fragments which, in the case of a linear configuration, are
described by the rigid rotors model. However, molecular
cryocrystals, as almost model objects, have a complicated
crystal structure with some sublattices and space rotor
rotation. A considerable simplification of their description,
while still keeping the basic physical features, is found by
application of chain models to the linear lattice dynamics and
thermodynamics of molecular cryocrystals [2].

Low dimensional systems are very important as models
as well as objects for applications. Real objects can be
adsorbed structures [3] or layered crystals [4]. Chain models
are a necessary stage in the investigation of the dynamics
and thermodynamics of more complex systems: crystals [5],
nonlinear dynamics of atomic and molecular lattices [6] and
their thermal conductivity [7]. The complexity of models
even for a 1D molecular chain requires some approximations

to simplify the system description. Such approximations
are in the model potential and 1D rotation of the molecular
rotors [2, 3, 7]. After these essential simplifications, analytical
consideration is constricted by the limits of small oscillation or
free rotation of rotors, i.e. the limits of low and high energies.
In the middle range of energies, especially in the vicinity of
the point of orientational melting, an analytical description
of the molecular rotor dynamics and thermodynamics
is absent.

In the present paper we investigate the rotational nonlinear
wave excitations of an ordered molecular chain in the range
from the low energy limit to the point of orientational
melting. The molecular chain consists of linear molecules with
realistic quadrupolar interaction [2]. It was natural to begin
investigation of this complex problem starting from simpler
cases such as linear rotational oscillations [8, 9] or the long-
wave limit for arbitrary amplitudes and nonlinearity [10] in our
previous works. Here we use the same model approximations
as in [8–10] and earlier in [2, 3]: one degree of freedom
for each molecule, and very hard translational potential, so
translational modes are frozen and can be neglected. The
rotational potential energy was obtained by supposing nearest
neighbour interaction only; the next neighbour contribution is
much less. The molecular chain energy was found to have a

minimum value for alternating ordering of the molecules:

$$(\phi_{2n} = \pi/2 + \pi j; \ \phi_{2n+1} = \pi j) \qquad \text{or}$$
$$(\phi_{2n} = \pi j; \ \phi_{2n+1} = \pi/2 + \pi j). \tag{1}$$

Here $i, j, n = 0, \pm 1, \pm 2, \ldots$, an angle ϕ_i is between the principal axis of a molecule and the direction of the radius-vector which connects the centres of inertia of the ith and $(i + 1)$th molecules. Therefore, the molecular system splits into two sublattices and index $i = 2n(i = 2n + 1)$ defines an even (odd) site. To research the time or space evolution of the molecular chain we must write the Lagrangian $L = K - U$ of the system. Here U and $K = \frac{1}{2}\sum J_i\dot{\phi}_i^2$ are potential and kinetic energies of the chain, the ith molecule has moment of inertia $J_i = J_0$ and angular velocity $\dot{\phi}_i$. Then the Lagrangian variation yields a system of equations for the chain motion in even (ϕ_{2m}) and odd (ψ_{2m+1}) sites:

$$\ddot{\phi}_i - \{2a\sin 2\phi_i + b[\sin 2(\phi_i - \psi_{i-1}) + \sin 2(\phi_i - \psi_{i+1})]$$
$$+ c[\sin 2(\phi_i + \psi_{i-1}) + \sin 2(\phi_i + \psi_{i+1})]\} = 0;$$
$$\ddot{\psi}_{i+1} - \{2a\sin 2\psi_{i+1} + b[\sin 2(\psi_{i+1} - \phi_i) \tag{2}$$
$$+ \sin 2(\psi_{i+1} - \phi_{i+2})] + c[\sin 2(\psi_{i+1} + \phi_i)$$
$$+ \sin 2(\psi_{i+1} + \phi_{i+2})]\} = 0.$$

Here the parameters of quadrupolar–quadrupolar interaction are $a = 5/4$, $b = 3/8$, $c = 35/8$, $\Gamma = 3Q^2/4R_0^5$, where Q is a quadrupolar moment of a molecule and R_0 is a distance between centres of inertia of the molecules. The dimensionless time is introduced: $t \to \tau = t\omega_0$ where $\omega_0^2 = \Gamma/J_0$ is a characteristic frequency.

Stability of the structure (1) was confirmed by analysis of the dynamical equations (2) as in the linear approximation [8, 9] and the long-wave limit for arbitrary amplitudes and nonlinearity [10] when all even or odd sites are equivalent. Previously we found the rotational excitations demonstrate a strong anisotropy in the angle space—directions of easy excitation ('valleys' on the effective potential) exist. By accounting for the strong anisotropy, it is possible to consider linear and nonlinear oscillations separately.

2. The continual equations for an inhomogeneous chain

The system of equations (2) is strongly nonlinear and differential-difference. Let us rewrite these equations for the two subsystems that follows from separation of the molecules into two sublattices and introduce new variables. Transformation from a discrete to a continual system of equations is not unambiguous. We suggest some set of steps (ansatz) which have to lead to a proper result.

(1) Here we use more convenient variables to account for the difference between the sites. It is natural to begin investigation of this complex problem by starting from the limiting case of small oscillations of molecules around the equilibrium positions [8, 9]. With this purpose new variables were introduced by the relations $\phi_{2m} = v_{2m}$; $\phi_{2m+1} = \pi/2 + u_{2m+1}$, where v_{2m} and u_{2m+1} are small deviations of the angles

from the equilibrium positions. After expansion of terms as power series in small perturbations v and u, the set of equations for the motion can be transformed into a linear system of differential-difference equations [8, 9]. Now we account for the cubic contributions in this expansion.

(2) Let us find expansion of the variables v and u around values in the ith and $i + 1$th sites. Then we introduce the dimensionless space coordinate:

$$\xi = \frac{x}{R_0}. \tag{3}$$

Let us note that $\Delta x = 2R_0$ and $\Delta\xi = 2$. Then expansions can be written as $v_{i+2} = v_i + 2v'_i + 2v''_i$; $u_{i-1} = u_{i+1} - 2u'_{i+1} + 2u''_{i+1}$. Here derivations are $v' = \partial v/\partial\xi$ and $v'' = \partial^2 v/\partial\xi^2$, the same formulae we have for u, u', u''. After substitution of expansions in the system (2) then grouping of the angles and their space derivations we obtain a system of continual dynamical nonlinear differential equations for the variables $v \equiv v_{2m}$ and $u \equiv u_{2m+1}$:

$$\ddot{v} + b_v v + 2du + du'' - \tfrac{2}{3}b_v v^3 - 4dv^2u - 4(b+c)vu^2$$
$$- \tfrac{4}{3}du^3 = 0;$$
$$\ddot{u} + b_u u + 2dv + dv'' - \tfrac{2}{3}b_u u^3 - 4du^2v - 4(b+c)uv^2 \tag{4}$$
$$- \tfrac{4}{3}dv^3 = 0.$$

Here parameters are $b_v = 4(-a + b + c) = 14$, $b_u = 4(a + b + c) = 24$, $d = 2(c - b) = 8$. We suppose relatively smooth changing of the orientation of the molecules. This means that derivations are relatively small: $v'', u'' \ll v', u' \ll v, u$. The system describes any nonlinear space- and time-dependent processes in the molecular chain for relatively large angular amplitudes.

(3) The attractive feature of the system (4) is symmetry in the coordinates v, u and the interaction parameters under pair exchange:

$$v, b_v \longleftrightarrow u, b_u. \tag{5}$$

We will explore this symmetry and the properties of the parameters in further simplification of the equations and investigation of nonlinear excitations.

3. Integral of the equations for an inhomogeneous chain

(4) With the aim of further progress, let us consider inhomogeneous stationary excitations when v and u depend on $x - Vt$. Here V is velocity. In dimensionless variables we have $v(\zeta), u(\zeta); \zeta = \xi - w\tau$. Here $w = v/v_0$ is the dimensionless velocity and $v_0 = R_0\omega_0$ is the characteristic one.

After introducing these coordinates the time-dependent terms are transformed into $\ddot{v} \to w^2v''$ and $\ddot{u} \to w^2u''$ where $v'' = \partial^2 v/\partial\zeta^2$ and $u'' = \partial^2 u/\partial\zeta^2$. Instead of the system of partial differential equations (4) we obtain the common differential one:

$$w^2v'' + b_v v + 2du + du'' - \tfrac{2}{3}b_v v^3 - 4dv^2u - 4(b+c)vu^2$$
$$- \tfrac{4}{3}du^3 = 0;$$
$$w^2u'' + b_u u + 2dv + dv'' - \tfrac{2}{3}b_u u^3 - 4du^2v \tag{6}$$
$$- 4(b+c)uv^2 - \tfrac{4}{3}dv^3 = 0.$$

The integral of this system still keeps symmetry, according to (5):

$$\frac{1}{2}w^2(v'^2 + u'^2) + \frac{1}{2}(b_v v^2 + b_u u^2) + 2dvu + dv'u'$$
$$- \frac{1}{6}(b_v v^4 + b_u u^4) - \frac{4}{3}dv^3 u - 8(b+c)v^2 u^2$$
$$- \frac{4}{3}dvu^3 = C. \tag{7}$$

4. Normal modes equations and solutions

(5) The variables v and u are entangled in the nonlinear system of equations (4) and (6). Besides different variables have the same or very close amplitudes for linear [8, 9] and nonlinear [10] excitations of the molecular chain. Meanwhile introduction of the normal coordinates [9] splits the linear system of equations for the chain oscillations into two independent subsystems of oscillations; amplitudes of the obtained normal modes differ considerably. The linear system of equations can be obtained by omitting cubic terms in the nonlinear equations (4) and (6).

Let us introduce a normal coordinates for the linear subsystem of equations (6). Then both quadratic forms for variables u, v and their derivations u', v' must be split in equations (6) and diagonalized in the integral (7). Operating with any of the equations (6) or (7) leads to the same result. We diagonalize the quadratic forms according [11]. The first step is diagonalization of the u', v' form. Let us introduce new variables by the coordinate rotation on the angle α_1. Their substitution into (7) diagonalizes the u', v' quadratic form for

$$u = \frac{u_1 + v_1}{\sqrt{2}}; \qquad v = \frac{u_1 - v_1}{\sqrt{2}}. \tag{8}$$

Then after transformation (finding their sum and difference), each of equations (6) contains only one second derivation. The second step is the space deformation of variables with the purpose of obtaining equal coefficients before derivations: $u_1 = u_2/\sqrt{w^2 + d}$; $v_1 = v_2/\sqrt{w^2 - d}$. As a consequence of this deformation any further rotations do not change the quadratic form of the derivations. The third step is rotation of coordinates on the angle α_3 which diagonalizes the u, v quadratic form. Coefficients before $u_3 v_3$ terms equal zero if the angle α_3 satisfies the condition

$$\cos 2\alpha_3 = \frac{G}{\sqrt{4(b_u - b_v)^2(w^4 - d^2) + G^2}};$$
$$G = (b_u + b_v - 4d)(w^2 + d) - (b_u + b_v + 4d)(w^2 - d). \tag{9}$$

As result of all transformations, the final view of equations (6) is:

$$v_3'' + \frac{1}{\lambda_+^2}v_3 - \frac{1}{3}b_{v3}v_3^3 + O(u_3) = 0;$$
$$u_3'' + \frac{1}{\lambda_-^2}u_3 + b_{uv2}u_3 v_3^2 + b_{u0v3}v_3^3 + O(u_3^2) = 0. \tag{10}$$

Here characteristic dimensionless lengths are

$$\lambda_\pm^2 = \frac{\sqrt{4(b_u - b_v)^2(w^4 - d^2) + G^2} \pm G_+}{4(b_u b_v - 4d^2)};$$
$$G_+ = (b_u + b_v - 4d)(w^2 + d) + (b_u + b_v + 4d)(w^2 - d). \tag{11}$$

The inequality $\lambda_+ \gg \lambda_-$ is satisfied. This means that normal variable v_3 is considerably softer than u_3 one. Therefore, a variation interval for v_3 is considerably wider than that for u_3: we can write an inequality $v_3 \gg u_3$ and neglect the higher powers $O(u_3)$ in equations (10). So the first equation in the nonlinear system (10) becomes independent. As one can see in relations (9), (11) and the definition of v_2, the obtained equations for nonlinear waves describe a situation with threshold velocity $w^2 > d$.

Coefficients $b_{v3}, b_{uv2}, b_{u0v3}$ before the nonlinear terms are very cumbersome to write here. Nevertheless, their physical sense is obvious. In the first equation, the term with coefficient b_{v3} describes nonlinearity of a soft normal mode with considerably large amplitude. In the second equation, the term with coefficient b_{uv2} slightly renormalizes the fast characteristic length λ_- (or frequency) in dependence on the slow variable v_3. In the second equation, the term with coefficient b_{u0v3} slightly shifts the equilibrium position of the fast oscillator u_3 in dependence on the slow variable v_3. According to the second equation of the system (10) the variable u_3 oscillates with a relatively small space period λ_- accounting for the influence of v_3.

The first equation in (10) can be transformed into a nonlinear Schrödinger one with well known solutions. The first equation in system (10) has negative parameter of nonlinearity, its periodic solution can be written according to [12] as

$$v_3(\zeta) = \frac{k\sqrt{g}}{4\delta_s} sn\left[\frac{g\zeta}{4\delta_s}, k\right]; \qquad k^2 = \frac{\gamma - \sqrt{\gamma^2 - \gamma_0^2}}{\gamma + \sqrt{\gamma^2 - \gamma_0^2}};$$

$$\delta_s = K(k) - E(k); \quad g = \frac{b_{v3}}{3}; \quad \gamma = \frac{3}{2b_{v3}\lambda_+^2}. \tag{12}$$

Here $K(k), E(k)$ are the complete elliptic integrals of the first and second order with elliptic module k, and $sn(x, k)$ is the elliptic sinus, γ_0^2 is the integral of equation (10a) which has the sense of energy. At $\gamma_0 \to \gamma$ for most of the time the molecules are far from the equilibrium positions (close to the saddle points of the effective potential [10]). At $\gamma_0 = \gamma$ the solution (12) transforms into a kink.

5. Conclusion

For the first time the nonlinear excitations close to the point of orientational melting were considered. We use the strong anisotropy of the molecular rotation on the plane of the angles ('valleys'). Building of the normal coordinates on the plane of the angles gives the possibility of splitting equations for linear and nonlinear molecular chain oscillations. The linear oscillations correspond to a stiffer subsystem and are stable. The nonlinear oscillations correspond to a softer subsystem and, therefore, easily reach an unstable states (bifurcation points of the dynamical system).

It would be interesting to apply the obtained results in the nonlinear dynamics of molecular crystals to investigate the thermodynamics and kinetic properties in regions close to orientational melting.

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