

7. Bustard, H. R., *Tiger Paper*, 1976, 3, 3.
8. Dash, M. C. and Kar, C. S. *The Turtle Paradise - Gahirmatha*, Interprint, New Delhi, 1990, p. 295.
9. Kar, C. S., *Tiger Paper*, 1982, 9, 6-7.
10. Pandav, B., Choudhury, B. C. and Kar, C. S., *A Status Survey of Olive Ridley Sea Turtle (*Lepidochelys olivacea*) and their Nesting Beaches along the Orissa Coast, India*, Wildlife Institute of India, Dehradun, 1994.
11. Pandav, B., Choudhury, B. C. and Kar, C. S., *Oryx*, 1997, 31, 32-36.
12. Pandav, B., Choudhury, B. C. and Kar, C. S., *Marine Turtle Newsletter*, 1994, 67, 15-16.
13. Bowen, B. W. and Witzell, W. N. (eds), *Proceedings of the International Symposium on Sea Turtle Conservation Genetics*, NOAA Technical Memorandum NMFS-SEFSC-396, 1996, p. 173.
14. Witherington, B. E. and Martin, R. E., *Understanding, Assessing, and Resolving Light-pollution Problems on Sea Turtle Nesting Beaches*, FMRI Tech. Rep. TR-2, Florida Marine Research Institute, St. Petersburg, Florida, 1996, p. 73.

Received 22 September 1998; accepted 24 September 1998

REVIEW ARTICLES

Non-equilibrium atomic dynamics in solids

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Atoms, molecules, electrons and impurities in solids are subjected to short-lived large energy fluctuations (SLEFs) arising from the background phonon-sea due to anharmonic interactions. These SLEFs arise from the 10-100 atoms situated within a few nanometer size volume surrounding the affected entity and have lifetimes of the order of a few picoseconds. The resulting dynamics is not in equilibrium with the remaining system over these space and time intervals; it results in unusual and fast atomic/cluster displacements and electronic transitions. The study of this 'fluctuations dynamics' has led to understanding 'abnormal' diffusion, desorption, chemical kinetics, ionic conductivity, etc. in solids especially in situations when the associated Arrhenius parameters are beyond the realm of conventional rate theory. This article reviews (a) advances made by the SLEF theory with a few examples drawn from literature and (b) results from computer experiments that reveal the microscopic nature of the fluctuations.

CONVENTIONALLY, the subject of 'lattice dynamics' deals with atomic and molecular vibrations in solids within the confines of harmonic approximation^{1,2}. Phonon spectra derived from theories of lattice dynamics and measured by experimental techniques of inelastic scattering of neutrons have played an important role in understanding the nature of various macroscopic thermodynamical properties of solids like specific heat, velocity of sound, thermal expansion, elastic moduli, temperature dependence of elasticity and thermal conductivity, etc. Equation of state of metals and alloys are

fairly predictable. In order to understand the temperature dependence of some of these properties one invokes 'quasi-harmonic approximation'. Phase diagrams of various systems are foreseen based on evaluation of the total energy of the systems as functions of temperature and pressure. However, many phenomena like evaporation, diffusion, viscosity or plastic deformation at high temperature, etc. cannot be understood within the scope of conventional lattice dynamics.

Frenkel studied this aspect of the subject by considering what is referred to as 'energy fluctuation dynamics'³, wherein the atoms and molecules in a solid possessing energy at least an order of magnitude greater than the average energy, as given by conventional dynamical approaches, were contemplated upon. His work has later on led to information concerning the nature of energy fluctuation of atoms in detail in terms of their temporal evolution, spatial localization and statistics. Another area that is influenced considerably is the study of heterophase fluctuations related to phase transitions^{3,4}.

In recent times Khait⁵ has provided a nanoscopic stochastic dynamic many-body theory of energy accumulation by an atom in any solid as a result of a directional flow of energy flux from the immediate causal nanometer environment of the atom during a time of the order of pico-seconds through correlated motion of the fluctuating atom and its surroundings consisting of a few tens or hundreds of atoms and electrons. (The dynamical treatment is in terms of interrelated statistical distribution functions governed by coupled integro-differential kinetic equations derived from the Liouville equation;

this brief review does not detail all the aspects covered in ref. 5.) It is difficult to investigate the details of this phenomenon, experimentally. However, computer simulation/experimental studies via molecular dynamics have thrown confirmatory light on this subject.

We shall review in this article some aspects of development of this subject, which deals with dynamics, essentially non-equilibrium in nature. The following section deals with the descriptive aspects of kinetic theory of short-lived large energy fluctuations (SLEFs) in solids. Salient features of the SLEF theory are outlined in the next section followed by results of a variety of experimental studies, which need one to go beyond conventional rate theory to the kinetic theory of SLEFs. The latter approach leads to a new understanding of 'abnormal' results. Computer experiments have confirmed various aspects of the transitory nature of the non-equilibrium atom dynamics and these results have helped in reconciliation of the 'anomalous' in terms of microscopic space-time behaviour of atoms in solids. The last section deals with a few chosen examples of these computer experimental studies followed by a summary.

Kinetic theory of short-lived large energy fluctuations (SLEFs) in solids

The energy of atoms in any condensed system does not deviate much, on an average, from the average kinetic energy, $3/2 kT$, where k is the Boltzmann constant and T the temperature of the solid. However, occasionally atoms do exhibit strong fluctuation in their kinetic energy. This fluctuation moves very fast, in the sense that the energy 'accumulation' (SLEF formation energy) is rather flash-like and the 'release of energy' (SLEF relaxation energy) is almost instantaneous. In a truly harmonic system, redistribution of energy between different normal modes is not allowed; hence the energy fluctuation in the system is a result of anharmonicity leading to interaction amongst various modes of the crystal. The energy fluctuations which are essentially energy/wave packets are believed to be of two types: (i) a transitory packet associated with one atom or (ii) a soliton-like migrating fluctuation. This model of energy fluctuation in solids has been confirmed by computer experiments.

The standard equilibrium theory of fluctuation and statistical physics are inadequate in case of short-lived large energy fluctuations of single atoms because of factors described in detail in ref. 5. The standard equilibrium statistical thermodynamics, describes mainly the behaviour of the majority of *particles* which determines averaged macroscopic parameters of subsystems containing a large number of atoms $N \approx 10^{10}$ to 10^{20} . Small fluctuations of such parameters, say, of thermal energy

$\Delta u_f = u_f - \langle u_f \rangle$, considered to be small corrections to the equilibrium values, are described by the probability density,

$$F(\Delta u_f) = \{1/\sqrt{(2\pi\sigma_u^2)}\} \exp\{-\Delta u_f^2/(2\sigma_u^2)\}. \quad (1)$$

Alternately, this equation can be written in the form,

$$f_1(\Delta \epsilon) = \{1/\sqrt{(2\pi\sigma_\epsilon^2)}\} \exp\{-(3N_f Z/2)(\Delta \epsilon/\langle \epsilon \rangle)^2\}, \quad (2)$$

where

$$\sigma_u^2 = \langle \Delta u_f^2 \rangle = 3N_f Z (kT)^2 \text{ and } \Delta \epsilon = \epsilon - \langle \epsilon \rangle = \Delta u_f / N_f, \\ \text{and } \langle \epsilon \rangle = \langle u_f \rangle / N_f = 3kZT. \quad (3)$$

Here σ_u^2 is mean square fluctuation energy, N_f the number of fluctuating particles involved, $3Z$ the number of degrees of freedom per particle, $\Delta \epsilon$ the energy fluctuation and $\langle \epsilon \rangle$ the mean thermal energy per particle.

This distribution of equilibrium statistical thermodynamics breaks down when $N_f \geq 1$ and $\Delta \epsilon_0 = \{\epsilon_0 - \langle \epsilon_0 \rangle\} \gg kT$ since, under these circumstances, the system is highly non-stationary. It may also be noted that equilibrium energy distributions neglect short-lived states of small minority of particles as they contribute negligibly to averaged macroscopic parameters. This is justified when one considers macroscopic parameters and their small fluctuations near mean values. However, these short-lived states involving a minority of particles can cause significant errors in calculated far-tails of such distributions and therefore in calculation of probability of occurrence of short-lived large energy fluctuations and short-lived large energy fluctuation-assisted processes.

Based on the vast amount of experimental data obtained in many fields, it is seen that behaviour of observed Arrhenius pre-exponential factors K_0 and activation energy ΔE in the Arrhenius equation,

$$K = K_0 \exp\{-\Delta E/kT\}, \quad (4)$$

that governs rate processes in solids and on their surfaces, cannot be explained by equilibrium rate theories. These include, for example,

(i) Self-diffusion of atoms at different temperature intervals along different crystallographic directions in materials such as Bi, Se, S, white phosphorus, α -Fe, γ -Fe.

(ii) Impurity diffusion of atoms of Ag, Mo, Sb, etc. in α -Fe, Ba in BaO, etc.

K_0 covers many orders and even tens of orders of magnitude. An empirical relation like

$$K = K_{00} \exp(g\Delta E^{\gamma}) \exp(-\Delta E/kT) \text{ with } \gamma \neq 1, \quad (5)$$

has explained such discrepancies by sometimes redefining K_0 . K_{∞} and γ are assumed to be temperature independent. This equation is referred to commonly as 'compensation effect' equation.

Vast literature exist that provide a database from which one can note several other discrepancies similar to what are given above⁶. The kinetic many-body theory of short-lived large energy fluctuations and associated rate processes based on quasi-classical physics has provided the basis through which a new understanding of the underlying mechanisms that control the rate processes has emerged. One can now rationalize and narrow down the differences between theoretical results and experimental data.

One of the important consequences of appearance of a short-lived large energy fluctuation in a solid is that it induces large transient coordinate fluctuations (LTCFs) of atoms. Some atoms can come close together and form transient local atomic clusters of pico-second lifetime; so much so that the inter-atomic distances are substantially smaller than the average distance between the atoms. Under these circumstances,

(i) the atoms can participate in reactions impossible otherwise, or

(ii) local transient point defects of pico-second lifetime can be formed, and

(iii) it is also noted that when large amplitude motions of individual atoms occur as a result of large energy associated with the SLEF, even electronic transitions can occur as in SLEF-assisted tunnelling processes which do not occur in the absence of SLEFs.

Salient features of SLEF theory

Some atoms in a solid at any temperature and at any instant of time come to possess SLEFs as is confirmed now by molecular dynamics studies. Referring to Figure 1, these energy fluctuations $\epsilon_{op} \gg kT$ and the SLEF lifetime $\Delta\tau = \tau_1 + \tau_2$. τ_1 is the SLEF formation time and τ_2 , the SLEF relaxation time. t_f , the mean time between two successive SLEFs is $\gg \Delta\tau$. τ_1 and τ_2 are typically of order of 10^{-13} s. During τ_1 , the strongly fluctuating atom receives thermal energy $\epsilon_{op} \gg kT$ from its immediate neighbourhood in nanometer vicinity of volume Ω_1 given by, $\Omega_1 = 4\pi/3\{(\rho_0 + l)^3 - \rho_0^3\}$ and radius $R_1 = \rho_0 + l$ which contains $\Delta N_1 = (\Omega_1/\Omega_0) \gg 1$ atoms. ρ_0 is the radius of volume $V_0 = 4\pi\rho_0^3/3$ occupied by the strongly fluctuating atom and Ω_0 , the average volume per atom. Here $l = c_0\tau_1$ is the maximum distance from which thermal energy ϵ_{op} can be delivered to the fluctuating atom during the time τ_1 ; c_0 is the energy transfer velocity in the atomic system typically of the order of sound velocity say, 6×10^5 cm/sec. The times τ_1 and τ_2 are given by,

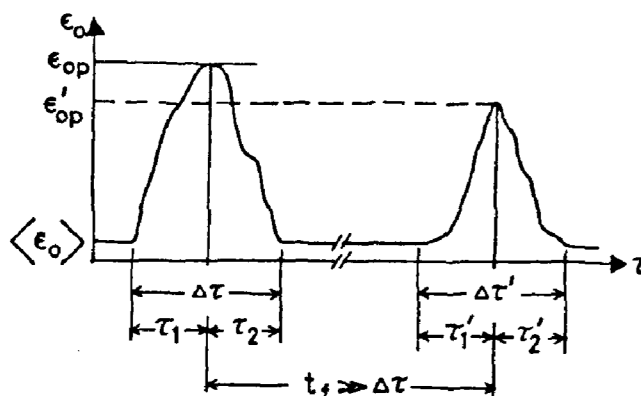


Figure 1. Schematic diagram of energy ϵ_0 versus time for two successive SLEFs of lifetimes $\Delta\tau$ and $\Delta\tau'$. $\Delta\tau = \tau_1 + \tau_2$, τ_1 is the SLEF formation time and τ_2 , the SLEF relaxation time. t_f is the mean time between the two successive SLEFs. $\langle\epsilon_0\rangle$ is the average thermal energy. ϵ_{op} and ϵ'_{op} are the peak SLEF energies of the two SLEFs.

$$\tau_1 \approx \tau_2 = B\{h/(\kappa k\Theta)\} \sqrt{\{\epsilon/(k\Theta)\}}, \quad (6)$$

where κ is the effective nearest number of neighbours, l a parameter ≈ 1 when the mass of the fluctuating particle (atom) is approximately equal to the mass of the neighbouring atoms. The SLEF probability per unit time and per atom is of the form,

$$W_f = (1/t_f) = (1/\Delta\tau) \exp\{-\epsilon_{op}/(kT)\}, \quad (7)$$

where t_f is the mean time between two successive SLEFs of peak thermal energy ϵ_{op} of the same atom. SLEFs of peak energy $\epsilon_{op}^{(m)}$ occur m times amongst ν atoms in a time τ_E if $\epsilon_{op}^{(m)}$ satisfies the relation,

$$\epsilon_{op}^{(m)} = kT \ln \{(\nu\tau_E)/(m\Delta\tau)\}, \quad (8)$$

with $m = 1, 2, \dots$ and $\tau = 1, 2, \dots$

The rate coefficient of SLEF induced thermally activated processes is given by,

$$K = K_0 \exp\{-E/(kT)\}, \quad (9)$$

where $K_0 = 1/\Delta\tau$ and $\epsilon_{op} > E > kT$. This equation is similar to that in conventional rate theory.

It should be noted that eqs (8) and (9) are obtained on the basis that only atomic vibrations are responsible for SLEF formation. However SLEF formation or relaxation may be associated with local atomic and electronic rearrangements. Under these circumstances, the local SLEF time inversion symmetry can be broken and SLEF probability can change considerably and is given by⁷,

$$W_f' = \exp\{\delta S/k\} \exp\{-(\epsilon_{op} + \delta E_1)/(kT)\}, \quad (10)$$

where δS is the change in local configurational entropy and δE_1 is the energy change associated with the atomic and electronic rearrangements.

The rate coefficient (probability per sec.) is now given by,

$$K = K_{00} \exp\{\delta S/k\} \exp\{-(E + \delta E_1)/(kT)\}, \quad (11)$$

for energy barriers of height $E \gg kT$. The effective measured activation energy and pre-exponential factors are $\Delta E = E + \delta E_1$ and

$$K_0 = K_{00} \exp\{\delta S/k\}. \quad (12)$$

Here $K_{00} = 1/\Delta\tau$.

Equations (11) and (12) enable one to explain a wide range of experimental data in thermally activated rate processes associated with *observed compensation effect* and abnormally large and small Arrhenius activation energies and pre-exponential factors found in several experimental studies of diffusion in solids, desorption, ionic conductivity, etc. Electronic effects are associated in this formalism, since δE_1 are related to electronic transition energies. Equations (10) and (11) show how SLEF based theory is an improvement over conventional rate theories that lead to results with large discrepancies in comparison with experimental data. The SLEF theory as given by eqs (10) to (12) give results in agreement with experimental data containing large compensation effects satisfactorily.

SLEF based analysis of experimental data

The initial observations of anomalous diffusion parameters referred to earlier in this article, led to development of SLEF theory based only on atomic vibrations. Subsequent studies, based on atomic vibrations and associated transient non-adiabatic electronic transitions, have satisfactorily explained observed abnormally small to abnormally large diffusion of atoms in several systems determined through a variety of experimental techniques, in different temperature intervals and under doping conditions. In this section we summarize results of a few of these studies.

Atomic diffusion in Si and Ge

Self-diffusion in Si, in the temperature range 1100–1600 K and that of Ge in the temperature range 950–1200 K have been studied by Borg and Dienes⁸ and that of Ge in Si in the temperature range 1400–1650 K by Handjicantis *et al.*⁹ and McVay and Ducharme¹⁰. The diffusion coefficient in the conventional diffusion theory is given by,

$$D = D_0 \exp\{-\Delta E/(kT)\}, \quad (13)$$

where D_0 is temperature independent pre-exponential factor and ΔE the diffusion activation energy. ΔE^{obs} and D_0^{obs} for self-diffusion in Si and Ge cover a broad range.

$$\begin{aligned} \Delta E_{\text{Si}}^{\text{obs}} &= 4.1 \text{ to } 5.13 \text{ eV}, \Delta E_{\text{Ge}}^{\text{obs}} = 2.6 \text{ to } 3.8 \text{ eV}, \\ D_0^{\text{obs}}_{\text{Si}} &= 8 \text{ cm}^2/\text{s} \text{ to } 9 \times 10^3 \text{ cm}^2/\text{s}; \\ D_0^{\text{obs}}_{\text{Ge}} &= 0.18 \text{ cm}^2/\text{s} \text{ to } 2.5 \times 10^4 \text{ cm}^2/\text{s}. \end{aligned}$$

The change in D_0 is as much as 10^5 when experimental conditions (temperature, sample and doping) change. The correlation between the activation energy and pre-exponential factor is empirically given by,

$$\ln D_0 = a\Delta E + c. \quad (14)$$

This linear dependence is referred to as compensation effect. The origin of the observed large variation in D_0 and ΔE as well that of the compensation effect is not clear within the framework of conventional theories.

The experimentally observed diffusion is modelled¹¹ in terms of a large number of SLEF-induced electron affected microscopic diffusion events. During the lifetime of the SLEFs, the fluctuating atom may receive enough energy to hop to neighbouring sites and initiate the diffusion process. In addition, electronic transitions in the nanometer vicinity of the SLEF-affected atom can take place in the valence and mobile electrons/holes. One can even consider local pico-second fluctuations in the temperature of the medium in the immediate vicinity. When these latter phenomena coincide with the SLEF-induced diffusion event, they can influence ΔE and D_0 considerably.

The diffusion coefficient for this kinetic SLEF-based and electron-assisted process is given by¹¹,

$$D = (\rho^2/6\Delta\tau) \exp\{-\Delta G/(kT)\}. \quad (15)$$

Here ρ is the diffusion jump distance nearly equal to the interatomic distance, ΔG the effective activation energy $E + \delta E - T\delta S$, with E the energy of the SLEF-affected atom, δE energy change due to the electronic transitions and δS the change in the local configurational entropy. The pre-exponential factor is now given by,

$$D_0 = (\rho^2/6\Delta\tau) \exp\{-\delta S/k\}. \quad (16)$$

Without going into further details, it may be stated that the modified pre-exponential factor and the activation energy are reconcilable with observed D_0^{obs} and ΔE^{obs} .

The theory¹¹ has also established experimentally verifiable relation between ΔE and D_0 on the one hand and the independently measured melting point T_m and melting entropy ΔS_m on the other. Coefficients a and c occurring in compensation effect are expressible in terms of T_m and ΔS_m in good agreement with experimental data.

Desorption of hydrogen from amorphous silicon (a-Si)

Hydrogenated amorphous silicon, denoted as a-Si:H possesses useful technologically important properties that are not found in pure a-Si, because of the high concentration of unsaturated dangling bonds in the latter. At a high temperature, hydrogen can get desorbed leading to deleterious effects in a-Si:H used in devices. The desorption process is controlled by the rate coefficient K given by,

$$K = K_0 \exp\{-\Delta E/(kT)\}, \quad (17)$$

where K_0 is the Arrhenius pre-exponential factor and ΔE the activation energy. Doping of a-Si:H also influences the rate of evolution of hydrogen. Khait *et al.*¹² have studied experimentally hydrogen effusion of doped and undoped a-Si:H at low substrate temperatures and obtained ΔE^{obs} and K_0^{obs} for hydrogen desorption. These vary over a very wide range,

$$\Delta E^{\text{obs}} = 0.3 \text{ eV to } 2.1 \text{ eV and } K_0^{\text{obs}} = 1 \text{ s}^{-1} \text{ to } 10^{15} \text{ s}^{-1},$$

whereas one expects 'normal' $K_{0,\text{norm}}$ to be nearly equal to 10^{13} to 10^{12} s^{-1} for desorption and a 'normal' $\Delta E_{0,\text{norm}} = 2 \text{ eV}$ for breaking a Si-H bond. The values ΔE^{obs} and K_0^{obs} can be related to each other by the compensation effect given by the empirical relation

$$\ln K_0^{\text{obs}} = c + a\Delta E^{\text{obs}}, \quad (18)$$

Khait *et al.*¹² have taken into account SLEF-related kinetic atomic and electronic processes and obtained the rate coefficient K given by,

$$K = (1/\tau_1) \exp(\delta S/k) \exp\{-\Delta E/(kT)\}, \quad (19)$$

without invoking equilibrium rate theory, but still formally similar to the rate coefficient K given by the equilibrium rate theory.

The Arrhenius activation energy ΔE and pre-exponential factor $K_0 = (1/\tau_1) \exp(\delta S/k)$ are expressed in terms of local parameters that characterize atomic and electronic processes induced by SLEFs of surface atoms. These processes occur in the vicinity of a desorbed H_2 molecule during the desorption event. Thereby these authors were able to explain the 'abnormally' large observed variations in the pre-exponential factors K_0 (nearly 15 orders of magnitude) and in the activation energy ΔE (by a factor of 7) caused by dopant variation but at low substrate temperatures. The kinetic compensation effect follows as a natural corollary.

Stability of a-Si and related materials

Khait and Weil¹³ have investigated the problem of crystallization kinetics in a-Si related materials and the deleterious effects of amorphous to crystalline transfor-

mation in devices based on amorphous materials. Effects of metal-contacts on material stability are of technological interest. Another related problem is crystallization of Si and Ge layers in Si_nGe_m superlattices disordered by ion implantation which was studied by Freiman *et al.*¹⁴

One of the important experimental observations is that the temperature dependence of the 'incubation time' (the delay in nucleation of crystallization) t_N and the rate coefficient for this process K_N are described by Arrhenius equations,

$$t_N = t_{0N} \exp\{+\Delta E/(kT)\} \text{ and}$$

$$K_N = 1/t_N = K_{0N} \exp\{-\Delta E/(kT)\}. \quad (20)$$

The activation energy ΔE and the pre-exponential factor K_0 found from experimental data cover a wide range

$$t_{0N} = 1.43 \times 10^{-12} \text{ s to } 7.2 \times 10^{-12} \text{ s} \\ \text{and } \Delta E = 0.4 \text{ to } 3 \text{ eV.}$$

Normally the pre-exponential factor $t_{0,\text{NORM}} = 10^{-13}$ to 10^{-12} s and $\Delta E_{0,\text{NORM}} = 2.5$ to 2.7 eV . Once again, as in earlier cases given above, K_{0N} and ΔE can be expressed by a compensation effect relation namely,

$$\ln K_{0N} = a\Delta E + c, \quad (21)$$

where a and c are empirical fitting parameters assumed to be independent of temperature. The conventional rate theory has failed to explain the wide range of experimental pre-exponential factors and activation energies as well as the compensation effect equation.

The dynamical semi-phenomenological approach, based on kinetic many body electron related theory of SLEFs and corresponding theory of SLEF-induced thermally activated rate processes in solids, has enabled Khait and Weil¹³ to calculate t_{0N} , ΔE and coefficients a and c (expressed in terms of material characteristics, namely bulk modulus and melting point) in agreement with experimental data. In formulating this approach, the authors have assumed that the formation of crystallization nuclei in a meta-stable disordered material, namely the amorphous material, is associated with a small number $\nu_A \geq 1$ of SLEF-induced 'diffusion' like jumps of Si atoms within $\Delta\tau$ over energy barriers to occupy more ordered positions. In addition to these atomic jumps, they considered rotation-like jumps of some 5 to 10 atoms around sites to more ordered states. These jumps are accompanied by electronic transitions in the vicinity of hopping atoms. The metal contacts with metals that do not form silicides can enhance the number of mobile carriers at the metal/semiconductor interface which in turn decrease ΔE and increase K_0 in agreement with experimental data. Metals that form silicides decrease the rate of crystallization. By detailed analysis, the authors have shown how to calculate Arrhenius parameters in the environment of local non-equilibrium

fluctuations in terms of material parameters and were able to find good agreement with experimental data. The compensation effect equations are given by,

$$\ln t_{0N}^{-1} = 9.17\Delta E \text{ (eV)} - 1.03,$$

for nucleation time and

$$\ln D_0 = 9.17\Delta E \text{ (eV)} - 35.55, \quad (22)$$

for diffusion coefficients in agreement with experimental observations.

In addition, the theory has also led to some experimentally verifiable predictions.

Anomalous impurity atom dynamics observed in Mössbauer spectroscopy and X-ray absorption fluorescence spectroscopy (XAFS)

XAFS experiments on Hg in Pb, and Mössbauer experiments of solid solutions of Sn in Pb, Ag and Au¹⁵ have revealed abnormal temperature dependence of XAFS spectra and of Mössbauer spectra at a certain temperature T_0 , substantially lower than the melting point of the host metal. The Mössbauer intensity varies logarithmically linearly with T at low temperatures as expected for harmonic vibrations. As the temperature increases the alloys show spectacular concentration and temperature dependence of intensity, the intensity falling rather precipitously. The spectral intensity falls below the expected Debye–Waller factor behaviour, namely,

$$f_M = \exp\{-Q\gamma^2\sigma_A^2\}, \quad (23)$$

where Q_γ is the wave-vector of the γ -photon and σ_A , the root mean square displacement of the impurity atom. At the T_0 s, impurity atoms are not expected to show any anomalous diffusion or unusual anharmonic behaviour. The intensity drop-off rate increases substantially beyond T_0 .

In order to examine these observations theoretically, the kinetic theory based on SLEFs associated with the impurity atoms and associated electronic transitions have been taken into account¹⁶. The SLEFs cause transient atomic displacements much larger than average atomic displacements but insufficient to cause impurity diffusive jumps within nanometer surroundings. The temperature dependence of Mössbauer spectral intensity is given by a new expression,

$$f_M(\Delta E_{ef}, T) = [1 - (\kappa + 1)\exp\{-\Delta G/(kT)\} \exp\{-Q\gamma^2\sigma_A^2\}], \quad (24)$$

which sets a lower limit to the SLEF-induced reduction of the Mössbauer spectral intensity. Here, ΔE_{ef} is the electron-affected activation energy, a sum of SLEF energy and local energy change due to electronic transitions and κ the number of nearest neighbours of the

impurity atom. $\Delta G_{ef} = \Delta E_{ef} - T\Delta S_{ef}$, with ΔS_{ef} being the electron-affected entropy change. Secondly, the SLEF-based theory is able to predict the critical temperature and concentration of impurities around which the anomalous intensity variation in Mössbauer spectra are observed. A notable feature of the related discussion pertains to the reversible nature of SLEFs involved and how they take part in percolation-like process in initiating the macroscopic observation of Mössbauer spectral intensity variation around T_0 .

Reduction of radiation damage in the presence of weak magnetic fields

Ion-implantation techniques have been used to effect changes in the material characteristics of semiconductors and high-temperature superconductors in recent times. Some efforts are directed to examine the nature of radiation damage that may occur during this process. Khait and Richter¹⁷ have considered the effects of weak static magnetic fields of strength 0.7 to 2 kOe on the semiconductor Hg–Cd–Te and in Sb bombarded by ions of moderate energy (200–400 keV) and ion dosage (10^{11} – 10^{13} cm⁻²). The post-irradiation radiation damage decreases by a factor of nearly 2 in these materials, in the presence of the magnetic field as confirmed by Rutherford back-scattering and X-ray diffraction studies. These experimental results are examined in the light of SLEF theory modified to take into account perturbations to local electron transport due to the weak magnetic field. The local electron transitions in the nanometer vicinity of fluctuating atoms reduce exponentially point defect formation and migration rates and this decreases the radiation damage. On the other hand, the post-irradiation damage in superconducting ceramics irradiated at room temperature can increase and change material properties.

Computer experiments (molecular dynamics)

Computer experiments relating to molecular dynamics are a very standard and powerful tool to study atomic or molecular dynamics in solids and liquids. A few such computer experimental studies have been undertaken to investigate the predictions of kinetic theory based on the concept of SLEF of individual atoms outlined in earlier sections. In other studies carried out without any knowledge of SLEF phenomena, one has observed closely similar results. Without going into the methodology, we summarize some results of both types of studies.

Studies of a-Si

In a detailed study by Silverman *et al.*¹⁸, an amorphous silicon (a-Si) system containing 256 Si atoms along with

a single fluorine atom was investigated using two-body and three-body F-F inter-atomic potential¹⁹ and the Si-F inter-atomic potential²⁰ both proposed by Stillinger and Weber. This sample was studied over a time equivalent to physical time of 2×10^{-11} s and the molecular dynamics integration time was 10^{-15} s $\ll 10^{-13}$ s, the characteristic atomic vibrational period. The objective of the study was to monitor the time evolution of coordinates of F and Si atoms to elucidate details of diffusion and ultimately the desorption of F from the a-Si surface. In these studies, the (first reported) short-lived fluctuations of spatial coordinates LTCFs of both F and of some Si atoms were observed. Two types of LTCFs were seen, one associated with an irreversible diffusion like displacement of F atoms over distances of the order of 1 Å. In some cases these were found to result in diffusion and as per SLEF theory could lead to re-crystallization of a-Si. In the second type of LTCFs, the displaced atom returns to its initial position after SLEF-induced LTCF of duration Δt ; these reversible displacements can induce a transient nonlinear motion of the fluctuating atom and 'mixing' of different types of vibrational modes. Figure 2 (from ref. 21) shows typical results observed. Both these types of LTCFs have been related to predictions based on the SLEF theory.

Study of 1-dimensional chain of atoms

Slustsker *et al.*²² have studied a 1-dimensional chain of atoms using a Morse type of potential of interaction

between atoms to examine various aspects of 'fluctuation dynamics'. They have investigated maximum energy of a fluctuation (separately, kinetic, potential and their sum), lifetimes of the fluctuation state of atoms, size of the fluctuation region, migration of fluctuations, etc. Since the studies are related to a 1-dimensional system, some of the results may be arch-typical. Special attention has been paid to the mechanism of formation of energy fluctuation. An interesting aspect of results of these studies is the space-time diagram of the atoms in the chain in the presence of a SLEF. Figure 3 (from ref. 22) shows the magnitude of the fluctuations of the total energy of atoms in the presence of one of the SLEFs as a function of time.

Nature of energy fluctuations (SLEFs) and coordinate fluctuations (LTCFs) in Pd-D

Rao and Chaplot²³ have reported investigation of SLEFs and LTCFs in a Pd-D lattice. The inter-atomic potential considered has Coulombic and short-range repulsive interactions, the parameters of which were obtained by relating calculated phonon dispersion relation of the system to neutron inelastic scattering data. In their computer experiments in a Pd-D lattice containing about 800 atoms at 300 K, Rao and Chaplot observed spontaneous, frequent but irregular occurrence of SLEFs of different energies, the largest of them being 20 times

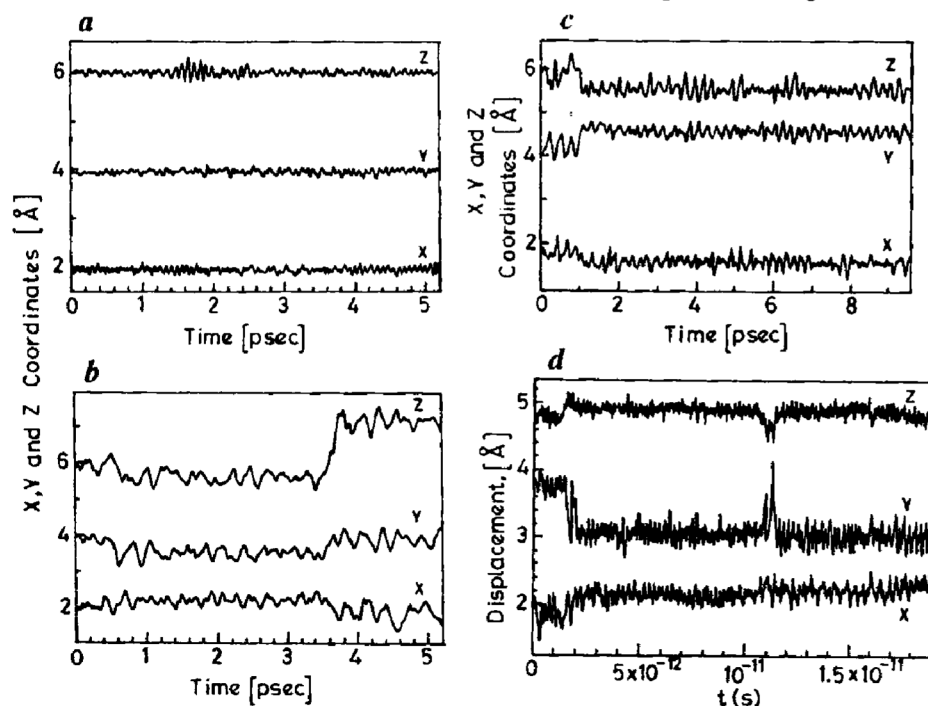


Figure 2. Space-time behaviour of (a) a silicon atom under 'normal' equilibrium fluctuation condition; (b) a silicon atom exhibiting LTCF at 3.5 psec as a consequence of occurrence of a SLEF; (c) another silicon atom exhibiting LTCF at 1.1 psec as a consequence of occurrence of a SLEF; (d) two different types of LTCFs are exhibited by a fluorine atom at 1.5 and 11×10^{-12} s (from ref. 2).

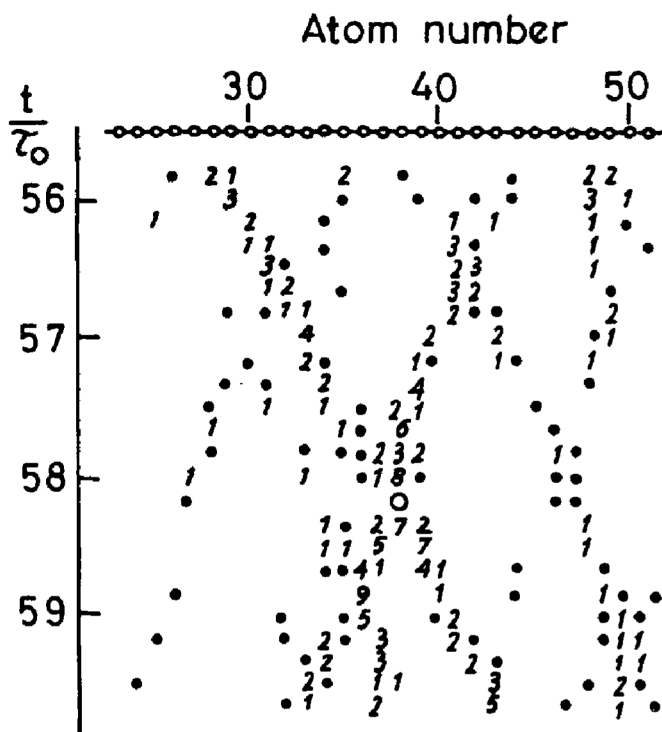


Figure 3. Space-time diagram of the total energy of atoms in a one-dimensional model with 100 atoms. E_n denotes the magnitude of the fluctuation of the total energy of an atom. Blank: $E_n < 1.5$ kT (\bullet): $E_n = (1.5 \text{ to } 2.0)$ kT; 1, $E_n = (2.0 \text{ to } 2.5)$ kT; 2, $E_n = (2.5 \text{ to } 3.0)$ kT; 3, $E_n = (3.0 \text{ to } 3.5)$ kT; 4, $E_n = (3.5 \text{ to } 4.0)$ kT; 5, $E_n = (4.0 \text{ to } 4.5)$ kT; 6, $E_n = (4.5 \text{ to } 5.0)$ kT; 7, $E_n = (5.0 \text{ to } 5.5)$ kT; 8, $E_n = (5.5 \text{ to } 6.0)$ kT; 9, $E_n = (6.0 \text{ to } 6.5)$ kT; o, $E_n > 7.0$ kT (from ref. 22).

as large as the average kinetic energy of atoms. Anomalous close encounters of atoms wherein inter-atomic distances decrease by as much as 1 to 1.5 Å were also observed. Typical energy fluctuations above 400 meV and representative pattern of coordinate fluctuations from this study are shown in Figure 4.

Simulation studies of glasses

(i) Sanyal and Sood²⁴ have carried out Brownian dynamics simulation experiments on binary colloidal mixture of particles containing 512 particles of two different diameters interacting via a repulsive DLVO potential. These studies are somewhat different from other studies since the space and time scales are quite different. The particle sizes are 545 Å and 1100 Å and the time step for integration is (3 to 7) 10^{-6} s. One of the results reported in this work is that of individual particle motions as a function of time. They noted four types of particle motions: vibrations of particles around local potential minima; hopping of particles by about inter-atomic distances to one of the neighbouring positions and persisting there till the end of simulation run; hopping of some particles to new positions and staying there for a short

while before hopping back to its original position; and motion similar to that in the third case but residence time in the hopped position being high. Figure 5 (from ref. 24) is a typical example of results from this study. These motions observed by Sanyal and Sood²⁴ are remarkably similar to the two types of motions observed by Khait *et al.*²¹. However, Sanyal and Sood have not examined the nature of the energy fluctuations. On the other hand, they have noted that a few particles have executed *jump motions cooperatively* at the same time and the particles persist in their new position for nearly 0.5 s before they hop back to their initial positions.

(ii) Miyazawa *et al.*²⁵ have investigated the dynamical aspects of glass transition by molecular dynamics (MD) simulations of equi-molecular soft-sphere mixtures with 500 atoms interacting through purely repulsive soft sphere potential,

$$V_{\alpha\beta}(r) = \epsilon \sqrt{(\sigma_{\alpha\beta}/r)}, \quad (25)$$

where $\sigma_{\alpha\beta} = (\sigma_{\alpha} + \sigma_{\beta})/2$ with $\alpha, \beta = 1, 2$. σ_1 and σ_2 are diameters of the two spheres of atoms. They could observe three types of jump motions of atoms: certain atoms jump to near neighbour local minima, remain there for nearly 20 MD time-steps and then return to their original positions; some atoms leave their positions without returning during the time scale of the MD simulation; and strongly correlated coordinated jump of several atoms jumping at successive times by permuting their positions. These are also the types of LTCFs noted by Khait *et al.*²¹ and Sanyal and Sood²⁴. However, Miyazawa *et al.*²⁵ have 'averaged' out all short time fluctuations calling them 'thermal noises'. In my opinion, they have missed the fundamental SLEF aspects in this process.

(iii) Wahnstrom²⁶ has also obtained similar results in his MD study of a supercooled two-component Lennard-Jones glassy system.

In this paper we have reviewed some of the features related to 'fluctuation dynamics', a concept aired for the first time by Frenkel in 1930s but followed extensively recently by several other studies. Notably, Khait and his coworkers have formulated the kinetic theory of rate processes based on SLEF dynamics of atoms and electrons in a variety of solids. The fluctuations are confined to nanometer vicinity of very few fluctuating atoms that can trigger electronic transitions up or down in a very short time scale of order of 10^{-12} to 10^{-13} s. These non-equilibrium dynamics of atoms and electrons can affect various processes like diffusion, effusion, crystallization, conductivity, compensation effect, etc. The theoretical analysis has helped in explaining many anomalous experimental observations in a variety of fields in physics and chemistry quantitatively.

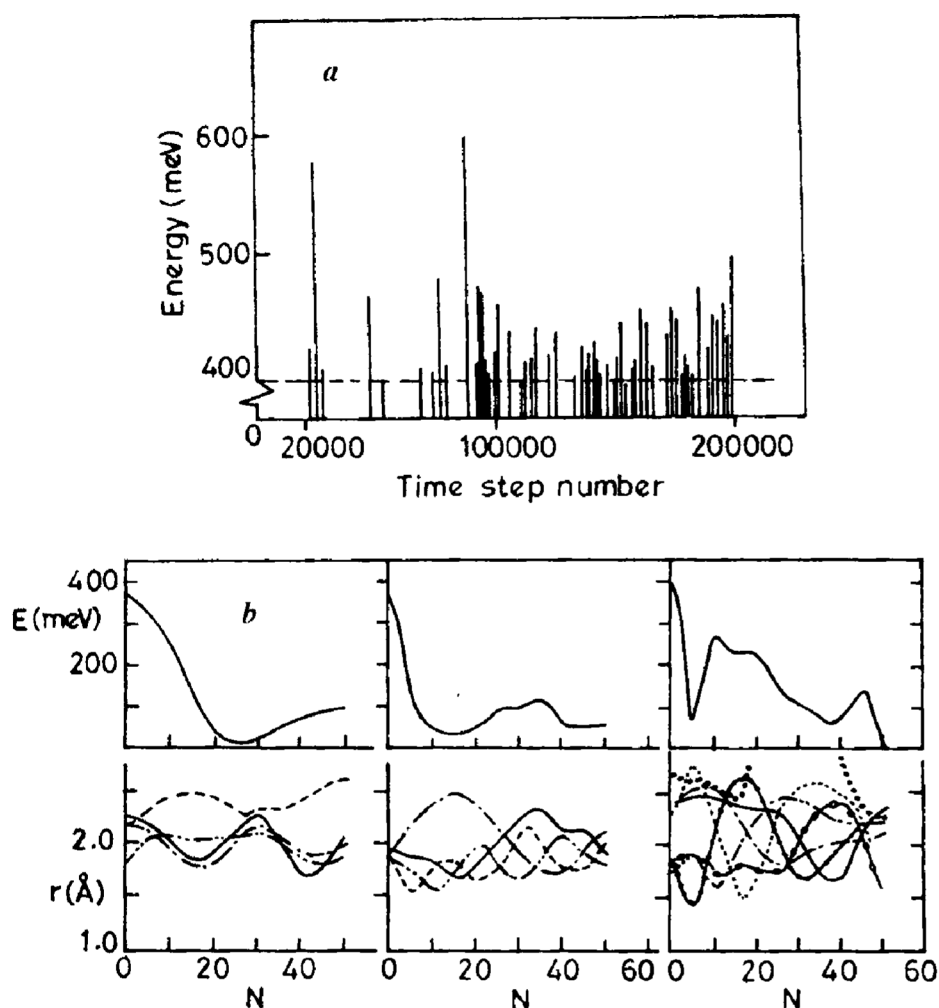


Figure 4. *a*, Temporal sequence of various SLEFs observed in a Pd-D system at 350 K in psec for energies > 390 meV; *b*, Three random SLEFs observed in a Pd-D system at 350 K. The upper row shows SLEF relaxation parts only as a function of N , the number of time steps in the computer experiment; the lower row shows corresponding LTCFs of atoms neighbouring the one associated with the SLEFs (from ref. 23).

This brief review could not go into detailed theoretical aspects given especially in ref. 5. It is important to comprehend that one of the key ideas of SLEF theory is that the study or application of individual SLEF's of even a single atom requires taking into account the transient correlated many-body behaviour of the causal nanometer environment of the fluctuating atom that includes tens or hundreds of atoms and electrons. The reader, who is interested in applications of the theory to particular materials and processes, may note that the final relations for SLEF-generated rate processes are simple and easy for applications; they are Arrhenius-like equations used along with some phenomenological parameters describing the dynamic behaviour of multi-atomic clusters of particles. There are many examples of such applications available in literature (see refs 5 and

11–17). We hope that this review will encourage readers for new investigations.

Computer simulation (molecular dynamics) studies, in a variety of materials like semiconductors, alloys and glassy systems, have not only revealed the presence of SLEFs and LTCFs in these systems – and such is the nature in any condensed matter system – but also led to the study of details of space-time behaviour of these exotic fluctuations.

Although the topic of 'fluctuation dynamics' dates back to about a century – for it is stated, that the initial suggestion is due to Boltzmann – it appears that not enough attention is paid to look at systems close enough, on truly microscopic space-time scales where and when the participants have not equilibrated. Further scope exists for making use of some of

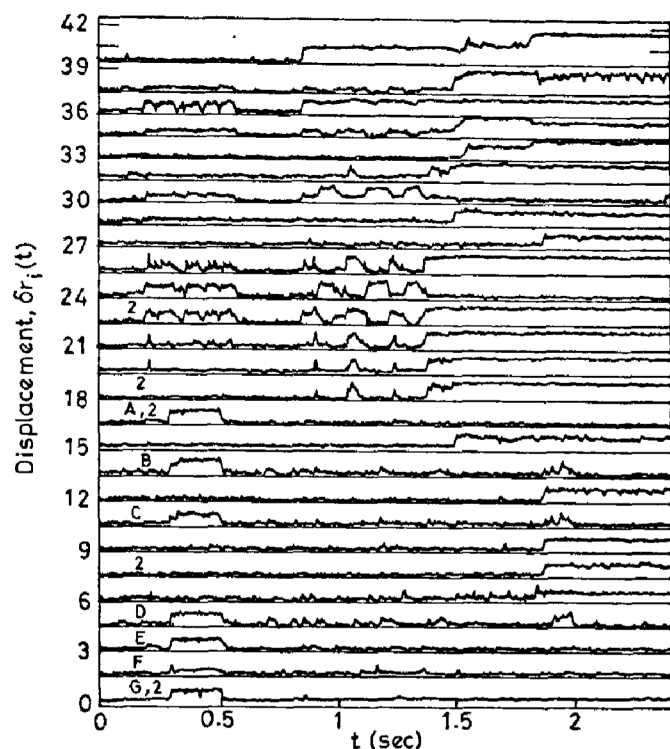


Figure 5. Individual particle motions studied by noting $\delta r_i(t) = r_i(t) - r_i(0)$ for a few representative particles in a simulation run. Maximum δr_i^{\max} decreases from top to bottom. Curves are shifted vertically by some multiple of the average inter-particle distance. Panels marked 2 are heavier particles and the rest are lighter particles. Note the particles A to G have executed jump motions cooperatively. Other types of motions described in the text can also be noted (from ref. 24).

these ideas in relating to and understanding many phenomena that seem to be 'anomalous' or depart from the ordinary.

1. Born, M. and Huang, K., *Dynamical Theory of Crystal Lattices*, Clarendon, Oxford, 1954.
2. Venkataraman, G., Sahni, V. C. and Feldkamp, K., *Dynamics of Perfect Crystals*, MIT Press, 1974.
3. Frenkel, Ya. I., *Kinetic Theory of Liquids*, Clarendon, Oxford, 1946.
4. Yukolov, V. I., *Phys. Rep.*, 1991, **208**, 395.
5. Khait, Yu. L., *Phys. Rep.*, 1983, **99**, 237; Khait, Yu. L., *Kinetics and Application of Atomic Diffusion in Solids - Nanoscopic*

Electron-affected Stochastic Dynamics, Scitec Publications Ltd, Brandrain, Switzerland, 1997, vol. 53.

6. Series of books on *Diffusion Rate and Defect Data* (ed. Wholbeir, F. N.), Trans. Tech. Publ., Ohio, 1967-1973; *Diffusion and Point Defects in Semiconductors* (ed. Boltacks, V. I.), Nauka, Moscow, 1972; Gutman, F. and Lyons, L. E., *Organic Semiconductors*, Wiley, New York, 1967.
7. Khait, Yu. L., in *Recent Progress in Many Body Theories* (eds Kallio, A. J., Pajanne, E. and Bishop, R. E.), Plenum, New York, 1988, vol. 1, p. 357.
8. Borg, R. G. and Dienes, G. J., in *An Introduction to Solid State Diffusion*, Academic Press, New York, 1990.
9. Handjicantis, V., Londos, C. A. and Eftakias, K., *Phys. Status Solidi*, 1988, **A105**, K-87.
10. Mcvay, G. L. and Ducharme, A. K., *Phys. Rev.*, 1974, **B9**, 627.
11. Khait, Yu. L., Besserman, R., Shaw, D. and Dettmer, K., *Phys. Rev.* 1994, **B50**, 14893.
12. Khait, Yu. L., Weil, R., Beserman, R., Beyer, W. and Wagner, H., *Phys. Rev.*, 1990, **B42**, 9000.
13. Khait, Yu. L. and Weil, R., *J. Appl. Phys.* 1995, **78**, 6504.
14. Freiman, W., Beserman, R., Khait, Yu. L., Shaanan, M., Dettmer, K. and Kessler, F. R., *Phys. Rev.*, 1993, **B48**, 2282.
15. Haskel, D., Shechter, H., Stern, E. A., Newville, N. and Yakoby, Y., *Phys. Rev.*, 1993, **B47**, 14032 and other references cited therein.
16. Khait, Yu. L., Snapiro, I. B. and Shechter, H., *Phys. Rev.*, 1995, **B52**, 9392.
17. Khait, Yu. L. and Richter, V., *J. Phys. D Appl. Phys.*, 1993, **26**, 1806; Khait, Yu. L., *Nucl. Inst. Meth.*, 1996, **B116**, 516.
18. Silvermann, A., Adler, J. and Weil, R., *Thin Solid Films*, 1990, **192/193**, 571.
19. Stillinger, F. H. and Weber, T. A., *Phys. Rev.*, 1985, **B31**, 5262.
20. Stillinger, F. H. and Weber, T. A., *J. Chem. Phys.*, 1990, **92**, 6229.
21. Khait, Yu. L., Silverman, A., Weil, R. and Adler, Joan, *J. Non-cryst. Solids*, 1991, **137** and **138**, 145; Khait, Yu. L., Silverman, A., Weil, R. and Adler, Joan, *Phys. Rev.*, 1991, **B44**, 8308.
22. Slutsker, A. I., Mihailin, A. I. and Slutsker, I. A., *Soviet Phys. Uspekhi*, 1994, **37**, 335.
23. Rao, K. R. and Chaplot, S. L., *Fusion Tech.*, 1996, **30**, 355.
24. Sanyal, Subrata and Sood, K. Ajay, *Prog. Theor. Phys. Suppl.* 1997, **126**, 163.
25. Miyazawa, H., Hiwatari, Y., Bernu, B. and Hansen, J. P., *J. Chem. Phys.*, 1988, **88**, 3879.
26. Wahnstrom, G., *Phys. Rev.*, 1991, **A44**, 3752.

ACKNOWLEDGEMENTS. I thank Prof. Yu. I. Khait for much correspondence during the course of our work on the Pd-D system which is also briefly summarized in this review. The collaboration with Dr S. L. Chaplot is gratefully acknowledged.

Received 14 July 1998; revised accepted 8 October 1998