1. Introduction

Due to advances in laser optics non-thermally affected phase transitions like non-thermal melting, vapor condensation, etc, resulting from electron excitations due to laser irradiation are of increasing interest [1]. Of course, in general the response to the electronic excitations, essentially of the bonding electrons, must be faster than the lifetimes of the excitations. This sheds light on nonequilibrium physics and phase transition dynamics. Conservation laws like energy or angular momentum conservation control the time during which the transitions occur. Since the photon induced effects result from weakening or strengthening of the bonding between the atoms or molecules transitions like solid/liquid, etc can be shifted in both directions. Photoinduced transitions will be discussed from a unified point of view.

(Some figures in this article are in colour only in the electronic version)
Electrons are excited out of the ground state (GS) by a laser, for (a) PES for photoinduced structural changes. (b) Illustration of excited electrons the system may not return to its original state. Note, irreversible transitions may occur. After relaxation of the excited electrons the system in equilibrium may or may not return to the original state. It is generally assumed to be spherical. Hence, changing the electrostatic interactions via an increase of dipole moments may affect, in particular for water, the transition of supersaturated vapor, etc relatively strongly. Electronic excitations might cause a considerable enhancement of the chemisorption like binding of water molecules to impurity molecules with strong water affinity. Examples are C₃H₄, C₆(H₂O)₇, etc molecules injected into vapor and acting then as seeds for nucleation.

Similarly, of course, strong effects are expected from photoinduced ionization, in particular, in highly polarizable dielectric material. Note, ionization causes locally quasi strong ionic bonding.

As already mentioned and physically expected, the photoinduced response must be shorter in time than the lifetimes of the excited electrons. This was noted and discussed already by Hensel et al when explaining the different responses of Hg and Cs vapor to light [6].

In general, the chemical potential, the thermodynamical potential per particle $\mu(t)$, controls the phase stability and phase transition and is, in general, changed if bonding varies due to electronic excitation [8]. This is the origin of non-thermal photoinduced effects on phase transitions. Of particular interest are, for example, the effects on supercooling, superheating or supersaturation. If no energy barriers stabilize the induced phase, the nonequilibrium state will relax in accordance with the lifetimes of the excited electrons.

In contrast to the case where many hot electrons are present which cause a significant change of the electron temperature, as is the case for non-thermal melting of Si and graphitization of diamond, we assume for simplicity, for photoinduced effects on supersaturation or supercooling, that the temperature remains at first nearly unchanged during nucleation and formation of nuclei. Of course, the generation of latent heat must be taken into account in order not to violate energy conservation. And this controls the dynamics, the time dependence of the transitions. If magnetism is involved angular momentum conservation must also be taken into account [1].

Generally, for transitions via precursor fluctuations involving small nucleation centers with $N$ particles of the growing new phase, the surface energy $\sigma$ of the nuclei must be included in the thermodynamical potential $G$. This is, for example, the case for small liquid droplets in vapor, for small crystallites in melt, etc. (Then the reaction coordinate in figure 1(b) is the radius of the nuclei which for simplicity is assumed to be spherical.)

In figure 1 the physics of photoinduced phase transitions is illustrated. After relaxation of the excited electrons the system may or may not return to the original state. It is generally occurring in covalent crystals, Ge, Si, GeAs, etc. Due to sp³ population changes and excitations into antibonding states the bonding is weakened [2–4]. Regarding photoinduced seeding, a particularly interesting case may be small diamond (or Si, etc) crystals in C-vapor with photoinduced s-, p- atomic populations like in diamond.

The opposite case of photoinduced bond strengthening may cause condensation of vapor, non-thermal condensation, or a transition of liquid into solid. Then, depending on the energy barrier between the phases, the induced phase may remain or may change, and relax again in accordance with the lifetimes of the excited electrons. Examples of photoinduced bond strengthening are the weak van der Waals interactions between Hg atoms changing into covalent or metallic ones upon exciting 6s electrons into 6p states, see theory by Pastor et al [5] and experiments by Hensel et al [6], and also the interaction increase between water molecules with weak H-bonding (van der Waals bonding) upon electron excitation. These possibly enhance the binding of water to impurity molecules, which act like nucleation seeds, and also enhance the interactions due to an increase of the water dipole moments. For example, photoactivated binding of water molecules to CO₂, SO₂, sugar, etc. Impurity molecules might cause particularly efficiently condensation of vapor, see [7].

In figure 1 the physics behind non-thermal and photoinduced phase transitions is illustrated for detailed discussion see [3, 4]. Note, irreversible transitions may occur. After relaxation of the excited electrons the system may not return to its original state. (a) PES for photoinduced structural changes. (b) Illustration of photoinduced changes of the potential energy surface (PES).
and occurs during 100 fs or so [2]. The results refer to Si, but thermal melting in covalent crystals. The transition is ultrafast may induce for saturated vapor a transition vapor close to an equilibrium phase boundary the electron excitations supersaturated or undercooled vapor. Note, in particular, that excitations. Results refer to $\xi$ of electron–hole excitations. Results refer to $\xi \approx 0.15$.

In figure 2 we illustrate photoinduced effects on non-thermal melting in covalent crystals. The transition is ultrafast and occurs during 100 fs or so [2]. The results refer to Si, but are similar for other covalent crystals. Si melts after a time of about 100 fs. The photoinduced transition depends of course on the density (fraction of excited electrons) $\xi$ of electron–hole excitations.

Important to achieve optically for example not only the transition crystalline $\rightarrow$ amorphous, but also amorphous $\rightarrow$ crystalline, etc.

In figure 3 we illustrate photoinduced effects on non-thermal melting in covalent crystals. The transition is ultrafast and occurs during 100 fs or so [2]. The results refer to Si, but are similar for other covalent crystals.

In figure 3 we illustrate, for example, what is expected for supersaturated or undercooled vapor. Note, in particular, that close to an equilibrium phase boundary the electron excitations may induce for saturated vapor a transition vapor $\rightarrow$ liquid, but also directly vapor $\rightarrow$ solid. In the case of photoinduced enhancement of the interactions amongst the water molecules, dipole coupling, the latter transition results from the energetically favored ordering of the dipole moments in the solid as compared to the liquid, see water versus ice. An increase of the coupling amongst the water molecules may be mediated by corresponding impurity molecules like SO$_2$, etc in impure (water) vapor. This is an interesting, but common physical mechanism.

In general change of bonding affects supersaturation, supercooling, etc.

The thermodynamical potential $\Delta G$ (the difference of $G$ between the two phases) determines the phase transition, see figure 1 and [8]. In the case of a transition $A \rightarrow B$ via forming precursor nuclei of the new phase B the phase transition rate $\Gamma = \Gamma(t)$ for forming nuclei is controlled by $\Delta G$ and it is

$$\Gamma_{A \rightarrow B} \propto \exp\left(-\alpha \Delta G\right),$$

with $\alpha = 1/\kappa T$ if the transition is a thermal one. Hence, there is a sensitive dependence on changes in the potential barrier $\Delta G$ due to electron excitations. $\Delta G$ refers to the difference between phases A and B. The dependence of the rate $\Gamma$ on time and fluence reflects the photoinduced effects.

Clearly, in general, the phase diagram will be affected by electron excitations. For example, the transition vapor $\rightarrow$ liquid occurs at higher temperatures if the photoinduced bonding is larger in the liquid phase.

2. Theory

In view of the equation for the transition rate $\Gamma$ one expects a sensitive dependence of thermodynamical processes on changes of the thermodynamical potential and thus on photoinduced changes of the (chemical) bonding. In the following details of the thermodynamical theory [8, 9] for photoinduced effects and of an electronic theory for this, for the effects of electron excitations on bonding, are given [1–4]. Irreversible thermodynamics is well suited to describing, in general terms, the influence of photoinduced bond changes on various processes and in particular on currents. Electronic theory might be particularly useful for understanding the dynamics, the time dependence of the transitions, and the significance of selective excitations. Depending on the photon energies the electron excitations may consist of low energy ones to high energy ones. Of particular interest are the excitations in bonding and antibonding states changing the interatomic binding strongly.
2.1. Thermodynamic theory for photoinduced phase transitions

Generally, the difference of the thermodynamical potential $\Delta G$ between phases A and B is for constant volume given by [6, 8]

$$
\Delta G = -\Delta S \Delta T - N \Delta \mu + \sigma \Delta s + \cdots.
$$

Here, $\Delta S$ is the entropy difference, $\Delta \mu$ is the difference of the chemical potential and $\sigma$ is the surface energy (per unit area) of the interface of A and B. This amounts to an energy increase. The surface energy $\sigma$ may change with photoinduced changes of the bonding. $N$ is the number of particles involved in the precursor fluctuation (in a nucleus, droplet). The first term may be rewritten as $(Nq/T) \Delta T$, where $q$ is the molecular latent heat. The latent heat should take into account the change in binding due to the electron excitations. Here, $\Delta T = T_0 - T$ gives the range of supercooling, temperature $T_0$ refers to the temperature at the phase boundary (or to the starting temperature) and condensation occurs at $T$ when the new phase nucleus arising from fluctuations has reached its critical size and continues to grow. In general one has a potential barrier in $G$ between phases A and B and electron excitations may lower this barrier thus causing the photoinduced effects. Clearly energy gain due to stronger interatomic bonding in one phase favors the transition into this phase.

The chemical potential change $\Delta \mu$ involves strengthening or weakening of the bonds between the particles. It is [8]

$$
\Delta \mu = T \ln(p/p_0) + \Delta \mu',
$$

where the last term describes the change of the bonding of the particles in phases A and B, both with electron excitations due to light of fluence $F$. $p_0$ is the pressure at the thermodynamical phase boundary. Summarizing, equation (2) can be rewritten as

$$
\Delta G = -(Nq/T) \Delta T - N T \ln(p/p_0) + N \Delta \mu' + \sigma \Delta s + \cdots.
$$

For a transition $A \rightarrow B$ all quantities refer to differences with respect to the two phases.

Clearly, $\Delta G = \Delta G_0 + \Delta G_{ph}$ and the photoinduced contribution $\Delta G_{ph}$ depends on the light (absorption) fluence $F$, since the probability to absorb a photon and to excite an electron should be proportional to $F$. Approximately one has

$$
\Delta G_{ph} \propto F
$$

(\ln \Gamma_{ph} \propto F/kT).$\text{Hence, from this one gets approximately, if }\Delta G_{ph} \text{ is not too large, for the rate (probability) of forming nuclei (} \Gamma \simeq \Gamma_0 + \Gamma_{ph} \text{)}

$$
\ln \Gamma_{ph} \propto F/kT + \cdots.
$$

The enhancement of the rate $\Gamma$ due to photon absorption is given by

$$
\Gamma = \Gamma_0 \exp(-\Delta G_{ph}/kT).
$$

Here, $\Delta G_{ph}$ is the decrease ($\Delta G_{ph} \leq 0$) of the potential barrier at critical radius $r_k$ of the nuclei, $r \approx r_k$. Then one obtains approximately, expanding $\exp(-\Delta G_{ph}/kT)$, $\Gamma \sim (1 + b \frac{kT}{\Delta G_{ph}} + \cdots)$ for small changes $\Delta G_{ph}$.

In the case of phase transitions involving phase fluctuations consisting of precursor droplet formation, small nucleation clusters of $N$ particles, one assumes for the nucleation center $N \sim$ volume and for calculating the surface energy $\sigma$ (per unit surface area) small spherical particles. The surface of the spherical nucleation center is $\Delta s = 4\pi r^2$. The particle density is $\rho = N/V$. (In thin films one has approximately $\Delta s \approx 2\pi r$.)

Then, for phase transitions occurring via (spherical) nucleation clusters having radius $r$ one gets approximately

$$
\Delta G \simeq -(4\pi/3)r^3(q/T) \rho \Delta T - (4\pi/3)r^3 \rho T \ln(p/p_0) + N \Delta \mu' + (4\pi)^{2/3} \sigma + \cdots.
$$

Here, $q$ is the molecular latent heat, $p_0$ refers to the equilibrium pressure at a flat surface and $(p - p_0)$ gives the range of supersaturation. $p/p_0$ is called supersaturation, $\rho$ is the particle density and $\sigma$ is the energy per unit surface area of the liquid droplet or crystal in the melt. $\Delta \mu'$ is the change of binding energy per particle with respect to phases A and B both under the influence of light with the same intensity [9, 10]. The photoinduced effect is proportional to the number of excited atoms or molecules in the nucleation cluster, its fraction is denoted by $\xi$, and may be determined by the absorption cross section and the light intensity, the fluence $F$. It is

$$
N \Delta \mu' \approx (4/3)\pi r^3 \rho \Delta \mu'_p.
$$

if we assume for simplicity a uniform change in the nucleus, that all particles in the nucleus have been excited. This will depend on the fluence $F$. If the fluence is not too large this will not be the case and the term should be calculated more correctly. For example, one may assume that the particle at the center of the nucleus absorbed a photon and caused electron excitations changing the cohesion. (The situation corresponds to the one of an impurity in a liquid or solid, or in the case of several excited particles in the nucleus to changes in cohesion like in an alloy.) $\Delta \mu'_p$ is the effective change of the energy per particle in the nucleus. (One may also express $N \Delta \mu'$ in terms of the bond energy changes due to electron excitations.)

In accordance with figures 1(b) and 4 one gets, from $\Delta G' = 0$, the critical size of the nucleus ($r = r_k$) of the precursor fluctuation (yielding the barrier in $\Delta G$). The nuclei grow when these reach a size larger than the critical one $r_k$. At $r_k$ the new phase occurs globally [8]. One gets, from $\Delta G' = 0$, that

$$
r_k = \frac{2\sigma/\rho}{(q/T) \Delta T - \Delta \mu' + \Gamma \ln(p/p_0)}.
$$

Hence, as physically expected, the greater the latent heat $q$ and supercooling $\Delta T = T_0 - T$, the bonding increase ($\Delta \mu' < 0$), and the supersaturation are the less the critical size of the nucleus is.

In summary, it follows from the above equation for $\Delta G$ that photoinduced increased cohesion decreases the critical size $r_k$ beyond which the nuclei grow and the new phase becomes stable. It is

$$
\Delta G_{ph} = \Delta G(r_{k,ph}) - \Delta G(r_k),
$$

(11)
be of the order of a few tenths, or less, of eV in the case of metallic
refers to photoinduced reduction of the potential barrier (which may
nucleation \( \Delta G \) involving nucleation, for example droplet formation. \( \Delta G \) depends on the supersaturation \( F \) and temperature \( T \). Here, \( r \) denotes the radius of the nucleus, for simplicity assumed to be spherical. The phase fluctuations accompanying the phase transition may consist of droplets which act as precursor of the new phase. At the critical radius \( r_k \) vapor condensation or crystallization occurs. The rate of nucleation \( \Gamma \) is determined by the potential barrier \( \Delta G_k \) which results from the interplay of surface energy and changes of cohesion. The rate \( \Gamma \) could be observed by Mie scattering. Photoinduced electron excitations may lower this barrier \( \Delta G \). The dashed curve refers to photoinduced reduction of the potential barrier (which may be of the order of a few tenths, or less, of eV in the case of metallic like cohesion) which is approximately proportional to light fluence \( F \). The electron excitations and light absorption should not increase the temperature within the nucleus much.

where \( r_k - r_{k, ph} \) is the change in the critical radius of the precursor droplet due to photoinduced electron excitations. For the analysis, to calculate the rate \( \Gamma \), it might be useful to expand \( \Delta G_{ph} \) in terms of the difference \( \delta = r_k - r_{k, ph} \).

Denoting by \( V_k \) the volume of a critical nucleus one expects approximately from the above theory

\[
V_k = (V_k)_0 - \alpha F, \tag{12}
\]

where the photoinduced change of the critical fluctuation size \( (V_k)_0 \) should be observable using a fast measurement (for example, Mie scattering).

Furthermore, one gets for critical supercooling (when the nuclei have reached the critical radius \( r_k \)) approximately\(^1\)

\[
\Delta T = \left( \frac{T}{q} \right) \left( 2\sigma/(\rho r_k) + \Delta \mu' - \ln \left( \frac{p}{p_0} \right) + \cdots \right). \tag{13}
\]

Hence, the critical supercooling \( \Delta T \) decreases for increasing excitations, fluence \( F \) and photoinduced increased cohesion. Note that, as discussed, \( \Delta \mu' \) results from electron excitations and accompanying changes of cohesion, ionization, or bond changes due to impurities.

\(^1\) A simple analysis gives approximately \( \Delta G_k \approx (4\pi/3) r_k^3 \sigma + \cdots \), with \( r_k = \frac{\rho_0 \sigma k T}{\Delta H_m} \). For pure water condensation upon irradiation besides ionization essentially the increase of the dipole coupling might matter and then \( \Delta \mu' \) results from this. Note, however, in water with impurities like SO\(_2\), etc. the establishment of chemical bonds with water condensation may essentially result from corresponding bond changes.

For critical supersaturation \( (p/p_0) \) one gets (see footnote 1)

\[
\ln \left( \frac{p}{p_0} \right) = 1/T (2\sigma/\rho r_k + \Delta \mu' + \cdots). \tag{14}
\]

One may rewrite this equation as

\[
p - p_0 \approx 2\sigma/\rho r_k + \Delta \mu' - (q/T) \Delta T. \tag{15}
\]

\( p_0 \) refers to the saturation pressure at a planar interface of the two phases. (Note, \( \sigma = \frac{4}{3} \sigma_0 \) and change of bonding may affect the surface energy. \( F \) denotes the free energy.) Hence, the supersaturation \( \ln \left( \frac{p}{p_0} \right) \) decreases with temperature \( T \) and becomes smaller for increasing cohesion, \( F \).

Note that it is \( \Delta \mu' < 0 \) for increased binding and hence as expected critical supercooling \( (T_0 - T) \) and supersaturation \( \frac{\rho_0}{F_0} \) or \( (p - p_0) \) decrease upon light absorption. Of course, the latent heat \( q \) should also reflect increased cohesion \( (\Delta \mu' \propto F) \).

Corresponding effects occur for decreased cohesion, \( \Delta \mu' > 0 \), resulting for excitations into antibonding states. For decreased binding the change of \( \mu' \) might be less than for bond strengthening.

Previous analysis supports physical intuition that photoinduced increase of cohesion, supercooling and supersaturation reduces the critical size, the radius \( r_k \) of the nucleus (droplet in vapor or crystallite in melt). Note that for size \( r > r_k \) condensation of vapor or crystallization occurs, since the nucleation center grows (if latent heat is sufficiently transferred). Also an overlap of nuclei (in the case of large fluence \( F \) or impurity concentration) accelerates the photoinduced transition. Furthermore, for example, for constant pressure and from \( \Delta G' = 0 \), one gets for the critical temperature \( T \) \( (T = T_0 - \Delta T) \) at which condensation of supercooled vapor occurs or the range of supercooling, see illustration in figure 10,

\[
T_0 - T \rightarrow 0, \tag{16}
\]

for increasing fluence \( F \).

In summary, both critical supercooling and supersaturation decrease with increasing light fluence \( F \).

The dynamics of the phase transition is controlled by energy, angular momentum conservation (see magnetic effects), etc. Then, if in supercooled melt there is a crystal nucleus with \( \mu_k < \mu_l \) it grows for some time, but the whole melt will not crystallize if heat cannot be removed (transferred) fast enough. For crystallization of the whole melt heat must be removed and this may take some time (ps or so) [9].

Close to the phase boundary the rate of forming nuclei is given by equation (1). Hence, the enhancement of the rate of condensation of vapor due to photon excitations is given by

\[
\Gamma = \Gamma_0 \exp \left( -\left( \frac{\Delta G - \Delta G_0}{kT} \right) \right), \tag{17}
\]

see equation (7), where \( \Delta G_0 \) refers to the case when no photoexcitations are present. The potential barrier of \( \Delta G \) is taken at \( r \approx r_k \). Thus, one gets approximately for supercooling and for the rate \( \Gamma \) the enhancement

\[
\Gamma \propto \exp \left[ \left( \frac{\Delta q}{kT} \right) \Delta T + \cdots \right]. \tag{18}
\]
Increase of latent heat \( q \), bond strengthening yields larger rate \( \Gamma \).

It is of interest to give in more detail, using standard thermodynamics [8] and previous equations, the expression for the formation rate of a nucleus in a (slightly) superheated or supercooled phase (see footnote 1)

\[
\Gamma \sim (\exp(4\pi r_0^3/kT)(\rho \Delta T/T + T \rho \ln(p/p_0) - \Delta \mu')) \\
\times (\exp[-(4\pi \rho r_0^2)/kT]) + \cdots ,
\]

(19)

where \( T \) may be written as \( T_0 - \Delta T \). Using then Clapeyron–Clausius \( \Delta p = \frac{T_0}{T} \Delta T \) one may express \( \Delta T \) also in terms of \( \Delta p \). For the critical radius of the precursor nucleus \( r_0 \) one uses the previously derived expression. This expresses the rate \( \Gamma \) for formation of a liquid droplet in vapor in terms of \( (p - p_0) \) and \( T - T_0 \). The molecular volumes \( v_1 \) and \( v_2 \) refer to the metastable phase and the nucleus, respectively [8, 9]. Clearly, \( \Gamma \) may depend sensitively on supersaturation \( \frac{p}{p_0} \).

Assuming that the size of the nuclei can be determined experimentally, it is useful to express the rate \( \Gamma \) as

\[
\Gamma \sim \exp \frac{\Delta G(r_0) - \Delta G(r_{k,ph})}{kT}.
\]

(20)

Here, frequently \( r_{k,ph} \sim r_k \) and this may be used for an expansion. Clearly, for smaller sized nuclei one gets that the transition rate increases.

In figure 4 we sketch the resulting \( \Delta G \) for nucleation, see also for comparison figure 1 and previous discussion by Hensel et al [6].

In summary, thermodynamics can relate the important parameters controlling the stability of a phase, including nonequilibrium phases, to bonding. Thus, for example, it becomes clear that changes from van der Waals bonding to metallic bonding cause a strong response regarding thermodynamical behavior. Due to their significance photoinduced changes of dipole coupling are treated in detail in the following.

2.2. Photoinduced effects due to enhancement of dipole coupling and ionization

In water and other liquids and systems with dipole coupling amongst the molecules, the photoinduced increase of bonding and resulting thermodynamical response could result from increasing dipole moments. It is straightforward to write down in the above equations explicitly the effects due to electron excitations yielding enhancement of dipolar coupling (or photoactivated impurity binding and accompanying changes of cohesion or ionization). Then one calculates the contribution \( \Delta G \) from the potential for dipole moments. Note, in unexcited pure water the dipole coupling may contribute to more than 70% of the cohesion [9].

It is

\[
\ln \Gamma_{ph} \sim \Delta G_{dipole} \propto F + \cdots .
\]

(21)

In the case of changing the relatively weak van der Waals coupling due to an increase of the dipole moments of the particles (water molecules), one must calculate \( \Delta G_{dipole} \) or \( N\Delta \mu' \) by using the corresponding potential which is proportional to the dipole moments of the interacting dipoles, their distance and temperature [8, 9]. Again, this gives a contribution to \( \Delta G_{dipole} \) proportional to \( (F + a F^2 + \cdots) \) and approximately one may use that \( \Delta G_{dipole} \) is enhanced by a factor \( \eta \) due to impurity mediated enhancement of the dipole coupling.

One may for simplification parameterize \( N\Delta \mu' \) in a way characterizing the molecule. Similarly many interactions can be treated as very local ones. A dependence of the transition on impurity concentration would be interesting, as mentioned already.

In general one might approximately assume for the dipole coupling

\[
\Delta G_{dipole} \approx \eta \Delta G_{dipole}^0 - \cdots ,
\]

(22)

where \( \eta \) denotes the induced enhancement of the van der Waals coupling and \( \Delta G_{dipole}^0 \) the corresponding thermodynamical potential due to dipole coupling in pure condensed vapor (water) and for \( F = 0 \). Note, above \( \Delta G \) refers to the difference between phases A and B. Hence we must subtract from the first term referring to phase A the corresponding one for phase B. Possibly for phase B this contribution is negligible. For simplicity we have not written explicitly the expression for \( \Delta G_{dipole} \). From the above equation one might easily calculate the condensation rate \( \Gamma \) and \( \ln \Gamma \propto \eta \). The enhancement factor \( \eta \) may result from impurity effects on binding or from the increase in dipole moments and may be estimated from the latent heat change and bond energy change, see equations for \( \Delta G \). In the case of supercooling \( \eta \) is approximately proportional to the ratio of latent heats of impure and pure substance (water), respectively.

Obviously already relatively small increases of the dipole coupling give large changes of the condensation rate, since \( \Gamma \) depends exponentially on the potential barrier \( \Delta G \). Note, the above equation (22) may be used for estimating the enhancement of the rate \( \Gamma \) due to photoinduced increase of the dipole moments.

Electron excitations change generally the charge distribution (within molecules, etc) and may enhance the dipole moment. Thus, the cohesion can increase and affect the vapor condensation, etc. This may apply to photoinduced water condensation, possibly mainly in relatively pure water. Using the previous equations dipole interactions are taken into account in the term \( \Delta \mu' \). Induced dipole moments contribute to \( \Delta \mu' \) a term increasing with \( p_0 \), where \( p_0 \) denotes the dipole moment. In polarizable systems it is \( p_0 \sim E \) where the dipole moment is induced by an electric field \( E \).

The contribution \( \Delta G_{dipole} \) due to dipole interactions is calculated from

\[
\Delta G_{dipole} \simeq \int 4\pi \rho^2 d\rho U_{dipole} ,
\]

(23)

where \( U_{dipole} = -r^{-6}[(2/3) p_0^2 p_{ph}^2/kT + a_1 p_{ph}^2 + \cdots] \) (Keesom) [9, 10]. The calculation of the thermodynamical potential due to dipole coupling is similar to in the case of ions. \( \Delta G_{dipole} \) refers to the difference of the two phases A and B with electron excitations present. Note, it might be necessary to take into account the ordering of the dipole moments, see for example water versus ice [9, 10], further lowering the energy.
Then, \( U_{\text{dipole}} = -r^{-6}(2/3)\rho_{00}^2 / kT \) at high temperature and \( U_{\text{dipole}} \approx -2\rho_{00}^2 / r^3 \) at low temperatures when \( kT \) is much smaller than the dipole coupling. Thus, one gets approximately in the case of photoenhanced dipole interactions (Keesom, ...)

\[
\Delta G_{\text{dipole}} \approx -a(r)p_d^3 / kT - \cdots, \text{ at high temperatures,} \tag{24}
\]

and

\[
\Delta G_{\text{dipole}} \approx -a'(r)p d' - \cdots, \text{ at low temperatures.} \tag{25}
\]

Here, \( p_d \) is the photoenhanced dipole moment at the center of the nucleus and \( p d' \) the moment of the surrounding ones. For a uniformly excited nucleus (same dipole moment \( p_d \) for all molecules) one gets \( \Delta G_{\text{dipole}} \propto p_d^3 \) at high temperatures and \( \Delta G_{\text{dipole}} \propto p_d^2 \) at lower temperatures. Both \( a(r) \) and \( a'(r) \) are approximately given by \((4/3)\pi r^3\). For very local interaction of the photoexcited dipole moment with the surrounding ones one has approximately that both coefficients \( a(r) \) and \( a'(r) \) are nearly constant.

One may write the dipole moment as \( p_d = p_{d0} + \Delta p_d \), where \( \Delta p_d \) denotes the photon induced change of the dipole moment. Approximately, \( \Delta p_d \propto F \). In both equations above \( \Delta G_{\text{dipole}} \) for phase B must be subtracted and possibly this may be negligible. For simplicity this is assumed in the following.

Summarizing, in the case of photoinduced changes of the dipole coupling one may rewrite the previous equation for \( \Delta G \) and has

\[
\Delta G \approx -(4\pi/3r^3)(q/v)\rho_0^2 \Delta T - (4\pi/3r^3)p_0^2 \kappa N \ln(p/p_0) \]

\[+ \Delta G_{\text{dipole}} + (4\pi)r^2\sigma + \cdots. \tag{26}\]

Here, of course the latent heat \( q \) includes contributions due to changes of the dipole coupling.

Thus, similarly to the case of radiation producing ionization photoinduced enhancement of the dipoles and their coupling may for example cause in pure vapor strong condensation (vapor \( \rightarrow \) liquid or of even vapor \( \rightarrow \) ice in the case of supercooling or supersaturation close to point M in the phase diagram, see figure 3).

Using the previous discussion

\[ \ln \Gamma_{\text{dipole}} \propto -(\Delta G)_{\text{dipole}} / kT, \tag{27} \]

with \((\Delta G)_{\text{dipole}} \propto (p_{d0})^2 / kT + \cdots\), at higher temperatures. It is interesting that at low temperatures the behavior changes and \( \ln \Gamma_{\text{dipole}} \propto p_d^2 + \cdots \) for \( T \rightarrow 0 \).

In the case of molecules with large polarizability \( \alpha \) one calculates \( \Delta G_{\text{dipole}} \) also from the potential for induced dipole moments \( p_{d0}, U_{\text{dipole}} \approx -2\alpha p_{d0} \).

Generally one gets that the rate of condensation \( \Gamma \) increases for increasing fluence \( F \), likely first linearly. For example,

\[ \ln \Gamma \approx \ln \Gamma_0 + \ln \Gamma_{\text{dipole}} \tag{28} \]

and (see equation (27))

\[ \ln \Gamma_{\text{dipole}} \approx -\Delta G_{\text{dipole}} / kT \propto F. \tag{29} \]

The condensation rate \( \Gamma \) also increases with supersaturation \( \Delta p_d \) or supercooling \( \Delta T \). It would be interesting to observe effects reflecting the number of particles excited within the nuclei, the fraction of excited particles \( \xi \).

Clearly, the photoinduced increase of binding and of the dipole moments is expected to be an important source for photoinduced condensation of vapor, dielectrics, and possibly also for pure water condensation. The photoinduced transition vapor \( \rightarrow \) ice may be preferred for supersaturated or supercooled vapor, for energetic reasons, see [9, 10]. The ordering of the dipole moments in ice yields stronger binding. Thus, supercooled (if \( \Delta T \) is large enough) or supersaturated water vapor may exhibit photoinduced condensation to ice.

Nucleation due to impurity molecules. In the case of nuclei forming around (injected) impurities like \( \text{CO}_2, \text{SO}_2, \text{CaH}_2 \), sugar molecules, etc \( \Delta \mu' \) describes the enhanced binding (quasi photoactivated chemisorption) of the material to these molecules. Then,

\[ N\Delta \mu' \approx v(r)\rho_{\text{eff}} + \cdots, \tag{30} \]

where the effective particle energy \( \epsilon_{\text{eff}} \) includes the binding energy to the impurity molecule and the change of the bond energies amongst the particles within the nucleus. It is \( v(r) \approx \rho_{\text{eff}} \) constant in the case of local coupling and \( v(r) \approx (4/3)\pi r^3 \) for uniform changes in the nucleus.

The binding to the impurity molecule should be proportional to the size, surface or length of the impurity molecule. Electrostatic effects like ionization or increase of dipole moments might play a role and \( \epsilon_{\text{eff}} \propto F + \cdots \). The binding energy is related to the affinity strength and is proportional to the reaction heat (for example \( \text{CO}_2 + n\text{H}_2\text{O} \rightarrow \text{CO}_2(\text{H}_2\text{O})_n + \text{heat} \)). One expects that the condensation rate \( \ln \Gamma \) is proportional to the binding energy plus bond energy changes. The basic behavior should be related to the reactions observed for example for water with \( \text{SO}_2 \), etc and activated by light. Obviously, excitations of the molecule electrons (water molecule as well as impurity molecule) may play a significant role.

Nucleation due to ions. In the case of nuclei due to ions resulting from photoinduced electron excitations one has for \( \Delta \mu' \)

\[ N\Delta \mu' \approx \epsilon_{\text{eff}}^{2/\epsilon} (1 - 1/\epsilon), \tag{31} \]

where \( \epsilon \) is the dielectric function and \( r \) the radius of the nucleus with the ion assumed to be at the center [8]. Note, the dielectric function may change due to electronic excitations. For simplicity one assumes that only one ion is involved in each nucleation process. (This of course depends on the density of ions and on the fluence.) Screening of the ion charge is taken into account by the dielectric function \( \epsilon \) of the material [8].

In summary, photoinduced condensation of saturated or supersaturated water may result from changes of dipolar coupling and from photoactivated binding to impurity molecules having strong affinity to water and which thus mediate a stronger coupling between water molecules. In pure water changes of dipolar coupling should dominate, while in impure water binding to foreign molecules (impurities) may play the dominant role. The dependence of the rate \( \Gamma \) or \( \ln \Gamma \) on light fluence \( F \) may reveal the mechanism for the photoinduced phase transition.
2.3. Photoinduced effects on droplet formation, phase diagrams, alloy mixing, and order–disorder transition

Droplet formation. Depending on the impurity molecules acting as nucleation seeds the size of a droplet in equilibrium with its surrounding vapor varies. One gets for the (equilibrium) pressure within the droplet

\[ p' = p + \frac{2\pi}{r} + \frac{\partial}{\partial V} (\Delta G_{ph}), \]

where \( p \) is the pressure of the saturated vapor and \( \Delta G_{ph} = \Delta G_{dipole} + \cdots \) (including bond changes), see [8]. This change of the pressure can be observed.

Phase diagram. Phase transitions without nucleation may occur depending on the interface structure. No supersaturation or supercooling should be observed.

Formation of nuclei within crystals may occur on melting, if a crystal is internally heated and the surface kept below melting temperature [8]. Then photoinduced effects occur as discussed for precursor nucleation.

Regarding phase diagrams, note that the Clapeyron–Clausius equation [8] gives \( \frac{dp}{dv_2} = -\frac{4}{v_2-v_1} \) where \( v_2 \) and \( v_1 \) refer to the volumes in the two phases 1 and 2. Here, phase 2 may be the gas one and phase 1 the liquid one. Photoinduced effects result from changing the latent heat \( q \) (for example of vaporization or melting, \ldots) due to electronic excitations. Increased bonding increases \( q \) and consequently for example the temperature at which melting or evaporation occurs. As known [8], one gets (approximately) for the transition liquid \( \rightarrow \) vapor

\[ p_s = \exp(-q/kT) \]

for the phase boundary, see figure 3. Here, one may write for the latent heat \( q = q_0 + \Delta q \) and approximately one gets for the photoinduced change \( \Delta q \propto F \).

Increased bonding increases also the temperature for evaporation (or melting). Non-thermal melting and evaporation should occur within a very short time, for example within 100 fs or so. Note also electron excitations, (many) hot electrons raise also the electron temperature and this must be taken into account.

Alloy mixing. Other important photoinduced effects occur regarding mixing, order–disorder transitions in alloys, segregation, etc [8]. Obviously the control parameter

\[ \varepsilon = \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} - \varepsilon_{AB} \]

characterizing alloying of atoms or molecules A and B depends on electron excitations. These may change possibly selectively the bond energies \( \varepsilon_{AA} \), etc. This influences strongly the mixing, ordering of the atoms on the sublattice sites [8].

Optical manipulation of atomic structure at surfaces and interfaces is of particular interest.

Dynamics of the phase transition. In general the dynamics (kinetics) of the photoinduced phase transitions, time dependence of the formation of nuclei, their growth, growth of crystal from melt, etc is important and reflects in particular energy conservation (latent heat transfer) and momentum conservation (for magnetism angular momentum transfer).

In figure 5 the expected time dependence of the transition rate \( \Gamma \) is sketched. Note, including atomic diffusion for crystallization one has \( \Gamma \propto \exp(-\frac{E_D}{kT}) \), where \( E_D \) denotes the activation energy for diffusion. Thus, \( \Gamma \) may decrease again for larger supercooling.

At the interface of crystal and melt the transition depends on interface structure. The growth of the crystal possibly proceeds discontinuously, since the first quasi two-dimensional nuclei are formed on the crystal face and then start to grow all over the interface. Electron excitations may influence the transition.

2.4. Electronic theory

The photoinduced electronic excitations change the bonding and consequently the chemical potential and this affects the phase transitions. Generally one expects that the number of electron excitations (or of excited atoms or molecules) is proportional to photon absorption, to the laser fluence \( F \), at least approximately. As a consequence one expects for the energy barrier \( \Delta G_k = (\Delta G_k)_0 + (\Delta G_k)_{ph} \) and \( (\Delta G_k)_{ph} \sim F + \cdots \), see figure 4.

2.4.1. Photoinduced structural changes. Interesting responses to laser irradiation are expected for systems where the electron excitations change the bond character like in covalent solids with \( sp^3 \) bonds changing to \( sp^2 \) ones or weaken the covalent bonds strongly enough that melting occurs. In general photoinduced excitations from bonding into antibonding states may cause structural transitions like graphitization of diamond, non-thermal ultrafast melting and ablation at surfaces. Ablation of an intact graphite plane...
may result at the surface of graphite due to laser irradiation. Repopulation of s and p$_z$ and p$_y$ states causes such responses. Thus, graphene can be produced optically [1, 3, 4]. This is a remarkable example of photoinduced transition.

One may use the Boltzmann equation to calculate the population of the electronic states by the excited electrons. The cohesive energy at nonequilibrium is given by, see [2],

$$E(T_{el}) = \int_{-\infty}^{\infty} d\xi \rho N(\xi, T_{el}) f(\xi, T_{el}) + E_i(r_{ij}) + \cdots$$

(35)

where $N$ is the electronic density of states, $f$ the Fermi distribution function and $E_i$ the repulsive energy between atoms at distances $r_{ij}$. $T_{el}$ is the temperature of the hot electrons. Then the dynamics of the atomic displacements at nonequilibrium follows approximately from the (classical) equation

$$M \ddot{u}_i(t) = -\frac{\partial}{\partial u_i} E_k(u_i, f, T_{el}).$$

(36)

The atomic displacements depend on $T_{el}$ and on the number of electron excitations, electron–hole pairs described by the parameter $\xi$. The temperature $T_{el}$ of the hot electrons depends on $\xi$ and may be determined due to the fast transitions approximately from $\Delta S(T_{el}) = 0$. Here, $S$ denotes the electron entropy which for ultrashort times remains constant, since no energy and entropy are transferred for example to the lattice.

As discussed by Garcia et al this analysis can be improved using a Lagrangian formalism which also applies if photoinduced transitions are accompanied by volume changes [3, 4]. Thus potential energy surfaces (PES) and nonequilibrium phase transitions are calculated.

In particular this analysis can be used to determine photoinduced structural changes in semiconductors. In covalent bonded semiconductors the photoinduced nonequilibrium state resulting from electron excitations is then characterized by the fraction $\xi$ of electrons excited across the energy gap between the valence and conduction bands. Excitations into antibonding states weaken the cohesion. Clearly, transitions sp$^3 \rightarrow$ sp$^2$ destroy covalent bonding. The characteristic band gap in the semiconductors decreases. Closing of the gap between conduction band and valence band yields metallic behavior.

In view of this, crystals with strong excitonic behavior are expected to exhibit strong photoinduced effects. Photoinduced creation of electron–hole pairs in graphene might be particularly interesting. To study this one may use the same analysis as for the graphitization transition and for ablation [3, 4].

Photoinduced changes of the bonding are expected for rare-earth and generally for crystals (nonmetals) with weak bonding due to a band gap as is typically the case for a filled outer electron shell. Vapor of mercury, etc might be an example. Then electron excitations across the band gap could change weak van der Waals like bonding to stronger metallic bonding.

### 2.4.2. Photoinduced strengthening of bonding

Due to electron excitations, interatomic or intermolecular interactions, binding may also increase. This may be the case for electron excitations out of a filled electronic shell, see for example Hg, Ba, Ce with 6s$^2$, Zn with 4s$^2$, lanthanides, etc. If these excitations live long enough the nonequilibrium population of the electron states may change the phase. In particular photoinduced increased cohesion of the nonequilibrium state should increase the melting temperature and favor condensation of vapor.

Photoinduced transition of a metastable state into a stable one deserves special attention. In particular supersaturation and supercooling, etc should be affected by photoinduced electron excitations. One expects photoinduced condensation of water and of mercury, etc, since the excited electrons increase cohesion, at least for some time depending on the lifetimes of the excited electrons. In vapor of Hg the weak van der Waals interactions change to covalent or even metallic interactions due to 6s$^2 \rightarrow$ 6s$^1$p$^1$ transitions [5, 6]. In water dipole coupling may increase strongly (within nuclei) upon electron excitations and thus enhance the weak intermolecular coupling of the vapor and the binding to (impurity) molecules acting as nucleation center.

Then, assuming that vapor condensation or crystallization results from fluctuations consisting of nucleation centers (liquid droplets or crystallites) one may use equation (4) or (8), and rewrite

$$\Delta G \simeq -\left(4/3\right) \pi r^3 \rho (q/T) \Delta T - 4\pi r^3 \rho T \ln \frac{p}{p_0} + N \Delta \mu' - 4\pi \sigma + \cdots,$$

(37)

where $p/p_0$ is the supersaturation (and where $p_0$ refers to the equilibrium pressure of a flat surface) and where the degree of supercooling is given by $\Delta T = T_0 - T$. Here, $T_0$ is the temperature at which the two phases coexist thermodynamically, at equilibrium. The (molecular) latent heat should refer to the case where electron excitations are present. One may write again $q = q_0 + \Delta Q$, where $\Delta Q$ is due to the electron excitations and is approximately proportional to the fluence $F$. $\Delta \mu'$ describes changes of the binding to impurity molecules and of dipole coupling. In pure vapor the increase of the dipole coupling might be most important. As mentioned already the difference $\Delta G$ refers to the one between phases A and B and for photoinduced electron excitations.

It is of interest to observe corrections due to inhomogeneous nuclei (hence corrections of the factor $(4/3)\pi r^3$ and acceleration of condensation, etc due to overlapping nuclei).

Photoinduced condensation (or crystallization) results as discussed already from a decrease in the barrier of $\Delta G$ [6].

One expects physically and as described by previous analysis that a photoinduced increase of cohesion, supercooling and supersaturation reduces the critical size, the radius $r_k$ of the nucleus (droplet in vapor or crystallite in melt). Note, for $r > r_k$ condensation of vapor or crystallization occurs, since the nucleation centers grow (if latent heat is sufficiently transferred). Also note that the overlap of nuclei (in the case of large fluence $F$ or impurity concentration) accelerates the photoinduced transition. (It is $\sigma = \frac{d\Delta G}{dt}$ and change of bonding...
may affect the surface energy. Here, $F$ denotes the free energy.)

In Hg nanostructures and thin films the gap between the 6s states and 6p states may be small enough so that a transition nonmetal $\rightarrow$ metal may result due to electron excitations into the 6p states, see [5]. Then the photoinduced effects get stronger. The increase in the coupling between the Hg atoms in the condensed nuclei can be related to the behavior of Hg clusters. Note, clusters and nuclei having about 15–20 atoms should have a nearly closed s–p ‘band gap’, optical measurements should reflect this, also the latent heat.

As discussed, photoinduced condensation of water vapor may result from increasing the relatively weak interaction amongst the water molecules via laser irradiation. Due to intraatomic electronic excitations the dipole moment of the water molecules may increase. In not so pure water the photoenhanced binding to impurity molecules, in particular if these have a strong affinity to water, causes stronger interactions. This binding to impurity molecules may be enhanced due to electron excitations, changing possibly the structure of the impurity molecule, electrostatic coupling, dipole moment, etc. This binding should increase as the surface of the impurity molecule increases. Longer molecules bind more water molecules, etc. The binding should be short ranged. Thus, its efficiency affecting the phase transition of saturated or supersaturated vapor depends on the critical size of the nuclei and thus on pressure and temperature and closeness to the thermodynamical phase boundary. To determine the physics one must know the dependence of the rate $\Gamma_1$ on the fluence $F$ and the impurity molecule. For same length molecules with stronger affinity, the binding energy to water is more effective, causing a larger enhancement of the rate $\Gamma$.

If changes of the intermolecular dipole coupling are most important, then one must add explicitly to $\Delta G$ the term due to dipole–dipole coupling. (Note, the dipole coupling is given by $\sim d_1 d_2$ + $\ldots$, here $d_{1i}$ may be the photoenhanced dipole moment and $d_{2i}$ the surrounding dipole moments, which are changed due to $d_{1i}$.)

The structure is different for ice and water, see Pauling and new studies [9, 10]. This could be the reason for getting sufficiently close to M in the phase diagram, see figure 3, the photoinduced transition vapor $\rightarrow$ ice rather than vapor $\rightarrow$ liquid. In the above equations contributions due to induced dipole moments via strong electric fields are only indicated by dots.

The increase of the dipole moment $p_d$ results from changing upon photon absorption the hybridization and population of the 1s and 2p states in H$_2$O. This might lead to a considerable strengthening of the bonding between the water molecules. Depending on the size, the radius $r$ of the condensed nucleus and light fluence $F$, a critical nucleus might involve one or more photoexcited molecules. Correspondingly the cohesion and latent heat $q$ increase.

In highly polarizable material a strong electric field $E$ causing $p_d = \alpha E$ is expected to increase also the dipole coupling. Then, for the dipole changes one has $\Delta p_d \propto E$.

One may write generally $p_d = p_{d0} + \Delta p_d$, where $\Delta p_d$ is photoinduced, see previous discussion. Approximately, one may assume again $\Delta p_d \propto F \propto \xi$. Here, as before $\xi$ is the fraction of excited atoms or molecules.

This photoinduced strengthening of the dipolar coupling may cause a strong condensation of water in supercooled very pure vapor and also for supersaturated pure water vapor. At sufficiently low temperatures ($T \leq q'$, where $q'$ refers to the latent heat for water $\rightarrow$ ice), as mentioned one might get for supercooled vapor, see figure 3, for energetic reasons a transition to ice. Here, $q'$ should take into account the increase of the dipole moment.

Of course, ionization may also play a role regarding the strengthening of the intermolecular coupling ($\Delta G \propto \frac{\epsilon^2}{2r^3} + \frac{\epsilon q}{r^3} + \ldots$).

The phase transition via precursor fluctuations consisting of nuclei refers to sufficiently pure substances. The photoactivated nucleation due to impurities may play an important role in not so pure substances.

Of course, one gets as mentioned already also photoinduced changes of phase transitions without nucleation, see previous discussion. If cohesion increases due to electron excitations caused by photon absorption, then one expects that ultrafast melting occurs at higher temperatures. Also, if for example saturated vapor is in contact with its liquid and the interface is planar, then condensation of the vapor occurs without nucleation and one has no supercooling. (Similarly for such an interface no superheating occurs [8].)

To observe photoinduced changes and for a quantitative analysis of this one should also study the Thompson droplet equation and corrections and relate this to bond changes.

Regarding photoinduced demixing or mixing enhancement (for example in alloys of type AB), note that electron excitations affect the bond energies ($\epsilon_{ij}$, $i, j = A, B$) and thus the control parameter $\epsilon (\epsilon = E_{AA} - E_{AB})$. Within molecular field theory one gets (for a simple two sublattice structure) as well known [8] for the energy (or similarly for the free energy) $E = E_0 - (z/4) NC X^2$, (38)

where $X$ is the usual order parameter ($X = 1$ is the state with atoms A only on one sublattice, $X = 0$ a mixed state with atoms A, B populating both sublattices, etc.), $z$ denotes lattice coordination. Thus, obviously (possibly selectively) photoinduced changes of the bond energies $\epsilon_{ij}$ affect the order–disorder transition (and mixing) and critical temperature $T_c = z\epsilon/2k$.

A similar analysis applies to solubility and segregation of alloys $A/B_{1-x}$. Note that $\epsilon > 0$ favoring ordering may change upon electron excitations into $\epsilon < 0$ and then $X = 0$ and mixing is favored.

It is of general importance that the electrons hopping on a lattice (see tight-binding approximation) may be strongly affected by electron excitations. Thus, the interatomic coupling changes, in particular the exchange coupling $J$ important for magnetism. Note, $J$ may change from ferromagnetic coupling $J > 0$ to antiferromagnetic coupling $J \leq 0$. Tunneling involving ferromagnets depends sensitively on the electron excitations. Applying Onsager theory ($J = LX$) to nanostructures one finds that the coupled induced currents by the forces $X$ may also respond sensitively to electron
excitations. Obviously, the gradient $X \propto (M_1 - M_2)$ of the magnetization $M$, where 1 and 2 refer to two neighboring ferromagnets, may be manipulated by light raising for example the temperature in one of the ferromagnets. Similarly, $X \propto \nabla \mu$ or $X \propto \nabla \mu_\sigma$ can be changed by manipulating optically the electron population. Here, $\mu_\sigma$ denotes the spin dependent chemical potential. This offers interesting possibilities for photoinduced electron transport, for a photoinduced Hall effect, etc.

3. Results

In the following we apply the analysis and present some characteristic results for phase transitions due to photoinduced bond changes:

1. structural transitions,
2. non-thermal melting of covalent crystals,
3. condensation of vapor,
4. condensation of water.

Results for the response to laser induced electron excitations due to weakening or strengthening of interatomic or intermolecular bonding are presented. Of particular interest are phase transitions like vapor/liquid, crystalline/amorph, etc. There are many interesting problems, for example optically induced transitions diamond/graphite, graphite/graphene and in general problems regarding agglomeration physics.

In general such optical studies may help to shed light on nonequilibrium physics and time resolved ultrafast phase transitions. For example, the time dependence of crystal growth, at equilibrium versus nonequilibrium.

3.1. Bond weakening

First we present results typical for photoinduced weakening of chemical bonding. Examples are structural changes in covalently bonded semiconductors and ablation at surfaces.

In figure 2 typical results obtained using an electronic theory, see [1, 2], for photoinduced transitions of covalently bonded semiconductors are shown. Depending on the light fluence $F$ or concentration $\xi$ of electron excitations, excitations into antibonding states, the covalent structure changes very fast, within about 100 fs, and conductivity increases, since the gap between the conduction and valence bands closes. In figure 5 we illustrate the dependence of the crystal growth rate $\Gamma$ on time $t$ and fluence $F$ which follows from applying the thermodynamical theory. Overlap of nucleation centers should speed up the increase of the rate.

In figure 6 the phase diagram of graphite is shown, since particularly interesting nonequilibrium behavior is expected regarding superheating, supersaturation, etc.

In figure 7 the photoinduced very fast transition diamond $\rightarrow$ graphite is shown, the results were obtained by Garcia and Jeschke [3, 4]. The graphitization occurs, since the photoinduced repopulation of the $s$, $p_x$, $p_y$, $p_z$ states lowers essentially the minimum of $G$ or PES of diamond, see figure 1(b). The minimum of the PES for graphite remains largely unchanged.

![Figure 6](image-url) (a) Pressure versus temperature phase diagram observed for carbon. The solid lines refer to equilibrium, B and C refer to very fast transition of graphite to diamond and diamond to graphite, respectively. For a discussion see [4]. These results referring to equilibrium thermodynamics should be compared with nonequilibrium behavior. (b) Phase diagram for lower pressures (? indicates controversial issues). Carbynes may refer to phases consisting of linear molecules. Supercooling and superheating, its dependence on $p$ and $T$, may exhibit particularly interesting behavior. It is of great interest also how to get the photoinduced transition graphite $\rightarrow$ diamond at nonequilibrium.

![Figure 8](image-url) Important results by Jeschke and Garcia [3, 4] are given for photoinduced ablation at the graphite surface. Note the coherent ablation of a graphite plane, quasi optical generation of graphene after about 1 ps. This result might be typical for layered structures with stronger intraplane bonding than interplane bonding. The photoinduced formation of graphene is stable (for larger sizes of graphene, simply due to the bending-energy barrier). In terms of general physics this is a consequence of structural anisotropy and consequently fluctuations do not destroy this two-dimensional structure. During and after emission of a graphene plane reconstruction within the plane of hexagons occurs shortening and strengthening the bonds to quasi compensate for the loss of interplane binding. This is in accordance with the Le Chatelier principle [8].
Figure 7. Ultrafast non-thermal graphitization of a (100) diamond crystal. Note, a 1.1 eV/atom is absorbed from the laser pulse of 20 fs duration. The transition is due to electron excitations. For details of the calculations see [4]. Note the time dependence of the transition. While for diamond $p_z$ orbitals are important for structure and cohesion, for graphite $2p_z$ states are not essential for binding. As a consequence the diamond minimum in PES, see figure 1(b), gets weaker and the one for graphite does not change much.

In figure 9 the mechanism for the coherent ablation of a whole plane is illustrated, for a detailed discussion see [3, 4]. This may have more general validity for ablation processes. In some cases depending on the crystal structure coherent ablation may depend on the laser pulse shape, duration of the pulse and wavelength and light polarization.

Detailed analysis reflects the role played by energy and momentum conservation regarding structural dynamics. Clearly, the coherent ablation is an interesting example of momentum transfer dynamics.

It is also of interest to study the optical response of graphene or a few layers of graphene. In particular, what is the momentum dynamics, the transfer of the photoinduced momentum, how long does it take to distribute the transverse one into the longitudinal one, etc? This sheds light on the stability of graphene, its wavy like structure, etc.

In general electron excitations will cause ultrafast (fs time scale) structural changes and phase transitions between different lattice structures. Non-thermal melting of Si, etc is a spectacular case demonstrating on what time scale the photoinduced transitions due to electron excitations occur in contrast to the usual much slower thermodynamical transitions. Clearly, similar photoinduced transitions are expected for ferromagnets or antiferromagnets having a sensitive dependence on lattice structure.

3.2. Bond strengthening

Electron excitations from a full band into states with stronger overlap between neighboring lattice sites cause generally stronger bonding. An example is mercury. Other examples are insulator metal transitions (see also photoassisted transitions). In Hg nanostructures and thin films the gap between the 6s states and 6p states may be small enough so that a transition nonmetal $\rightarrow$ metal may result due to electron excitations into the 6p states, see [5]. Then the photoinduced effects get stronger. The increase in the coupling between the Hg atoms in the condensed nuclei can be related to the behavior of Hg clusters. Clusters and nuclei having about 15–20 atoms should have a nearly closed s–p ‘band gap’, optical measurements should reflect this, also the latent heat. Photoinduced crystallization due to increased bonding should also occur close to the liquid/crystal phase boundary.

In figure 10 we illustrate how supercooling decreases for increasing light intensity. For example, such a dependence
Figure 8. Typical results for non-thermal ablation at a graphite surface. Note, 2.4 eV/atom is absorbed from the laser pulse acting for 20 fs. The light density is below the critical one destroying graphite planes. After about 160 fs the light energy is transferred to the atoms causing strong coherent vibrations of the surface planes and ultimately even a detachment of whole intact graphite planes (graphene) with (somewhat time delayed) shortened intraplane atomic distances as expected for energetic reasons. This optical production of graphene first calculated by Jeschke et al [4] was later observed. Conditions for coherent ablation of two or more planes need be studied.

Figure 9. Illustration of the mechanism responsible for the photoinduced formation of graphene, see calculations by Jeschke et al [4]. The photoinduced vibrational motion of the graphene planes causes strong repulsive interactions between the graphene planes. This then results in coherent ablation of intact atomic planes of the anisotropic crystal, an interesting example of coherent momentum transfer.

Figure 10. Schematic illustration of the decrease of critical supercooling $\Delta T = (T_0 - T)$ as a function of the laser fluence $F$ (or the fraction of excited electrons). Condensation occurs at temperature $T$ and $T_0(p)$ refers to the thermodynamical phase boundary at pressure $p$. Also, generally $\ln \Gamma_{\text{ph}} \propto F$.

on fluence $F$ is expected for water (or ice) condensation. As discussed, supercooling $(\Delta T = T_0 - T)$ decreases for increasing fluence $F$. The range of supercooling decreases as $q$ or $F$ increases. In order to keep the temperature nearly constant during nucleation the fluence probably needs to be limited and not to be too strong, regarding supersaturation and supercooling.

Results by Hensel et al [6] for Hg may be typical for photoinduced condensation of vapor due to bond strengthening. The effects should enhance in nanostructures of Hg, thin Hg films, when the gap between 6s and 6p states gets smaller, see nonmetal $\rightarrow$ metal transition in Hg clusters [5]. In satisfactory agreement with experiments by Hensel et al one gets from the previous thermodynamical theory and its equations a reduction of supercooling $\Delta T$, of supersaturation $\ln \frac{p}{p_0} \propto 1/T$, and $\Gamma_{\text{ph}} \propto F$. Also the rate $\Gamma$ depends sensitively on $p/p_0$ as predicted by the thermodynamical theory. Previous
thermodynamic theory yields for the enhancement of the rate

$$\ln \Gamma \propto \frac{\Delta G}{kT} \sim \ln \frac{p}{p_0} + \cdots. \quad (39)$$

Thus, one obtains in reasonable agreement with experiment [6] that much smaller values of the critical supersaturation yield already condensation rates $\Gamma$ as in the absence of electron excitations. This should be the case for other substances as well.

In figure 11 it is illustrated how for mercury vapor the condensation rate $\Gamma$ increases with light fluence $F$. For an estimate we assume a change of $\Delta G_{ph}$ by about 0.02 eV as the light intensity doubles. One expects that the slope of $\ln \Gamma$ versus fluence $F$ increases if the gap between 6s and 6p states becomes smaller. Note, similar behavior is expected for the enhancement of water condensation due to photons. The slope becomes smaller. Note, similar behavior is expected for the photoinduced enhancement of water condensation. The dots should indicate possible deviations for larger fluences.

Close to the triplepoint, see figure 3, supercooled or supersaturated vapor may exhibit a transition to ice rather than liquid water, for energetic reasons related to the latent heat of the water/ice transition. This is in accordance with the thermodynamical theory outlined before. Note, at lower temperatures the dipole–dipole coupling becomes temperature independent, see previous discussion [9].

In impure water one gets approximately

$$\Gamma \sim \exp - \eta (\Delta G_k)_{dipole}, \quad (41)$$

where here $\eta$ denotes the enhancement due to impurity molecules. $\eta$ may be estimated from the change of the latent heat due to impurity molecules. For example $\eta \sim 2$ would cause already a large increase of $\Gamma$. We estimate for a change of the barrier $\Delta G$ by about 0.1 eV (or less by about a few hundreds of eV) at a temperature of about 500 K already the enhancement $\Gamma \sim 10$.

The dependence on fluence $F$ may characterize the photoinduced condensation of water. Experiments (dependence of condensation on sort and concentration of ‘impurity’ molecules) must determine what the main reason for photoinduced condensation of supersaturated, etc vapor to water or ice is. Generally one expects, as discussed already,

$$\ln \Gamma_{ph} \propto F + \cdots. \quad (42)$$

Note, a different dependence on fluence $F$ could reflect interesting physics.

If the photoinduced changes $\Delta \mu'$ result from an increase in binding between water molecules induced by the binding between molecules like SO$_2$, CO$_2$, C$_6$H$_{14}$(H$_2$O)$_m$, C$_n$H$_m$, etc and water, then one expects a possibly strong increase of the condensation rate $\Gamma$ and $\ln \Gamma_{ph} \propto F + \cdots$.

One also expects that the condensation rate $\Gamma$ increases with the affinity between the water and the molecules acting as impurities and agents for forming nucleation centers. As mentioned already, the dependence of $\Gamma$ on the concentration of these impurity molecules is interesting. Furthermore, in particular $\Gamma_{ph}$ should also increase with length and surface of the molecules with strong affinity to water. Generally the photoeffects should result mainly from activating electrostatic (dynamic) interactions causing dipole enhancement, etc.

If also ions are produced upon laser irradiation these play a role and should be included in $(\Delta G)_{k}$ and $\Gamma$ as discussed before. The Coulomb field of the ions affects (the surrounding) bonds and may also change dipole moments.

In figure 12 we sketch the significance of photoassisted electron charge transfer. As discussed already for photoinduced enhancement of dipole moments, electron excitations affect electron charge transfer processes. Examples are charge transfers at surfaces, between chemisorbed atoms, molecules and surface of a crystal, and between two quantum dots, for details see [3]. In general, photoassisted hopping between potential wells and tunneling is important. As already suggested by the Hubbard Hamiltonian ($H = H_0 + U n_{i+1} n_{i+1} + \cdots$, $H_0 = \sum c_i^+ c_i$) the transfer and hopping may be spin selective and optically determined population controls this. The magnetic properties of atoms (molecules) having
For the corresponding interplay of momentum and energy dynamics one might achieve rather easily optical production of graphene and other atomic planes of layered compounds (likely lateral momentum correlations within the surface atomic plane might be important). Roughly speaking the intraplane bonding must be stronger than the interplane bonding. This is an interesting example of selective optical bond-breaking.

As spin–orbit coupling in the case of 2d magnetism, structural anisotropy is responsible for the observed stability of the 2d lattice, see [1–4, 12]. It is interesting that photoinduced formation of graphene via coherent ablation from graphite was discovered and calculated by Jeschke, Garcia and Bennemann (and then experimentally confirmed by Zewail et al) already several years before the most elegant quasi mechanical production of graphene by Geim et al [13]. Related problems are the photoinduced transitions nanotubes \( \leftrightarrow \) graphene as a result of the competing surface- and bending-energy interplay. Calculations by Kerner and Bennemann show that a quasi flat graphene piece is stabilized due to the bending-energy barrier and reconstruction [14].

Many important thermodynamical processes change upon photon induced manipulation of chemical bonding. For example, one may observe photoinduced demixing of alloys, segregation (in CuNi alloys, etc), continuous and discontinuous changes of bond character (involving a critical fluence) and effects on magnetism. For example, due to electron excitations and the accompanying increase in electron temperature the Curie temperature \( T_C \) changes and also depending on the band structure the Heisenberg exchange integral \( J(T_\ell, \ldots) \) may change from ferromagnetic to antiferromagnetic coupling. At film interfaces, for example, FM/FM may change to FM/AF, etc. In general interesting effects may occur due to photoinduced changes of angular momentum. Then regarding dynamics this is also controlled by angular momentum conservation.

Of course, electron currents are influenced by electron excitations and hence one expects (in particular for nanostructures) photoeffects on thermoelectricity, the Hall effect and all other nonequilibrium thermodynamical processes. The currents, \( j = LX \), see Onsager theory [15, 16], are optically influenced due to changes in the generalized (thermodynamical) forces \( X \) resulting from gradients in temperature, magnetization (\( VM \sim \sin \Delta \psi(r) + \cdots; \Delta \psi \) refers to phase difference), spin dependent chemical potential of the electrons, etc [16]. Clearly, temperature gradients, inhomogeneous magnetization, etc can be changed by varying the population of electron states and (locally) the electron temperature [17]. In tunnel junctions involving superconductivity and magnetism, for example, photoinduced quenching of magnetism causes rapidly fluctuating currents, in particular of the spin polarization [17].

In the case of phase transitions via precursor nuclei formation it is of interest to observe an acceleration of the phase transition due to overlap of the nuclei if photoinduced electron excitations are mainly responsible for the formation of the nuclei.

A challenging open problem is the optically induced condensation of carbon atom vapor to diamond (via...
agglomeration to small cluster nucleation centers) or optically induced reversal of graphitization. The use of small diamond crystallites or sp3 bonding favoring impurities may be an option. Photoinduced preparation of nonequilibrium carbon atoms with s- and p-state population like in diamond may help the agglomeration of diamond. It remains to be seen which physical conditions permit this.

Photoinduced charge transfer, for example between chemisorbed atoms or molecules and the surface of solids, and photoassisted tunneling between quantum dots, for illustration see figure 12, may yield many interesting results, see [3]. The interplay of current density and light field, the dependence on light pulse shape and pulse duration are of interest, see [3]. Generally, the phase dependent coupling between quantum dots, lattice sites of an optical lattice or a solid state lattice may be varied optically (via electron excitations) and the resultant phase gradients cause Josephson like currents (transitions) and for an ensemble of sites state transitions.

As suggested already by figure 12 photoassisted and photoinduced tunneling promises interesting effects. Thus the coupling between two attractive potentials (double well potential system) can be manipulated optically, changing the hybridization of electron states in the potential wells and the interference pattern of transitions. Application to optical lattices may offer a method for optical tuning of phase transitions within such lattices (BEC, BSC, magnetism). It follows from figure 12(b) (via varying the population of the states, in view of the Pauli principle) that photon assisted tunneling can be spin selective.

From a general point of view it is of interest to study how phase transitions, in particular the fluctuations accompanying phase transitions, are affected by photoinduced electronic excitations (nonequilibrium behavior). The starting point could be the previous theories by Stampfli et al, see in particular the Ginzburg–Landau type expansion at nonequilibrium of the free energy in terms of the dominant atomic displacements caused by electronic excitations, and [2–4], for both cases of bond weakening and bond strengthening, and modern versions of Ginzburg–Landau theory including beyond molecular field theory fluctuations, see for example lecture notes by Nogueira [18]. Thus an electronic theory for the nonequilibrium physics of supercooling, supersaturation, etc may be obtained.

Also photoinduced effects on the metallization of hydrogen gas (note that electron excitations into states with larger interatomic overlap) and superfluidity, in particular for small sized Cooper pairs and larger distances between them, and on BEC on a lattice may be interesting. Here also optically manipulated population of the states seems possible and interesting dynamics may result. In such a way interesting population patterns are possible.

Of course, photoinduced structural changes of interesting molecules playing an important role in biology like DNA etc are of eminent significance and these in principle may be calculated using the theory outlined for the photoinduced structural changes of the semiconductors diamond, silicon etc.

Acknowledgments

I thank C Bennemann for help in preparing this paper. Many useful and enlightening discussions, reactivating my interest, with F S Nogueira and Professors M Garcia, L Wöste and in particular with H Baumgärtel helped me. I am grateful to P Stampfli, M Garcia and H Jeschke for results. Finally, I dedicate this study to Professor J L Beeby.

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