§26. An Application of Landau Dumping to Chemical Reactions and Phase Transitions in Dense Matters under Intense Microwave Irradiations

Sato, M. (Faculty of Engineering, Chubu Univ.),
Fukushima, J. (Dept. of Appl. Chem., Tohoku Univ.),
Takayama, S.

Introduction A theoretical hypothesis is proposed for explaining the mechanism of chemical reactions and phase transitions under the intense microwave irradiations to dense matters. The electromagnetic wave excites electro-kinetic wave, possibly acoustic and/or spin waves, in which the phase velocities are in the order of several tens m/s as closer to the ion thermal vibration velocities in lattices of solids and in clusters of liquids. If the kinetic motions at the microwave frequency could grow up by collision-less damping in the velocity space, the accumulated kinetic energy would perturb the velocity distribution functions. Introducing the perturbed velocity function to the Eyring's chemical kinetics model, the theoretical analysis could explain the enhanced reactions in good agreements with the reported experimental results.

Excitation of Ultrasound Wave by External Microwave

Materials are heterogeneous in nature consisting of such as grain boundaries, magnetic domains in poly-crystals, powders and clusters. The electrons can move more widely on the surface than in the body of crystals. Fig. 1 shows a schematic of sound wave coupling with microwave on the surface of permittivity material. The set of equation of motion of non-isotropic elasticity (depend on Hooke's low) and alternating electro-magnetic field (Maxwell's equations) give the chains of compression and decompression. M. Steele and B. Vauel [(1)] showed the relations between stress and strain;

$$\rho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial T_{ij}}{\partial x_j} \qquad (1)$$

Where, T_{kl} are the components of the second-rank stress tensor $\boldsymbol{T}$. In the absence of piezoelectricity, $\boldsymbol{T}$ is r

Using eqs. (2) and 7), the equation of motion of lattice becomes

$$(-\rho\omega^2 + C_{44}k^2)u_x = ik\bar{e}E_z. \qquad (2)$$

The microwave accelerates particles in their translations in z-axis, that is one freedom of motion in the six motions, namely, three translations and three rotations belongs to x, y and z-axis. In the following discussions, the velocity v denotes the translation velocity v_z. The Maxwell-Boltzmann velocity distributions function $f(v)$ is perturbed as shown in the second term in the following eq. (13),

$$f(v) = f_0(v) + f_0(v)(v - v_{\mathrm{ph}})g(v). \qquad (3)$$

If the microwave has the delta fluctuation, the other approximation of delta function is the normal function shown as;

$$g(v) = \frac{1}{\sqrt{2\pi\xi^2}} \exp\left(\frac{-(v-v_{\mathrm{ph}})}{2\xi^2}\right). \qquad (4)$$

The physical images are that the stress induces electric fields E_z that propagate to z direction with an acoustic velocity. If the thermal motions of the particles are a little slower than the acoustic velocity, the static electric field E_z accelerates charged particles to z directions. On the other hand, faster particles push the wave. As the thermal velocity is slower than the sound velocity in a crystal, the numbers of particles getting energy is larger than that loosing energy. The form of eq. (4) is symmetric at $v = v_{\mathrm{ph}}$. As the velocity distribution function has a first order perturbations, Landau damping transfers energy from the vibrations in eq.(2) to the certain ions with the velocity near the phase velocity of the wave and it growths the amplitude of the kinetic motions ξ. The variance ξ^2 corresponds to the velocity spread by the accumulation of ordered motions near median v_{ph} that synchronizes to the phase velocity of electro-kinetic wave.

Applying eq.(3) and (4) to the Eyring's theory of absolute reaction rate, the reaction rate K*can be written as follows;

$$k^* = \frac{q^\dagger}{q_a q_b}\left[\frac{RT}{h} + \frac{m^*\xi^2}{h}\right]\exp\left(\frac{-E^*}{RT}\right). (5)$$

In eq. (5), the first term $RT{=}h$ in a bracket [ ] is the thermal reaction. The second term $m^*\xi^2/h$ is the kinetic energies of the ordered motions of molecules and lattices. It is not the thermal energy. The eq. (5) clearly shows that the rate of reaction is managed both by thermal energy and by the ordered motion induced by intense microwave. From a thermodynamic point of view, the second term suggest that reduced entropy give an acceleration of the particles passing by a col of activated complex.

(1) Steele, M.C., B. Vural, Wave Interactions in Solid State Plasmas, *McGrow Hill*, 1968.