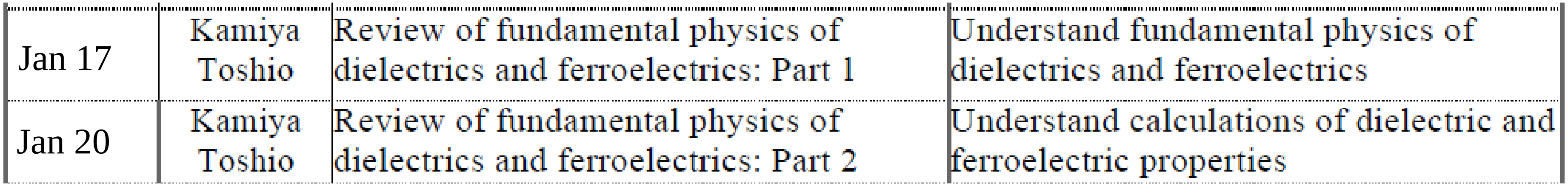
Introduction to Solid State Science

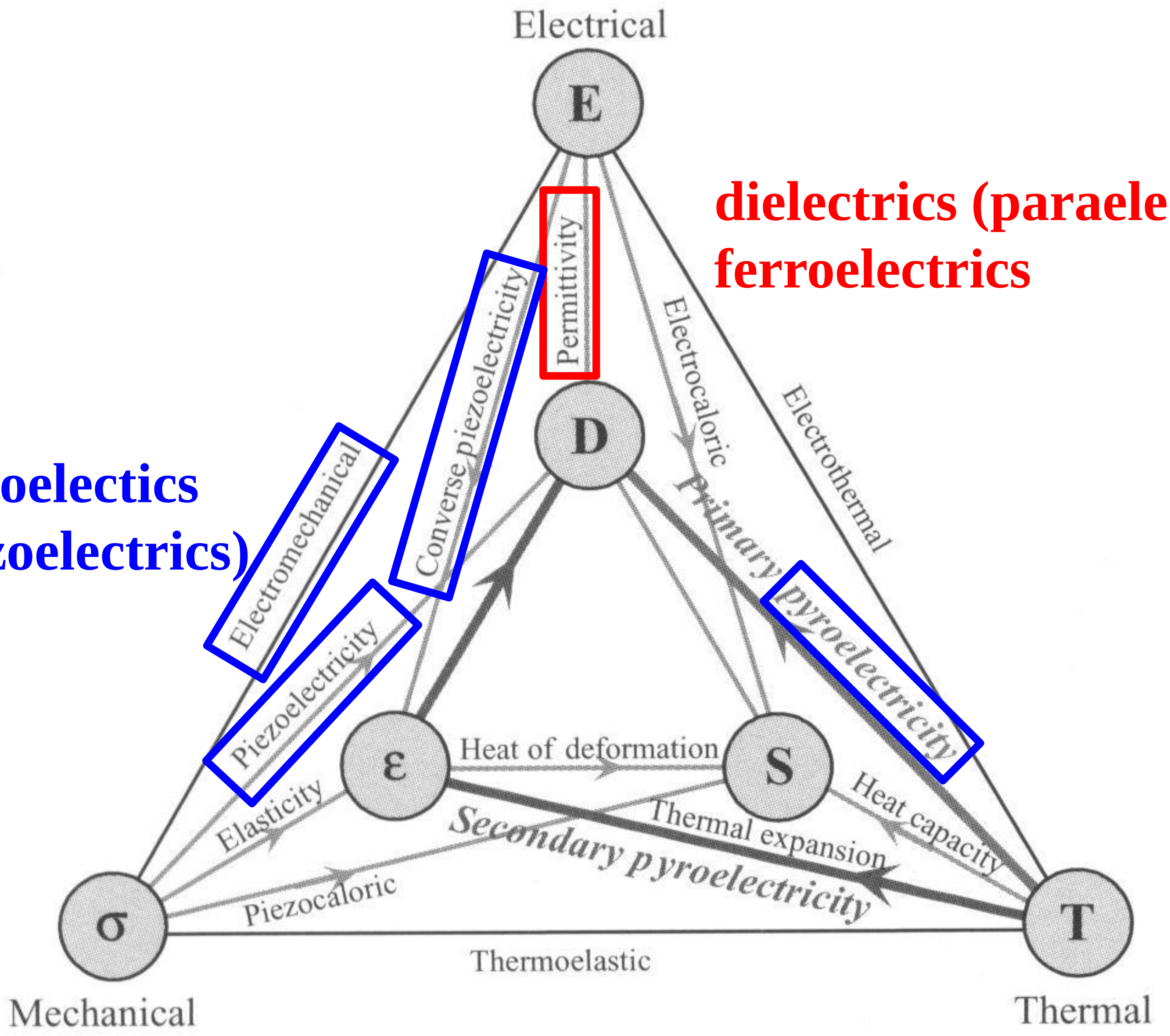
Toshio Kamiya



Jan 17	Kamiya Toshio	Review of fundamental physics of dielectrics and ferroelectrics: Part 1	Understand fundamental physics of dielectrics and ferroelectrics
Jan 20	Kamiya Toshio	Review of fundamental physics of dielectrics and ferroelectrics: Part 2	Understand calculations of dielectric and ferroelectric properties

What are material properties / functions?

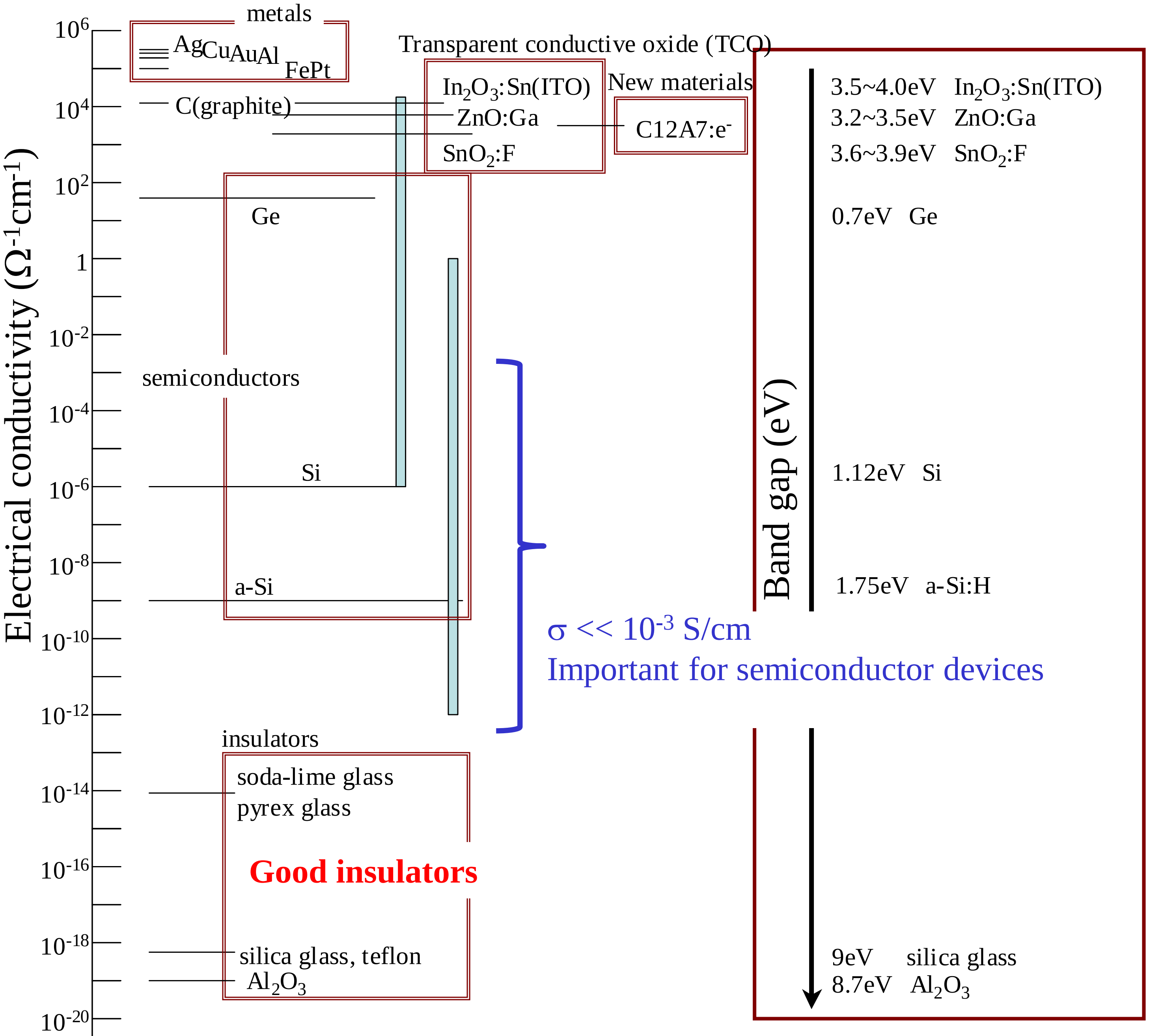
Hadis Morkoc and Umit Ozgur, Zinc Oxide, Wiley-VCH



dielectrics (paraelectrics)
ferroelectrics

Ferroelectics
(piezoelectrics)

What is dielectrics?: Conductor vs insulator



$\sigma << 10^{-3}$ S/cm

Important for semiconductor devices

Good insulators

What is dielectrics?

Electrical conductor (semiconductor, metal)

Characterized by electrical conductivity σ
(typically > 10^{-8} S/cm)

$$\mathbf{j}_\mathbf{e}(\mathbf{r},t) = \sigma\mathbf{E}(\mathbf{r},t)$$

Insulator

Characterized by very small electrical conductivity σ
(typically << 10^{-8} S/cm)
and by dielectric constant ε

$$\mathbf{D}_\mathbf{e}(\mathbf{r},t) = \varepsilon\mathbf{E}(\mathbf{r},t)$$

Dielectrics

Good dielectrics (usually)

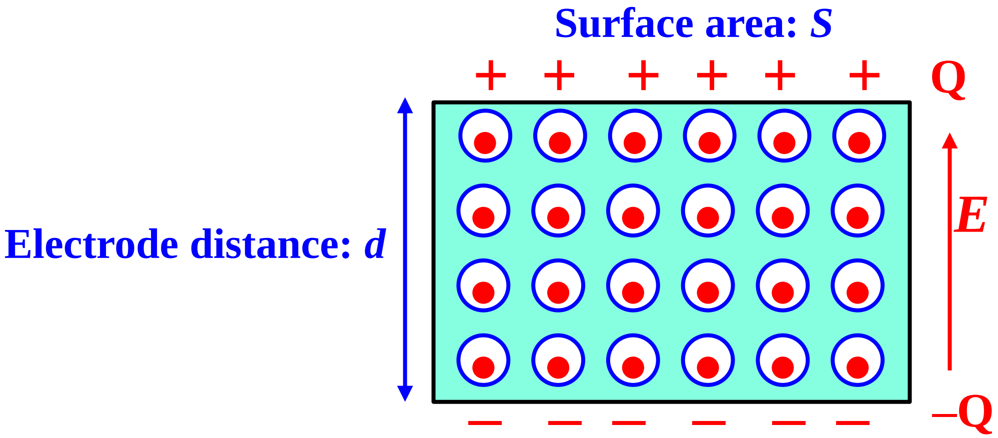
- **are good electrical insulator (very small σ)**
  to minimize dielectric loss and leakage current
- **have high ε**
  to storage large charges at low applied voltage

Classified to

paraelectics (dielectrics), ferroelectrics, anti-ferroelectrics

Function of Dielectrics

Induce / Storage electric charge ***Q*** by external electric bias ***V***



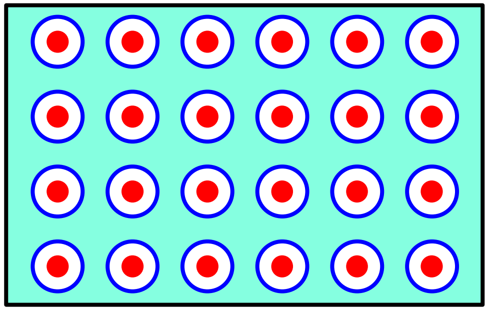
$$\boldsymbol{D} = \varepsilon \boldsymbol{E}$$

$$Q = |\boldsymbol{D}|S = \varepsilon S|\boldsymbol{E}| = \frac{S}{d}\varepsilon V$$

ε: Dielectric permittivity
(Dielectric constant)

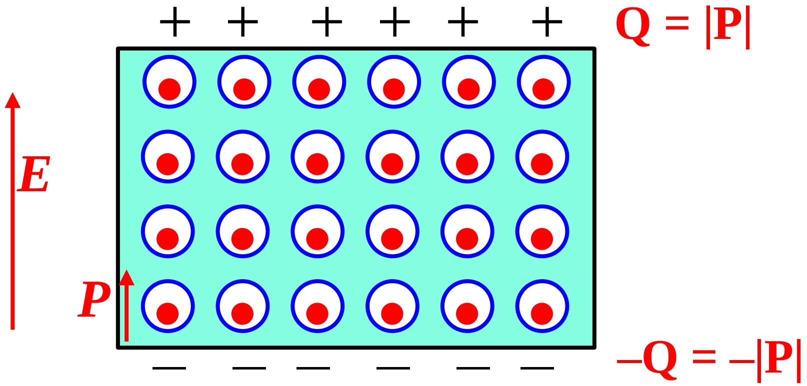
Dielectric permittivity

No electric polarization without external field ***E***



Macroscopic polarization $\boldsymbol{P} \neq \mathbf{0}$ is induced by external field

Uniform ***P*** in the bulk region produces the surface charge **Q = |P|**



$$\boldsymbol{P} = \chi_e \boldsymbol{E}$$

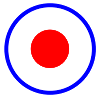
$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} = (\varepsilon_0 + \chi_e)\boldsymbol{E} = \varepsilon \boldsymbol{E}$$

$\varepsilon = \varepsilon_0 + \chi_e$: Dielectric permittivity (Dielectric constant)

χ_e : Dielectric susceptivity

Types of Dielectrics

Electron cloud ne^-

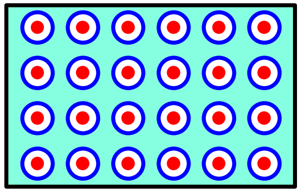


Nuclear (ne^+)

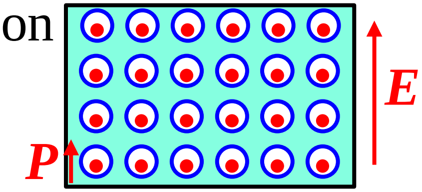
(Ionic) polarization
due to asymmetric local structure

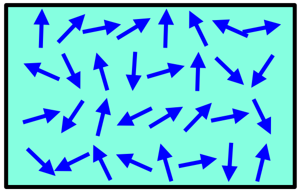
Paraelectics (dielectrics)

No electric polarization
without external field ***E***
Spontaneous polarization
$P_s = 0$

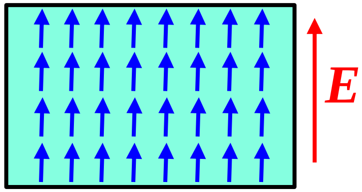


Macroscopic polarization
$P \neq 0$ is induced by
external field



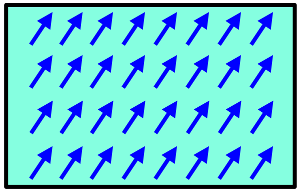


Local polarizations
are aligned by
by external field

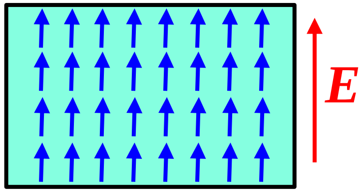


Ferroelectrics

Finite polarization
exists without external field
$P_s \neq 0$

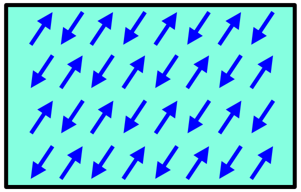


Local polarizations
are aligned
by external field

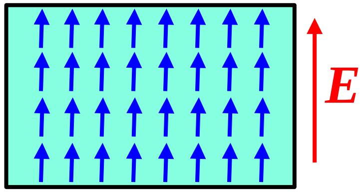


Anti-ferroelectrics

Local polarizations are
ordered in anti-parallel
$P_s = 0$



Local polarizations
are aligned by
strong external field



Electromagnetism equations

Maxwell equation

Gauss law $\mathrm{div}\, \boldsymbol{E}(\boldsymbol{r},t) = \frac{1}{\varepsilon_0}\rho_e(\boldsymbol{r},t)$

Ampere-Maxwell law $\mathrm{rot}\, \boldsymbol{H}(\boldsymbol{r},t) = \boldsymbol{i}_\mathbf{e}(\boldsymbol{r},t) + \frac{\partial \boldsymbol{D}(\boldsymbol{r},t)}{\partial t}$

Non-existence of magnetic monopole

$$\mathrm{div}\, \boldsymbol{B}(\boldsymbol{r},t) = 0$$

Electromagnetic induction law

$$\mathrm{rot}\, \boldsymbol{E}(\boldsymbol{r},t) + \frac{\partial \boldsymbol{B}(\boldsymbol{r},t)}{\partial t} = 0$$

Derivatives

Electric field and electrostatic potential

$$\boldsymbol{E}(\boldsymbol{r},t) = \frac{\partial \varphi(\boldsymbol{r},t)}{\partial \boldsymbol{r}}$$

Poisson equation $\nabla^2\varphi(\boldsymbol{r},t) = -\frac{1}{\varepsilon_0}\rho_e(\boldsymbol{r},t)$

Charge conservation law $\mathrm{div}\, \boldsymbol{i}_\mathbf{e}(\mathbf{r},t) + \frac{\partial \rho_e(\boldsymbol{r},t)}{\partial t} = 0$

Electromagnetism equations

Constitutive equations (material equations)

Ohm's law $\mathbf{j_e}(\mathbf{r},t) = \sigma\mathbf{E}(\mathbf{r},t)$

(Electrical conductivity)

Electric susceptibility $\mathbf{P_e}(\mathbf{r},t) = \chi_e\mathbf{E}(\mathbf{r},t)$

Dielectric permittivity
(Dielectric constant) $\mathbf{D_e}(\mathbf{r},t) = \varepsilon\mathbf{E}(\mathbf{r},t)$

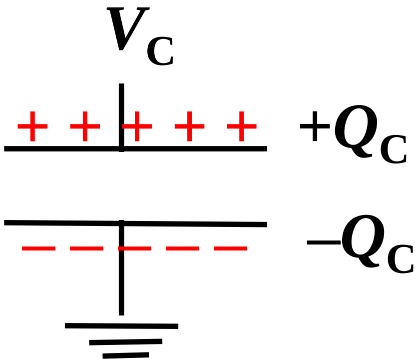
Relative dielectric permittivity (constant) $\varepsilon_r = \dfrac{\varepsilon}{\varepsilon_0}$

Magnetic susceptibility $\mathbf{M}(\mathbf{r},t) = \chi_M\mathbf{H}(\mathbf{r},t)$

Magnetic permeability $\mathbf{B}(\mathbf{r},t) = \mu\mathbf{H}(\mathbf{r},t)$

Application of dielectrics: Capacitor

Capacitor: Storage charges by applied voltage *V*

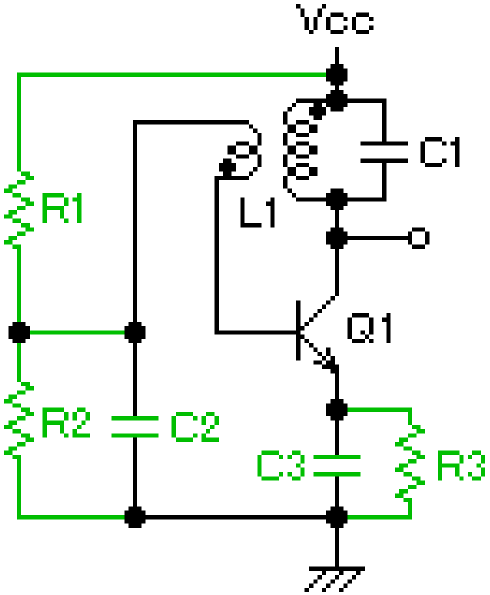


$$Q_C = |P| = CV_C = \varepsilon_r \varepsilon_0 \frac{S}{d} V_C$$

ε_r: **Relative dielectric constant**
S : Electrode area of the capacitor
d : Electrode distance

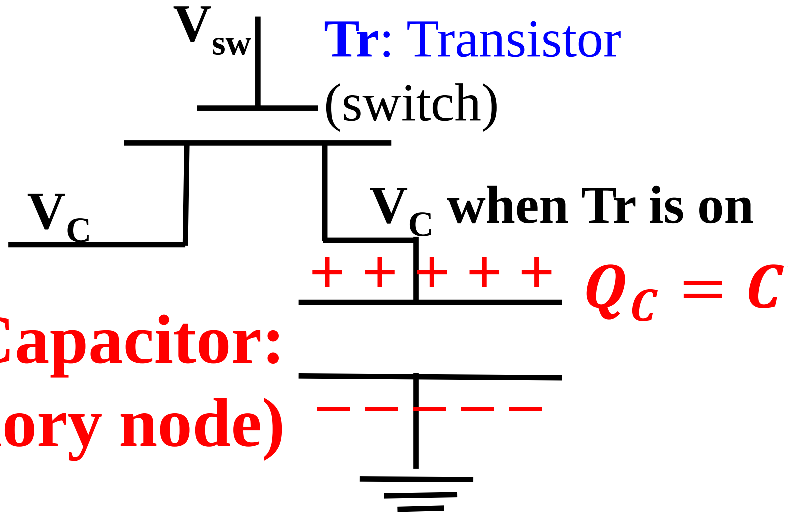
Circuits: Low (High) pass filter
Oscillator

Combined with resistor, inductor



Application of dielectrics: DRAM

DRAM (dynamic random access memory)

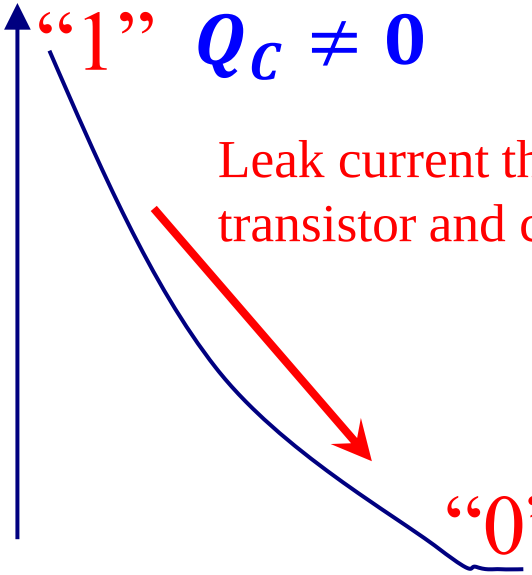


Tr: Transistor (switch)

V_C when Tr is on

$$Q_C = CV_C = \varepsilon_r \varepsilon_0 \frac{S}{d} V_C$$

Capacitor: (memory node)



$Q_C \neq 0$

Leak current through transistor and capacitor, I_{off}

$Q_C = 0$

Retention time

$$t_r \sim Q_C / I_{off}$$

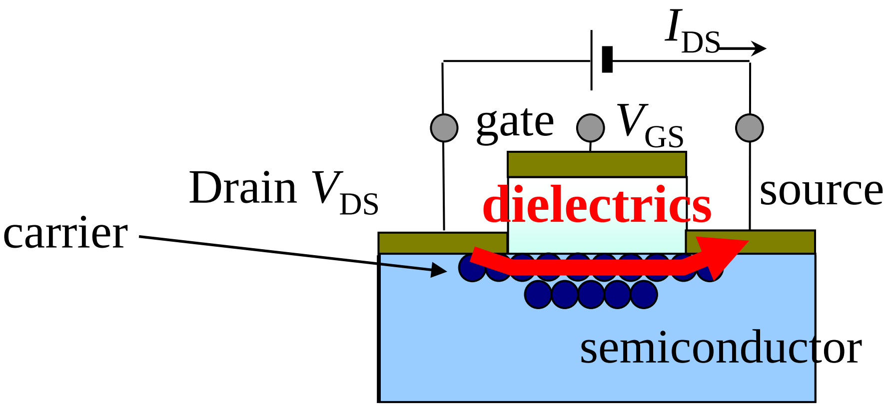
$$= \varepsilon_r \varepsilon_0 \frac{S}{d} \frac{1}{I_{off}} V_C$$

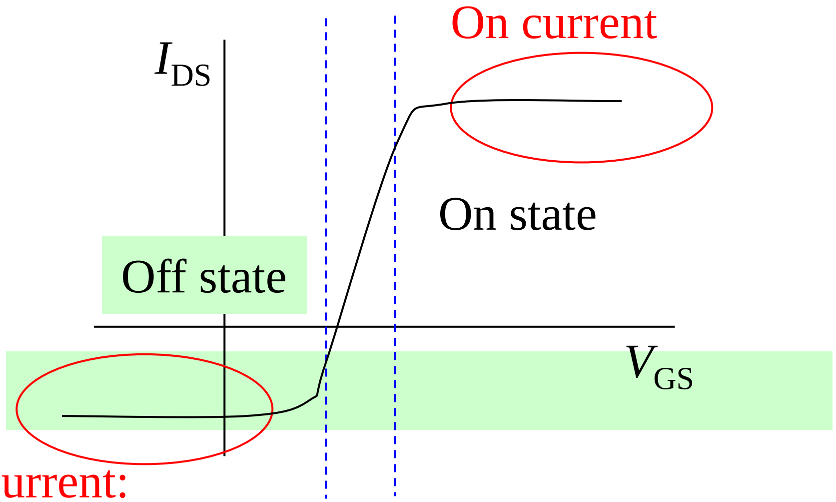
Application of dielectrics: FET

FET (Field-effect transistor)

Two representative functions of transistor

1. Amplification Use linear region ($I_{DS} \propto V_{GS}$)
2. Switching Use large on/off current ratio





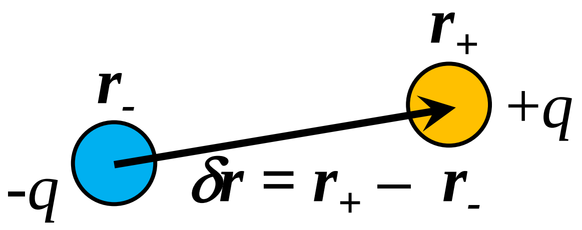
Leak current:
power consumption

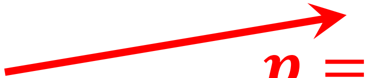
At V_{GS} = 0V
On state: Normally-on
Depletion-type
Off state: Normally-off
Enhancement-type

Electric polarization

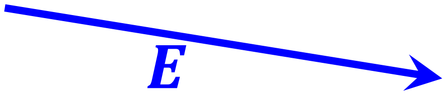
Definition of electric polarization *p*

Two point charges $+q$ and $-q$ are located at $\boldsymbol{r}_+$ and $\boldsymbol{r}_-$, respectively.





$$\boldsymbol{p} = +q\boldsymbol{r}_+ + (-q)\boldsymbol{r}_- = q\delta\boldsymbol{r}$$



$$\Delta U_{p-E} = -q\boldsymbol{r}_+ \cdot \boldsymbol{E} - (-q)\boldsymbol{r}_- \cdot \boldsymbol{E} \\ = -\boldsymbol{p} \cdot \boldsymbol{E}$$

General definition of electric polarization density, *P*

N point charges with q_i are located at $\boldsymbol{r}_\mathrm{i}$, respectively, in the volume V.

$$\boldsymbol{P} = \frac{1}{V}\sum_{i=1}^{N} q_i \boldsymbol{r}_i$$

Note: Uniquely defined only when the charge neutrality is satisfied.

Representative dielectric crystals

ε_r of representative crystals

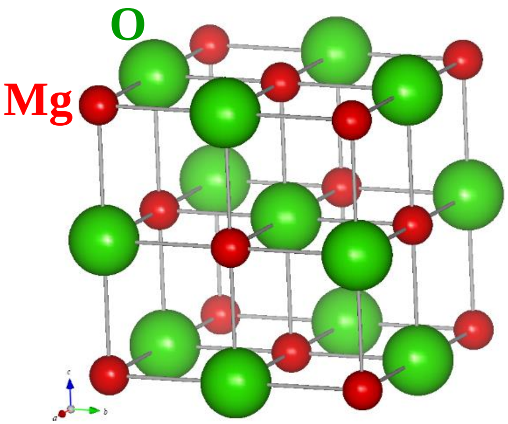
CaO	11.8	MgO	9.8
SrO	13.3	KBr	4.78
KCl	4.68	KF	6.05
KI	4.94	LiI	11.03
LiCl	11.05	NaCl	5.62

TiO_2 (rutile)	//*c*: 173, in *a*-*b*: 89
SnO_2 (rutile)	//*c*: 9.9, in *a*-*b*: 14
$Pb(Zr_{0.52}Ti_{0.48})O_3$ (25°C)	up to 1600

General trend (there should be many exceptions)

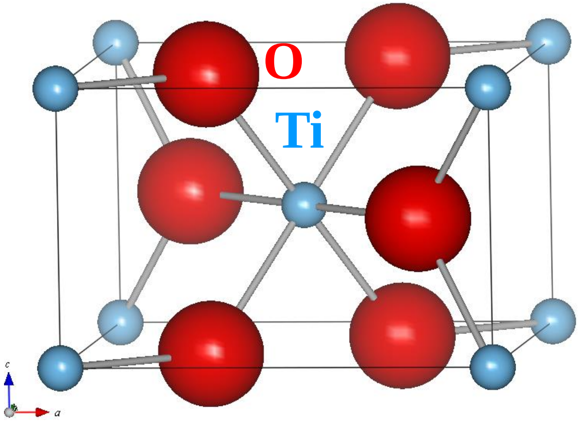
Rock-salt structure

(usually ε_r < 10)



Rutile structure

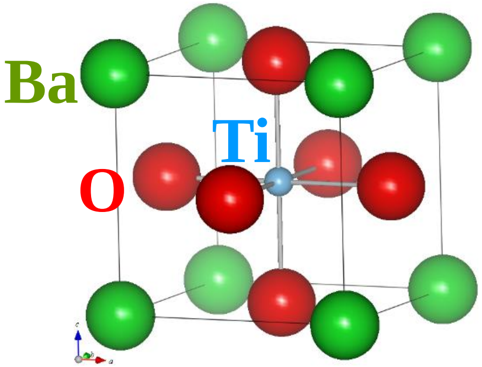
TiO_2 have large $\varepsilon_{r//c}$ ~180



Perovskite structure

Many extraordinary high $\varepsilon_r > 10^3$

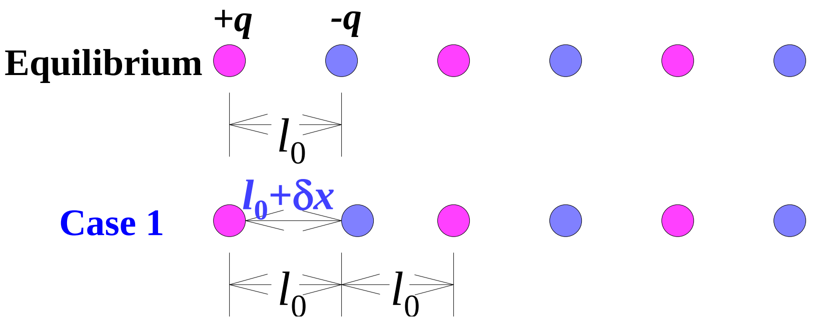
(anti-)ferroelectrics, piezoelectrics



Simple model: 1D ionic crystal at 0 K

Ion polarization

Polarization formed by ion displacement induced by external electric field ***E***.



Calculation of ion replacement

Internal energy without ***E***:

$$U_0 = \sum U_{ij}\left(r_{ij}\right) = \sum \frac{1}{2} k\left(x_i - x_{i-1} - l_0\right)^2$$

x_{i}: Coordinate of i-th ion

k: Force constant (spring constant)

If ions are displaced by ***E***, internal energy will be:

$$U = \sum \frac{1}{2} k\left\{\left(x_i - x_{i-1} - l_0\right)\right\}^2 - \sum q_i x_i E$$

Mechanical equilibrium condition at 0K

$$\frac{\partial U}{\partial x_j} = 0 = k\left(x_j - x_{j-1} - l_0\right) - k\left(x_{j+1} - x_j - l_0\right) - q_j E = 2k\delta x_j - q_j E$$

$$=> \delta x_j = \frac{q_j}{2k} E$$

Simple model: 1D ionic crystal at 0 K

Ion displacement $\boldsymbol{\delta x_j = \frac{q_j}{2k} E}$ => Polarization density $\boldsymbol{P}$

$$P = \frac{\sum q_j \delta x_j}{2l_0} = \frac{q^2}{4l_0 k} E$$

Dielectric constant

$$D = \varepsilon E = \varepsilon_0 E + P$$

$$\varepsilon = \varepsilon_0 + \frac{q^2}{4l_0 k} \qquad \left(\varepsilon_r = 1 + \frac{q^2}{4l_0 k \varepsilon_0} \right)$$

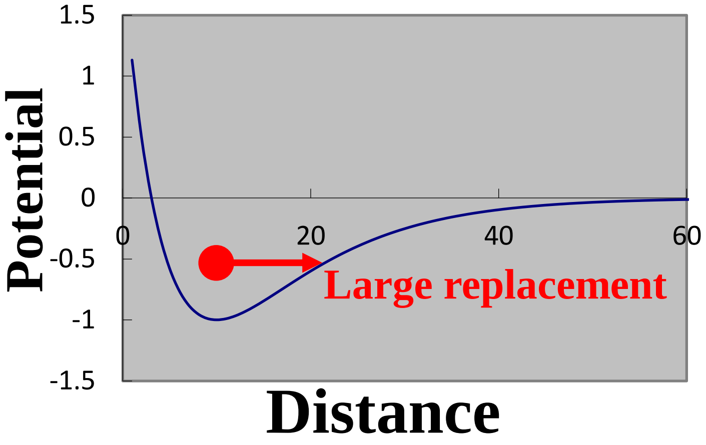
Dielectric constant is determined by ***k***

k**:** Force constant, or

Curvature of ion potential $\boldsymbol{k = \frac{1}{2} \frac{\partial^2 U}{\partial {x_i}^2}}$

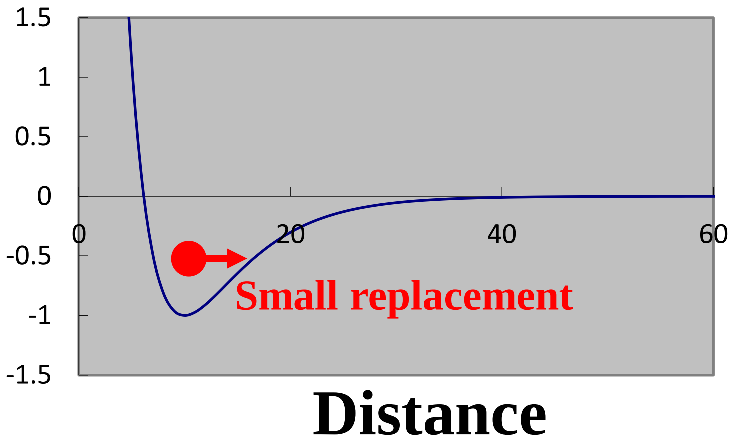
Dielectric constant vs potential curvature

Gentle potential



Large replacement

Sharp potential

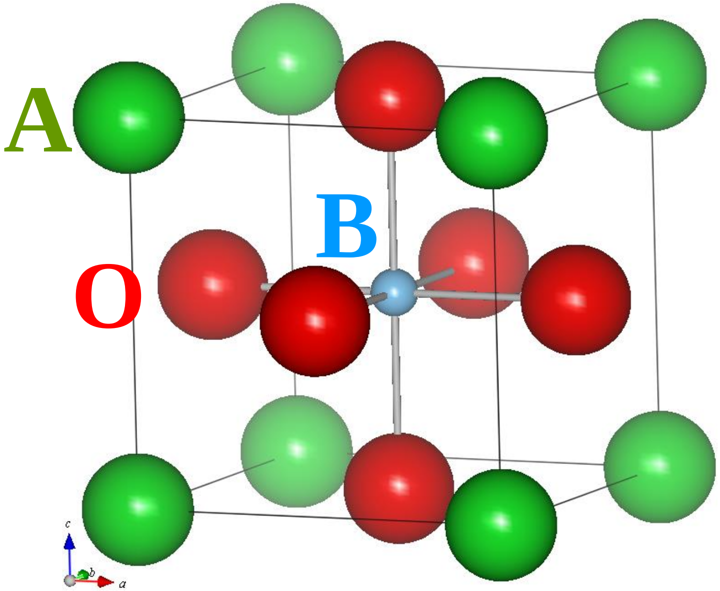


Small replacement

$$\varepsilon = \varepsilon_0 + \frac{q^2}{4 l_0 k}$$

	Gentle potential	**Sharp potential**
Potential **curvature** *k*	**Small**	Large
Ion displacement	Large	Small
Dielectric constant	**Large**	Small

Why perovskite-type crystals exhibit high ε?



For ideal cubic perovskite structure:

Each ion makes just contact with neighbor ions if their ion radii satisfy

$$a=\sqrt{2}\left(r_A+r_O\right)=2\left(r_B+r_O\right)$$

$$t=\frac{r_A+r_O}{\sqrt{2}\left(r_B+r_O\right)}=1.0$$

Tolerance factor

For *t* apart from 1.0, the cubic structure would be distorted:

t	**Lattice**	**Explanation**	**Example**
>1	Hexagonal	Large r_{A} Small r_{B}	$BaNiO_3$
0.9-1	Cubic	Ideal contact	$SrTiO_3$, $BaTiO_3$
0.71 - 0.9	Orthorhombic Rhombohedral	Small r_{A} in B ion interstitial	$GdFeO_3$ (Orth.) $CaTiO_3$ (Orth.)
<0.71	Different structures	Samll r_{A}, r_{B}	$FeTiO_3$ (Tri.)

Structural instability by the sub-lattice structure

Case 1:

Unit cell is stabilized by B-O

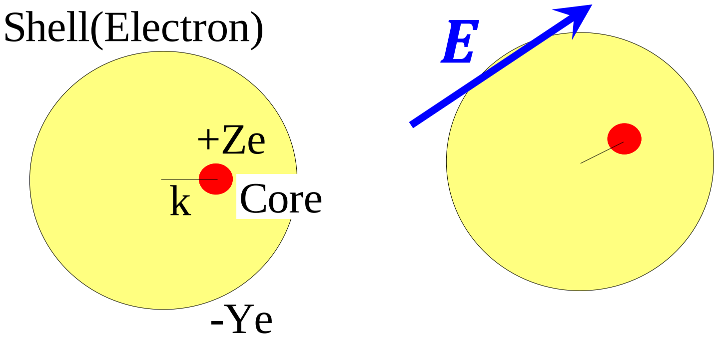
A ion is **loosely embedded**

Case 2:

Unit cell is stabilized by A-O

B ion is **loosely embedded**

How to incorporate electronic polarization: Shell model



$+Ze$: **Effective core charge** of ion

$-Ye$: **Charge of valence electron**
contribute to polarization
(electron cloud)

$(Z - Y)e$: Ion charge

1. Ion is separated to ‘effective core’ and ‘electron cloud’, which are bound by spring with the force constant k.
2. The core and the electron cloud have their own charges, $+Ze$ and $-Ye$, respectively.

=> The electron cloud can be treated as if it is a rigid ion.
The previous 1D model@0 K is applied.

Electronic polarization of an ion: $$\alpha_{ion} = \frac{Y^2}{k}$$

Extension to 3D model @ 0 K, non-harmonic interionic potential

Internal energy without ***E***:

$$U_0 = \frac{1}{2}\sum_{i,j} U_{ij}(\mathbf{r}_{10}, \mathbf{r}_{20}, \ldots)$$

$\boldsymbol{r}_{i0}$: Equilibrium coordinate of <u>*i*</u>-th ion

$\boldsymbol{U_{ij}(r_k)}$: Interionic potential between *i*-th and *j*-th ions

If ions are displaced by ***E***, internal energy will be:

$$\begin{aligned} U_{pE} &= U_0(\mathbf{r_{10}} + \delta\mathbf{r_1}, \ldots) - \sum_i q_i \delta\mathbf{r_i} \cdot \mathbf{E} \\ &= U_0 + \frac{1}{2}\sum_{i,s,j,s'} \frac{\partial^2 U_0}{\partial x_{i,s} \partial x_{j,s'}} \delta x_{i,s} \delta x_{j,s'} - \sum_i q_i \delta\mathbf{r_i} \cdot \mathbf{E} \\ &= U_0 + \frac{1}{2}\sum_{i,s,j,s'} W_{i,s,j,s'} \delta x_{i,s} \delta x_{j,s'} - \sum_i q_i \delta\mathbf{r_i} \cdot \mathbf{E} \end{aligned}$$

$\delta \boldsymbol{r_i}$: Ion displacement by ***E***

$\delta x_{i,s}$: *s* direction component (*s* = *x*, *y*, *z*) of
i-th ion replacement

$\boldsymbol{W_{i,s,j,s'} = \frac{\partial^2 U_0}{\partial x_{i,s} \partial x_{j,s'}}}$: **Hessian matrix (potential curvature)**

Extension to 3D model @ 0 K, non-harmonic interionic potential

$$U_{pE} = U_0 + \frac{1}{2}\sum_{i,s,j,s'} W_{i,s,j,s'}\delta x_{i,s}\delta x_{j,s'} - \sum_{i} q_i \delta\mathbf{r}_\mathbf{i}\cdot\mathbf{E}$$

Mechanical equilibrium condition at 0K

$$\frac{\partial U_{pE}}{\partial x_{i,s}} = 0 = \sum_{j,s'} W_{i,s,j,s'}\delta x_{j,s'} - q_j E_s = 0$$

Ion displacements are calculated easily by the matrix calculation:

$$\left(\delta x_{j,s'}\right) = \left(W^{-1}{}_{i,s,j,s'}\right)\left(q_j E_s\right)$$

(*cf.* 1D case: $\delta x_j = \frac{q_j}{2k}E$)

Dielectric constant tensor $\varepsilon_{ss'}$

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon_0\mathbf{E} + \frac{1}{V}\sum_{j} q_j \delta\mathbf{r}_j$$

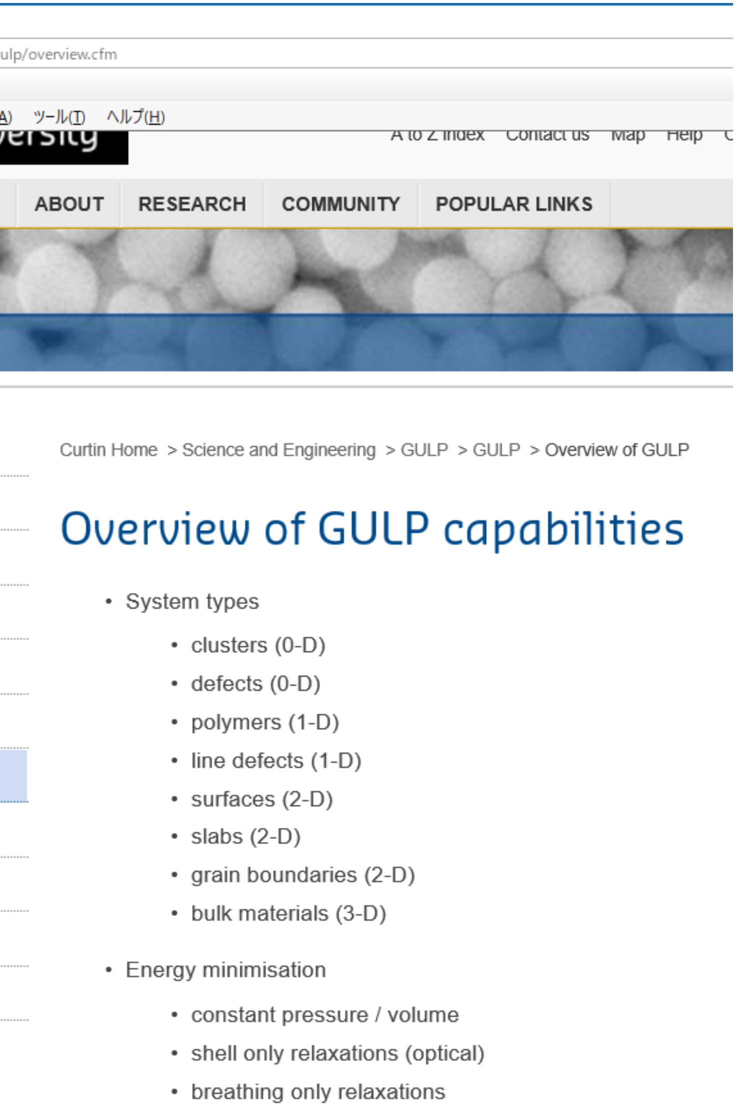
$$= \varepsilon_0\mathbf{E} + \frac{1}{V}\sum_{j} q_j \sum_{i,s'}\left(W^{-1}{}_{i,s',j,s}\right)\left(q_i E_{s'}\right)$$

$$D_s = \sum_{s'}\varepsilon_{ss'}E_{s'} = \sum_{s'}\left(\varepsilon_0\delta_{ss'} + \frac{1}{V}\sum_{i,j,s'} q_j q_i W^{-1}{}_{i,s',j,s}\right)E_{s'}$$

$$\boxed{\varepsilon_{ss'} = \varepsilon_0\delta_{ss'} + \frac{1}{V}\sum_{i,j,s'} q_j q_i W^{-1}{}_{i,s',j,s}}$$

Lattice dynamics simulation:
GULP - General Utility Lattice Program

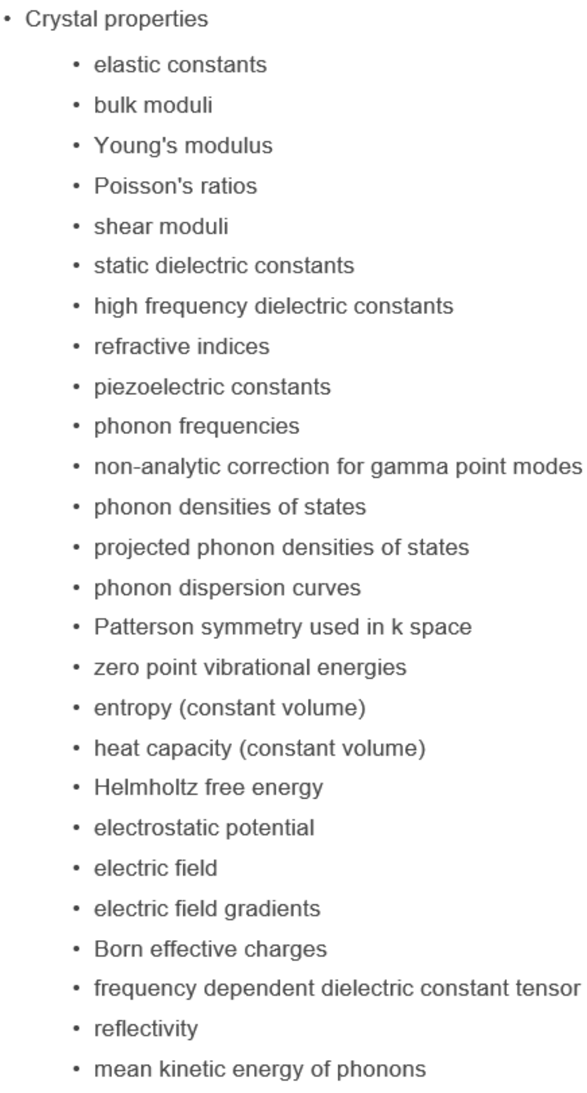
http://gulp.curtin.edu.au/gulp/



Curtin Home > Science and Engineering > GULP > GULP > Overview of GULP

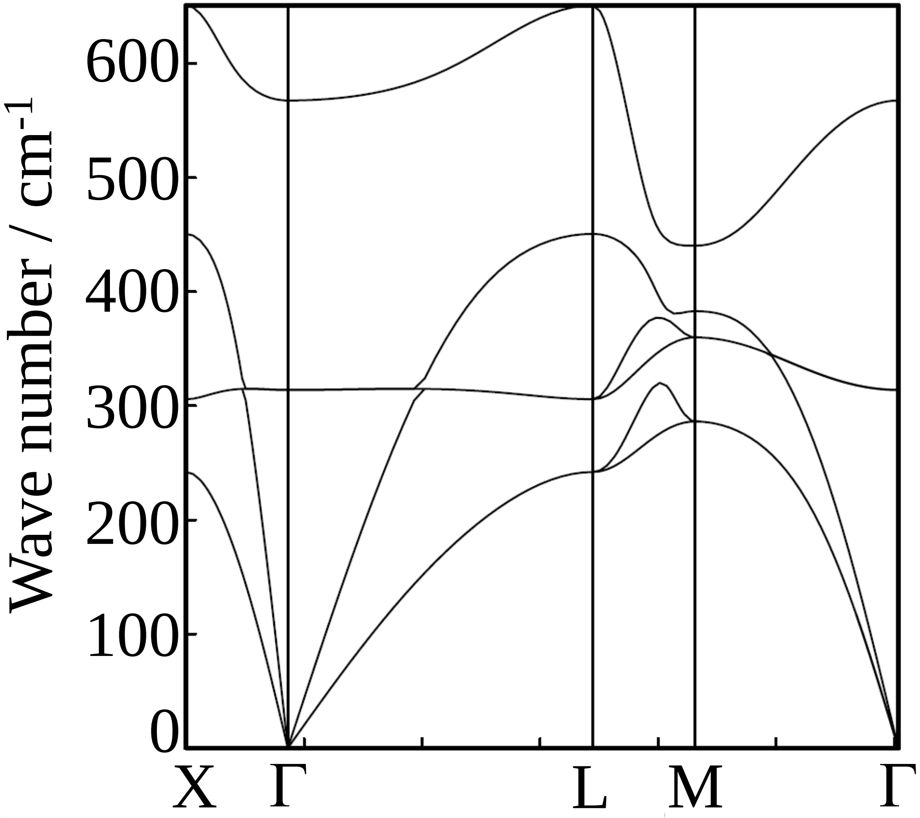
Overview of GULP capabilities

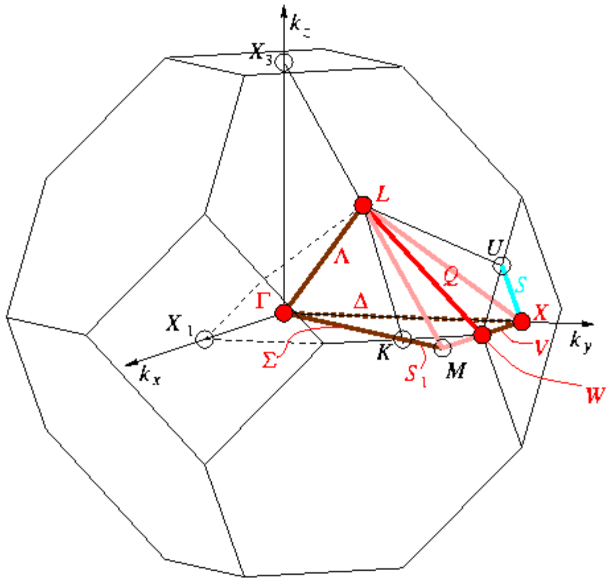
- System types
    - clusters (0-D)
    - defects (0-D)
    - polymers (1-D)
    - line defects (1-D)
    - surfaces (2-D)
    - slabs (2-D)
    - grain boundaries (2-D)
    - bulk materials (3-D)
- Energy minimisation
    - constant pressure / volume
    - shell only relaxations (optical)
    - breathing only relaxations

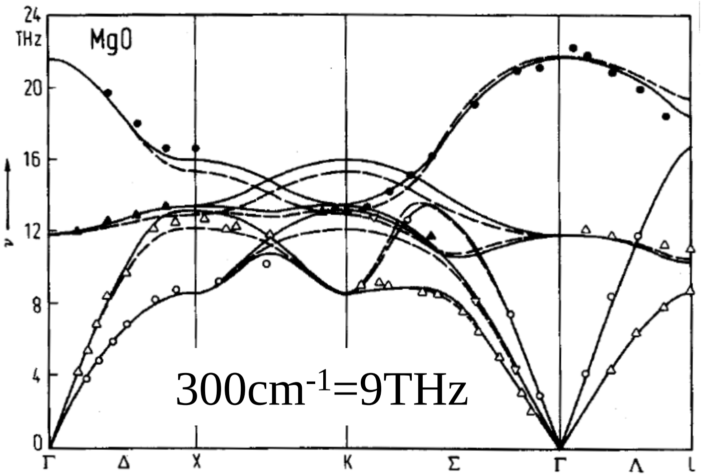


- Crystal properties
    - elastic constants
    - bulk moduli
    - Young's modulus
    - Poisson's ratios
    - shear moduli
    - static dielectric constants
    - high frequency dielectric constants
    - refractive indices
    - piezoelectric constants
    - phonon frequencies
    - non-analytic correction for gamma point modes
    - phonon densities of states
    - projected phonon densities of states
    - phonon dispersion curves
    - Patterson symmetry used in k space
    - zero point vibrational energies
    - entropy (constant volume)
    - heat capacity (constant volume)
    - Helmholtz free energy
    - electrostatic potential
    - electric field
    - electric field gradients
    - Born effective charges
    - frequency dependent dielectric constant tensor
    - reflectivity
    - mean kinetic energy of phonons

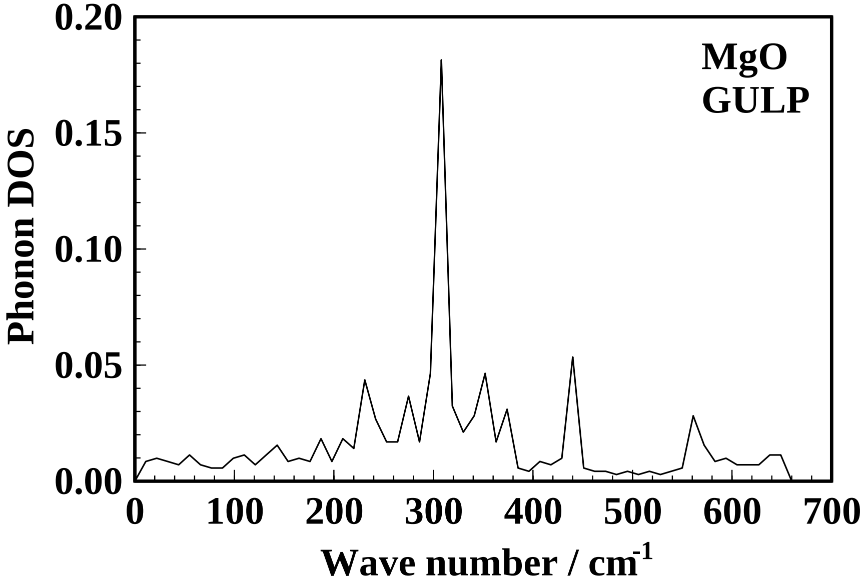
GULP (Phonon)







300cm^{-1}=9THz



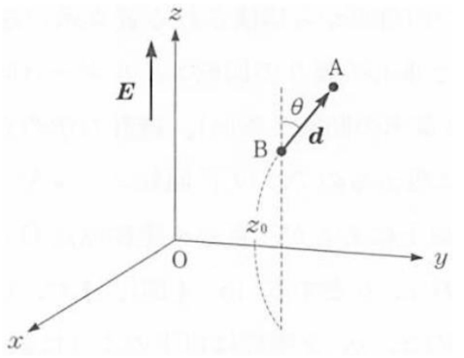
Polarization of polar molecules at finite *T*

Polar molecule like HF: H and F are charged with +$q|e|$ and -$q|e|$, respectively, and form electrical dipole $\boldsymbol{p_0} = q\boldsymbol{d}$ (d is the chemical bond vector).

When ***E*** **is applied along the *z* direction and *p*$_0$ is declined from the *z* axis by *θ* degree as shown in Fig. 1**:

$$\boldsymbol{U_p = -p_0 \cdot E = -p_0 E\cos\theta} \qquad \textbf{(5.28)}$$

Fig. 1 Dipole in electric field *E*



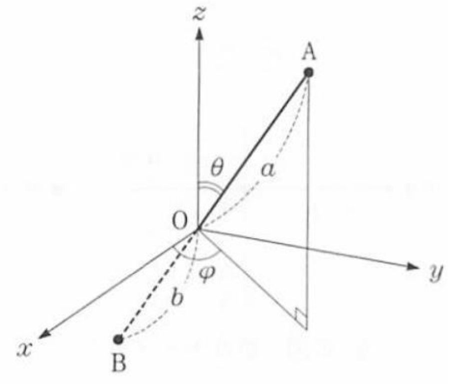
Polarization density *P*:

$$P = \frac{N}{V}\frac{\int p_0\cos\theta\cdot\exp(\beta p_0 E\cos\theta)\sin\theta d\theta d\varphi}{\int \exp(\beta p_0 E\cos\theta)\sin\theta d\theta d\varphi}$$

Replace by $\beta p_0 E = \alpha$ and $\cos\theta = x$, and integrate w.r.t. φ:

$$P = \frac{N}{V}p_0\frac{\int x\exp(\alpha x)dx}{\int \exp(\alpha x)dx}$$

Fig. 2 Polar coordinates



Partial integration gives $\int x\exp(\alpha x)dx = \frac{\exp(\alpha x)}{\alpha^2}(\alpha x - 1)$:

$$\boldsymbol{P = \frac{N}{V}p_0 L(\alpha)} \qquad \textbf{(5.49)}$$

$$\boldsymbol{L(\alpha) = \coth(\alpha) - \frac{1}{\alpha}} \qquad \textbf{Langevin function}$$

Polarization of polar molecules at finite *T*

Electrical susceptibility χ: $P = \chi E = \frac{N}{V} p_0 L(\beta p_0 E)$

$$L(\alpha) = \coth(\alpha) - \frac{1}{\alpha} \quad \text{Langevin function}$$

$$\coth(\alpha) = \frac{e^{\alpha}+e^{-\alpha}}{e^{\alpha}-e^{-\alpha}}$$

$$L(\alpha) \sim \frac{\alpha}{3} - \frac{\alpha^3}{45} + \cdots \quad (\alpha = \beta p_0 E \ll 1)$$

$$L(\alpha) \sim 1 \quad (\alpha = \beta p_0 E \gg 1)$$

=>

Low T / High ***E***: asymptotic to $P \sim \frac{N}{V} p_0$

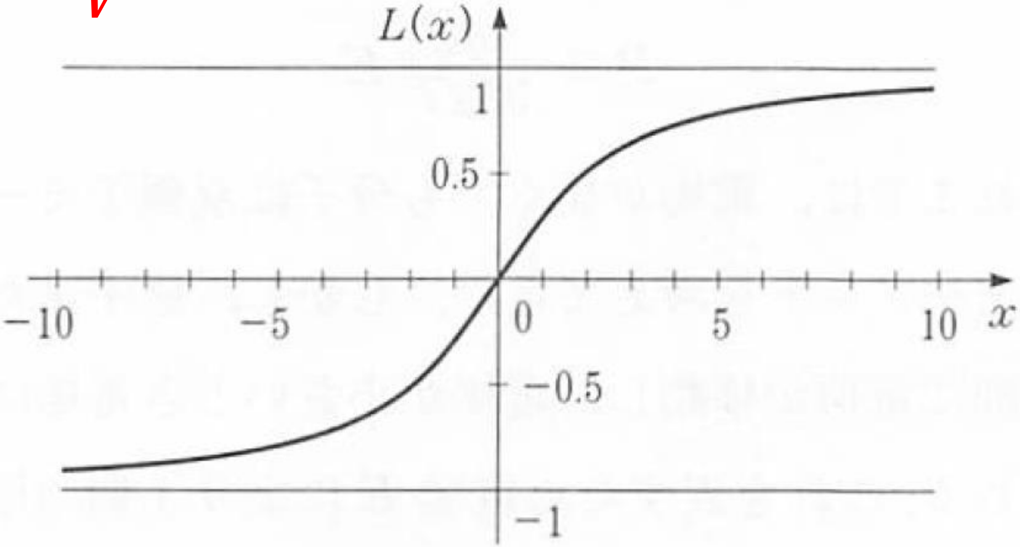
High T / Low *E*: $\chi \sim \frac{N/V}{3k_B T} {p_0}^2$

Dielectric constant ε:

$$\varepsilon E = \varepsilon_0 E + P$$

$$\varepsilon = \varepsilon_0 + \frac{N/V}{3k_B T} {p_0}^2$$

Fig. 3 Langevin function



Dielectric permittivity

Definition of electric flux density *D*

$$\mathbf{D_e}(\mathbf{r},t)=\varepsilon_0\mathbf{E}(\mathbf{r},t)+\mathbf{P}(\mathbf{r},t)$$

Electric susceptibility $\mathbf{P_e}(\mathbf{r},t)=\chi_e\mathbf{E}(\mathbf{r},t)$

$$\mathbf{D_e}(\mathbf{r},t)=(\varepsilon_0+\chi_e)\mathbf{E}(\mathbf{r},t)=\varepsilon\mathbf{E}(\mathbf{r},t)$$

ε : Dielectric constant (permittivity)

$\boldsymbol{\varepsilon_r=\frac{\varepsilon}{\varepsilon_0}}$**: Relative dielectric constant**

ε_r of representative crystals

CaO	11.8	MgO	9.8
SrO	13.3	KBr	4.78
KCl	4.68	KF	6.05
KI	4.94	LiI	11.03
LiCl	11.05	NaCl	5.62
TiO_2 (rutile)			//*c*: 173, in *a*-*b*: 89
SnO_2 (rutile)			//*c*: 9.9, in *a*-*b*: 14
$Pb(Zr_{0.52}Ti_{0.48})O_3$ (25°C)			up to 1600