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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

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PAIR POTENTIALS IN AMORPHOUS METALLIC ALLOYS: ORDER, STABILITY AND DYNAMICS

Lecture I

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PAIR POTENTIALS IN LIQUID AND AMORPHOUS ALLOYS

ORDER, STABILITY AND DYNAMICS

1. PAIR POTENTIALS IN METALS AND ALLOYS
   - REDUCTION OF THE ELECTRON-ION HAMILTONIAN
   - PSEUDOPOTENTIALS
   - SCREENING, ELECTRONIC MANY-BODY EFFECTS
   - CHEMICAL EFFECTS IN THE PSEUDOPOTENTIAL FOR ALLOYS

2. PAIR-POTENTIALS AND PHASE-STABILITY IN CRYSTALLINE METALS AND ALLOYS
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   - MIXED CRYSTALS
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3. STRUCTURE AND THERMODYNAMICS OF LIQUID METALS AND ALLOYS
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       - PURE METALS
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     - BEYOND HARD SPHERES
       - SOFT REPULSIVE POTENTIALS — WCA
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4. FROM A HAMILTONIAN TO A PHASE DIAGRAM

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6. GLASS-FORMING ABILITY
   - THERMODYNAMICAL ASPECTS
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     - EQUATION-OF-MOTION TECHN.
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   - INELASTIC STRUCTURE FACTOR
   - ELECTRON-PHONON COUPLING

REDUCTION OF THE ELECTRON-ION HAMILTONIAN

$$H = H_{i-i} + H_{e-e} + H_{e-i}$$

Adiabatic approximation

$$\tilde{H}_{i-i} = H_{i-i} + E_e(\{\vec{R}_\ell\})$$

↑ electronic ground state energy for fixed ionic positions $\{\vec{R}_\ell\}$

$$H_e = H_{e-e} + H_{e-i}(\{\vec{R}_\ell\})$$

Expansion in powers of the electron-ion interaction W

$$E_e = E_0 + E_1 + E_2 + E_3 + \ldots\ldots$$

$$E_n = \Omega_0 \sum_{\vec{q}_1 \ldots \vec{q}_n \neq 0} \Gamma^{(n)}(\vec{q}_1, \ldots \vec{q}_n) \cdot W(\vec{q}_1) \ldots W(\vec{q}_n)\, \delta(\vec{q}_1 + \ldots + \vec{q}_n)$$

$\Gamma^{(n)}$ .. multi-pole-functions, depend only on the electron-electron interaction

Factorization of the electron-ion ME

$$W(\vec{q}) = w(\vec{q})\, N^{-1} \sum_\ell \exp(i\vec{q}\vec{R}_\ell) = w(\vec{q})\, S(\vec{q})$$

form factor

structure factor

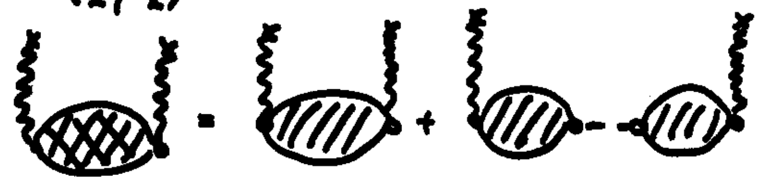
$$\lim_{q \to 0} w(\vec{q}) = \frac{b}{\Omega_0}$$

CALCULATION OF THE MULTI-POLE FUNCTIONS

$\Gamma^{(1)}(0)$:

$$\Gamma^{(1)}(0) = -[2i/(2\pi)^4] \int d^4p\, G(p) = n_0$$

$\Gamma^{(2)}(\vec{q}, -\vec{q})$:



π

proper irreducible part polarization operator

RPA: empty "polarization loop"

$\pi = \chi(q)$ ... Lindhard function

$$\Gamma^{(2)}(+\vec{q}, -\vec{q}) = -\frac{1}{2}\chi(q)/\epsilon(q)$$

$$\epsilon(q) = 1 + \frac{4\pi e^2}{q^2}\chi(q)$$

static dielectric function

Higher-order multipole functions:

General structure (Brovman + Kagan JETP 30, 883 (1970))

$$\Gamma^{(n)}(\vec{q}_1, \ldots \vec{q}_n) = \Lambda^{(n)}(\vec{q}_1, \ldots \vec{q}_n) / \epsilon(q_1) \ldots \epsilon(q_n) \qquad n > 2$$

EXPANSION OF THE GROUND-STATE ENERGY

$$E_0 = Z\, E_{eg}$$

$$E_1 = b Z / \Omega_0$$

$$E_2 = -\frac{1}{2} \Omega_0 \sum_{\vec{q} \neq 0} \frac{\chi(q)}{\epsilon(q)} |w(\vec{q})|^2 |S(\vec{q})|^2$$

$$E_n = \Omega_0 \sum_{\substack{\vec{q}_1 \ldots \vec{q}_n \\ \neq 0}} \frac{\Lambda^n(\vec{q}_1, \ldots \vec{q}_n)}{\epsilon(q_1) \ldots \epsilon(q_n)} w(q_1) \ldots w(q_n) \cdot S(\vec{q}_1) \ldots S(\vec{q}_n)\, \delta(\vec{q}_1 + \vec{q}_2 + \ldots \vec{q}_n)$$

EFFECTIVE IONIC HAMILTONIAN

$$\hat{H}_{i-i} = T_i + E_\Omega + \frac{1}{2!\, N} \sum_{i \neq j} V^{(2)}(|\vec{R}_i - \vec{R}_j|)$$

$$+ \frac{1}{3!\, N} \sum_{i \neq j \neq k} V^{(3)}(|\vec{R}_i - \vec{R}_j|, |\vec{R}_i - \vec{R}_k|, |\vec{R}_j - \vec{R}_k|)$$

$$+ \ldots\ldots$$

2nd ORDER:

Energy-wavenumber characteristic

$$F(q) \equiv -\frac{1}{2} \Omega_0 \frac{\chi(q)}{\epsilon(q)} |w(\vec{q})|^2$$

$$E_2 = \sum_{\vec{q} \neq 0} |S(\vec{q})|^2 F(q)$$

$$= \frac{1}{N} \sum_{i<j} \underbrace{\left\{ \frac{2!}{N} \sum_{\vec{q}} e^{i\vec{q}(\vec{R}_i - \vec{R}_j)} F(q) \right\}}_{V^{(2)}_{ind}(|\vec{R}_i - \vec{R}_j|)} + \underbrace{\frac{1}{N} \sum_{\vec{q}} F(q) - F(0)}$$

indirect ion-electron-ion interaction

contributes to the volume energy

$$\underline{E = E_\Omega + E_p}$$

$$\underline{E_\Omega = Z E_{eg} + b Z / \Omega_0 + \frac{1}{N} \sum_{\vec{q}} F(q) + \lim_{\vec{q} \to 0} \left(\frac{4\pi Z^2 e^2}{\Omega_0 q^2} + F(q) \right)}$$

$$\underline{V^{(2)}_Z(R) = \frac{Z^2 e^2}{R} + \frac{2!}{N} \sum_{\vec{q}} e^{i\vec{q}\vec{R}} F(q)}$$

3rd ORDER

$$F^{(3)}(\vec q_1,\vec q_2,\vec q_3) \equiv \Omega_0 \frac{\Lambda^{(3)}(\vec q_1 \vec q_2 \vec q_3)}{\epsilon(q_1)\,\epsilon(q_2)\,\epsilon(q_3)}\, w(\vec q_1)\, w(\vec q_2)\, w(\vec q_3)$$

Three-body potential

$$V_3^{(3)}(|\vec R_i-\vec R_j|, |\vec R_j-\vec R_k|, t) = \frac{3!}{N^2}\sum_{\vec q_1,\vec q_2} F^{(3)}(\vec q_1,\vec q_2,-\vec q_1-\vec q_2)\, e^{i\vec q_1(\vec R_i-\vec R_j)}\, e^{i\vec q_2(\vec R_j-\vec R_k)}$$

$$t = \frac{(\vec R_i-\vec R_j)(\vec R_j-\vec R_k)}{|\vec R_i-\vec R_j|\,|\vec R_j-\vec R_k|}$$

Third-order contribution to the two-body potential

$$V_3^{(2)}(R) = \frac{3\cdot 2!}{N^2}\sum_{\vec q_1,\vec q_2} F^{(3)}(\vec q_1,\vec q_2,-\vec q_1-\vec q_2)\, e^{i\vec q_1\vec R} - \frac{3\cdot 2!}{N}\sum_{\vec q_1} F^{(3)}(\vec q_1,-\vec q_1,0)\, e^{i\vec q_1\vec R}$$

Third-order contribution to the volume-energy

$$E_{\Omega,3} = \frac{1}{N^2}\sum_{\vec q_1,\vec q_2} F^{(3)}(\vec q_1,\vec q_2,-\vec q_1-\vec q_2) - \frac{3}{N}\sum_{\vec q_1} F^{(3)}(\vec q_1,-\vec q_1,0) - F^{(3)}(0,0,0)$$

~ n-body interaction $V^{(n)}$ is given by

$$V^{(n)}(\{\vec R_i\}) = \sum_{k\geq n} V_k^{(n)}(\{\vec R_i\})$$

DENSITY-DEPENDENCE OF THE INTERIONIC POTENTIALS

THE COMPRESSIBILITY PROBLEM

a) Static bulk modulus

$$B = \Omega \frac{\partial^2 F}{\partial \Omega^2}$$

$$\frac{\partial}{\partial\Omega} = \frac{\partial}{\partial\Omega_0}\Big|_{\vec R_j, n} + \frac{\vec R_j}{3\Omega}\frac{\partial}{\partial \vec R_j}\Big|_{\Omega, n} - \frac{n_0}{\Omega}\frac{\partial}{\partial n_0}\Big|_{\Omega, R_j}$$

b) dynamical bulk modulus via calculation of the speed of sound at constant volume

WARD IDENTITIES

$$\epsilon(0)\,\Gamma^{(n+1)}(\vec q_1,\dots,\vec q_n,0) = -\frac{1}{n+1}\frac{d\Gamma^{(n)}(\vec q_1,\dots,\vec q_n)}{d\mu}$$

or

$$\frac{\Lambda^{(n+1)}(\vec q_1,\dots,\vec q_n,0)}{\epsilon(\vec q_1)\dots\epsilon(\vec q_n)} = -\frac{1}{n+1}\frac{d\Gamma^{(n)}(\vec q_1,\dots,\vec q_n)}{d\mu}$$

$n=1$ $\qquad \chi(0) = \frac{dn_0}{d\mu}$

$n=2$ $\qquad \frac{\Lambda^{(3)}(\vec q,-\vec q,0)}{\epsilon(q)^2} = \frac{1}{6}\frac{d}{d\mu}\left(\frac{\chi(q)}{\epsilon(q)}\right) = \frac{\chi(0)}{6}\frac{d}{dn_0}\left(\frac{\chi(q)}{\epsilon(q)}\right)$

$n=3$ $\qquad \frac{\Lambda^{(4)}(\vec q,-\vec q,0,0)}{\epsilon(q)^2} = -\frac{1}{24}\frac{d^2}{d\mu^2}\left(\frac{\chi(q)}{\epsilon(q)}\right) = -\frac{\chi(0)^2}{24}\frac{d^2}{dn_0^2}\left(\frac{\chi(q)}{\epsilon(q)}\right)$

STATIC BULK MODULUS

$$B = B_0 + B_1 + B_2 + B_{3,4}$$

$$B_0 = \frac{n_0^2}{\chi(0)} \qquad \text{Bohm-Staver}$$

$$B_1 = \frac{2+z}{\Omega_0}$$

$$B_2 = \frac{1}{\Omega_0} \sum_{\vec{q}\neq 0} |S(\vec{q})|^2 \left[V(\vec{q}) + \frac{5}{9} q_\alpha \frac{\partial V(\vec{q})}{\partial q_\alpha} + \frac{1}{18} q_\alpha q_\beta \frac{\partial^2 V(\vec{q})}{\partial q_\alpha \partial q_\beta} \right]$$

$$V(q) \equiv FT\left[V_2^{(2)}(R)\right] = \frac{4\pi z^2 e^2}{\Omega_0 q^2} + 2F(q)$$

$$B_{3,4} = -\sum_{\vec{q}\neq 0} |S(\vec{q})|^2 \Big[\frac{1}{2} n_0^2 |w(q)|^2 \frac{\partial^2}{\partial n_0^2} \left(\frac{\chi(q)}{\epsilon(q)} \right)$$
$$+ 2 n_0 |w(\vec{q})|^2 \frac{\partial}{\partial n_0} \left(\frac{\chi(q)}{\epsilon(q)} \right)$$
$$+ \frac{4}{3} n_0 q_\alpha \frac{\partial}{\partial q_\alpha} \left[|w(q)|^2 \frac{\partial}{\partial n_0} \left(\frac{\chi(q)}{\epsilon(q)} \right) \right] \Big]$$

$B_{3,4}$ .. contribution from $V_3^{(2)}, V_4^{(2)}$

Note

$$\lim_{q\to 0} \frac{w(q)}{\epsilon(q)} = -\frac{n_0}{\chi(0)} = -\frac{2}{3} E_F$$

$$\lim_{q\to 0} \frac{\partial}{\partial q} \frac{w(q)}{\epsilon(q)} = \emptyset$$

ASSYMPTOTIC FORM OF THE INTERIONIC POTENTIALS

Assymptotic behaviour of FT determined by singularities of integrand.

$$\text{RPA:} \quad \chi_0(q) = \frac{3}{2} \frac{n_0}{E_F} \left\{ \frac{1}{2} + \frac{1}{4} \frac{1-z^2}{z} \ln \left| \frac{1+z}{1-z} \right| \right\}$$

$$z = q/2k_F$$

RPA + Exchange and correlation

Polarizability χ

$$\chi(q) = \frac{\chi_0(q)}{1 - (4\pi e^2/q^2)\, G(q)\, \chi_0(q)}$$

Effective electron-electron-interaction

$$v_{eff}(q) = (1 - G(q)) \frac{4\pi e^2}{q^2}$$

$$\epsilon(q) \Rightarrow \tilde{\epsilon}(q) = 1 + \frac{4\pi e^2}{q^2} (1 - G(q))\, \chi_0(q)$$

Singularity at $q = 2k_F$

$$\curvearrowright \quad V_2^{(2)}(R) \sim \frac{\cos(2k_F R)}{k_F^3 R^3}$$

FRIEDEL-OSCILLATIONS

MULTI-ION INTERACTIONS

$$V_n^{(n)}(\vec{R}_1, \dots \vec{R}_n) \sim \sum \frac{\cos(k_F(R_{12}+R_{23}+\dots R_{n1}))}{R_{12}R_{23}\dots R_{n1}(R_{12}+\dots R_{n1})}$$

sum over all $(n-1)!$ independent rings which can be formed by rearranging the sequence of the n ionic positions

$$V^{(n)}(\vec{R}_1, \dots \vec{R}_n) = \sum_{k \geq n} V_k^{(n)}(\{\vec{R}_e\})$$

phase shift in the asymptotic behaviour

(Harrison,
Lloyd + Oglesby)

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