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SPRING COLLEGE IN MATERIALS SCIENCE

ON

"METALLIC MATERIALS"

(11 May - 19 June 1987)

COMPUTER SIMULATION OF DEFECTS AND MECHANICAL PROPERTIES

(Lectures II and III)

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COMPUTER SIMULATION OF POINT DEFECTS AND DIFFUSION

THEORY

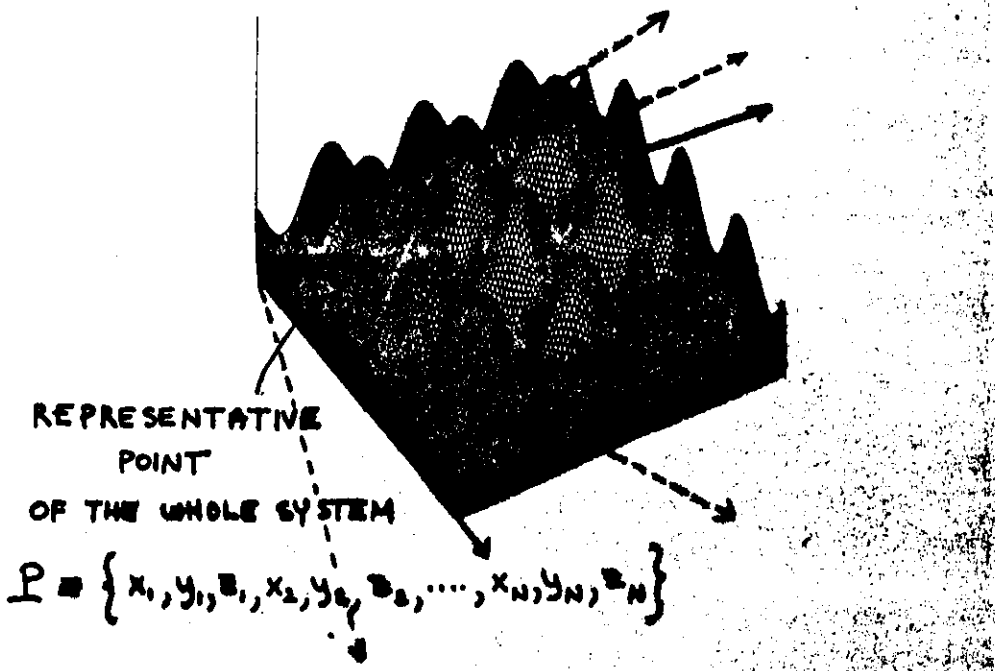
1. QUANTUM FREE ENERGY : HARMONIC
2. CLASSICAL FREE ENERGY : HARMONIC, ANHARMONIC
3. DEFECT FORMATION
4. DIFFUSION
5. EQUILIBRIUM JUMP RATE
6. TEMPERATURE DEPENDENCE : ν_L^{α} for

CALCULATIONS

1. FINDING EXTREMA : EQUILIBRIUM AND SADDLE POINT
2. QUASI-HARMONIC LATTICE DYNAMICS
3. MONTE CARLO
4. RESULTS FOR VACANCY IN ARGON (!)
5. MIGRATION : VINEYARD-SLATER
6. CURVATURE OF THE BARRIER
7. CONVERSION COEFFICIENT
8. ISOTOPE EFFECT

POTENTIAL-ENERGY HYPERSURFACE IN N-DIMENSIONAL SPACE

$$U(x_1, y_1, z_1, x_2, y_2, z_2, \cdots, x_N, y_N, z_N)$$



FACT SHEET 1

1. Diagonalization of Quadratic form

Taylor expand $U(\bar{s})$ about the minimum of U at $\bar{s}_0$

$$U(\bar{s}) = U_0 + \frac{1}{2}\sum_{i,j,\alpha,\beta} \left(\frac{\partial^2 U}{\partial s_{i\alpha}\partial s_{j\beta}}\right)_0 (s_{i\alpha} - s_{i\alpha 0})(s_{j\beta} - s_{j\beta 0}) + \cdots\cdots$$

By comparing terms the RHS can always be written

$$U(\bar{s}) = U_0 + \sum_i \frac{1}{2} m_i \omega_i^2 q_i^2$$

with $q_i = \sum_j a_{ij}(s_j - s_{j0})$ a rotation of coords.

2. Gaussian Integrals

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2/2}\, dx = \sqrt{2\pi/\alpha}$$

$$\int_{-\infty}^{+\infty} x\, e^{-\alpha x^2/2}\, dx = \alpha^{-1}$$

$$\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2/2}\, dx = \sqrt{2\pi/\alpha^3}$$

FACT SHEET 2

1. Free energy of harmonic oscillator

With energy levels $E_n = (n+\frac{1}{2})\hbar\omega$, the free energy is given by:

$$e^{-F/kT} = \sum_n e^{-E_n/kT} = e^{-\frac{\hbar\omega}{2kT}} \sum_{n=0}^{\infty} e^{-n\hbar\omega/kT}$$

$$= e^{-\hbar\omega/2kT}\left(1 - e^{-\hbar\omega/kT}\right)^{-1}$$

i.e. $$F = \frac{1}{2}\hbar\omega + kT \ln\left(1 - e^{-\hbar\omega/kT}\right)$$

2. Classical limit of oscillator energy

As $x \to 0$, $\quad 1 - e^{-x} \to 1 - 1 + x - \frac{1}{2}x^2 + O(x^3)$

$$\to x\left(1 - \tfrac{1}{2}x\right) + O(x^3)$$

Hence: $F = \frac{1}{2}\hbar\omega + kT \ln\left(1 - e^{-\hbar\omega/kT}\right)$

as $\frac{\hbar\omega}{kT} \to 0 \longrightarrow kT\left[\ln(\hbar\omega/kT) + O(\hbar\omega/kT)^2\right]$

QUANTUM FREE ENERGY

x_{di} is coordinate i of atom d, mass M_d.

$U(x_{11} \cdots x_{N3})$ is the potential energy.

The Hamiltonian is:

$$H = -\sum_d \frac{\hbar^2}{2M_d} \nabla_x^2 + U(x_{11} \cdots x_{N3})$$

Define $\quad s_{di} = M_d^{\frac{1}{2}} x_{di}$

Transform to normal coordinates q_j $(j = 1, \cdots 3N)$

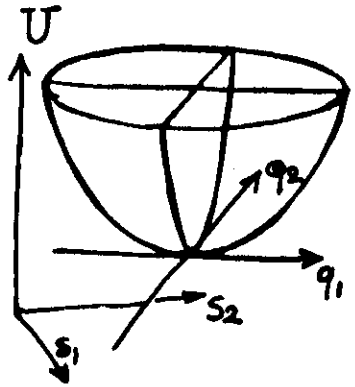
Then: $M_d^{-1} \nabla_x^2 = \nabla_s^2$; $\quad \sum_d \nabla_s^2 = \sum_j \frac{\partial^2}{\partial q_j^2}$

$$U(\bar{x}) \to U(\bar{q}) = U_0 + \tfrac{1}{2} \sum_j \omega_j^2 q_j^2$$

Thus: $H - U_0 = \frac{1}{2} \sum_j \left(\omega_j^2 q_j^2 - \hbar^2 \frac{\partial^2}{\partial q_j^2} \right)$

$$\phi(\bar{q}) = \prod_j \phi(q_j, \omega_j, n_j)$$

$$E = \sum_j (n_j + \tfrac{1}{2}) \hbar \omega_j$$



Free energy:

$$F = \sum_j \left[\tfrac{1}{2} \hbar \omega_j + kT \ln \left(1 - e^{-\hbar \omega_j / kT} \right) \right]$$

CLASSICAL FREE ENERGY

Definition:

$$e^{-F/kT} = \text{const} \int d\bar{p}\, d\bar{x}\; e^{-E(\bar{p},\bar{x})/kT} = \int dP$$

P is the probability. Use the transformation:

$$dp_{di}\, dx_{di} = d(M_d \dot{x}_{di})\, dx_{di} = d\dot{s}_{di}\, ds_{di}$$

$$d\bar{s} \to d\bar{q} \quad \text{(rotation to norm. coords.)}$$

$$\text{const} \to h^{-3N}$$

Harmonic system

$$U(x_1 \cdots x_{N3}) \to U(\bar{q}) = U_0 + \sum_j \tfrac{1}{2} \omega_j^2 q_j^2$$

$$T = \tfrac{1}{2} \sum_{di} \dot{s}_{di}^2 = \tfrac{1}{2} \sum_j \dot{q}_j^2$$

$$E(\dot{\bar{q}}, \bar{q}) = U_0 + \tfrac{1}{2} \sum_j (\dot{q}_j^2 + \omega_j^2 q_j^2)$$

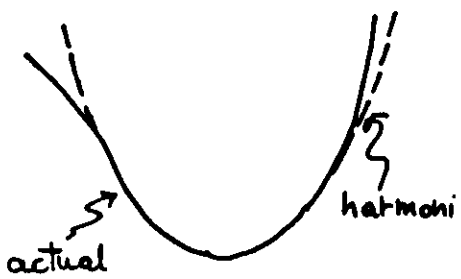
Thus $e^{-F/kT} = h^{-3N} e^{-U_0/kT} \prod_j I_j J_j$ $\quad \begin{cases} I_j = \int dq_j\, e^{-\omega_j^2 q_j^2 / 2kT} \\ J_j = \int d\dot{q}_j\, e^{-\dot{q}_j^2 / 2kT} \end{cases}$

The free energy is

$$F = U_0 + kT \sum_j \hbar \omega_j / kT$$

CLASSICAL FREE ENERGY (CONT.)

Anharmonic system



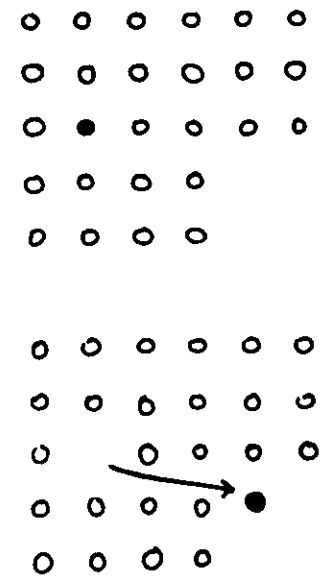
$\int dP$ cannot in general be calculated.

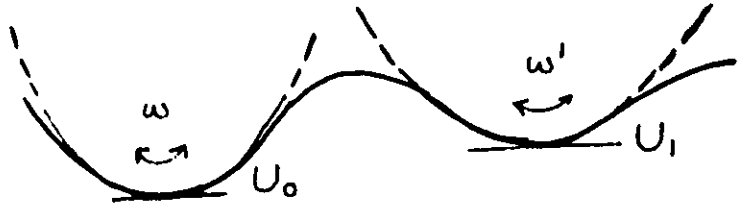
1. Use the approximate harmonic form (and exact expression for the free energy given above)

2. Sample q space. For 100 atoms, 300 D!
   → MONTE CARLO
   and evaluate directly the integral in the definition of the free energy.

DEFECT FORMATION

A vacancy defect forms in the crystal. What is the free energy change?





$$F_0 = U_0 + kT \sum_j \ln(h\omega_j/kT)$$

$$F_1 = U_1 + kT \sum_j \ln(h\omega'_j/kT)$$

$$f = F_1 - F_0 = U_1 - U_0 + kT \sum_j \ln(\omega'_j/\omega_j)$$

This is again the harmonic result. The real anharmonic problem requires detailed sampling near U_0 and U_1.

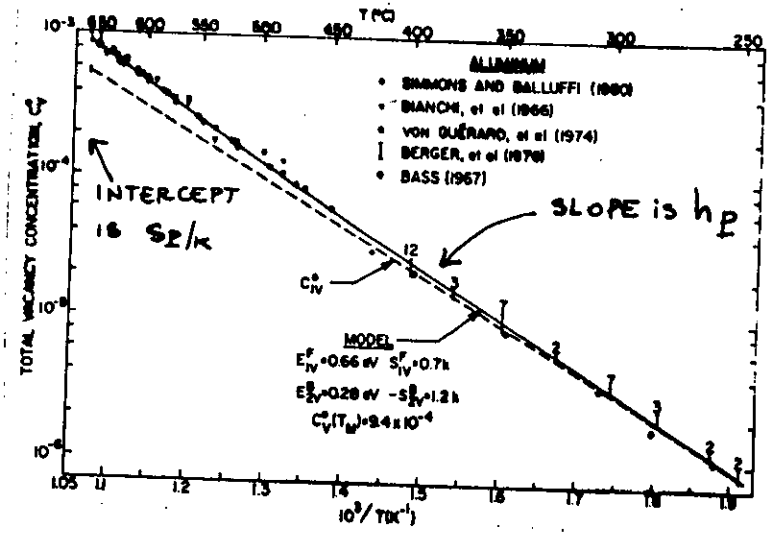
Note defect concentration $c \sim e^{-f/kT}$

TEMPERATURE DEPENDENCE

$$c = e^{-G/kT} = e^{S/k} \cdot e^{-h/kT}$$

↑ Gibbs free energy $G = F + PV$

EXPERIMENTS : P = const.



when a vacancy is formed at constant pressure, the crystal expands (or shrinks) a little. But:

$$v = V/N$$

$$f_{IF} = F'(v') - F(v) = F'(v') - F(v) + (v - v')\left(\frac{\partial F}{\partial v}\right)_T$$

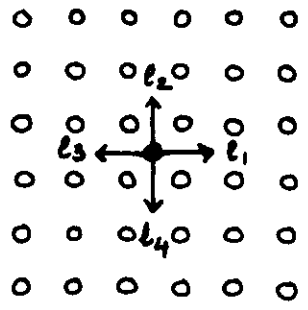
$$= \{F'(v') + P v'\} - \{F(v) + P v\}$$

$$= G'(v') - G(v) = g_F \rightarrow h_F = u_v + T(s_F - s_v)$$

The same work is required to form a single defect at constant volume and at constant pressure in large sample.

DIFFUSION

As a defect diffuses, the crystal vibrates about one site before hopping to the next along one of several jump steps $\vec{l}_i$



After N jumps the mean square displacement is

$$\vec{r}\cdot\vec{r} = (\vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots \vec{l}_N)\cdot(\vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots + \vec{l}_N)$$

$$= N l^2 + \sum_{i \neq j} \vec{l}_i \cdot \vec{l}_j$$

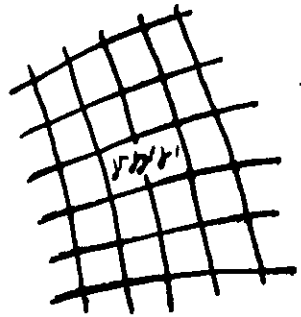
$\sum_{i \neq j} \vec{l}_i \cdot \vec{l}_j = 0$ if randomized so no memory of last jump

Einstein $\quad \langle x^2 \rangle = \frac{1}{3}\langle r^2 \rangle = 2Dt = \frac{1}{3} N l^2$

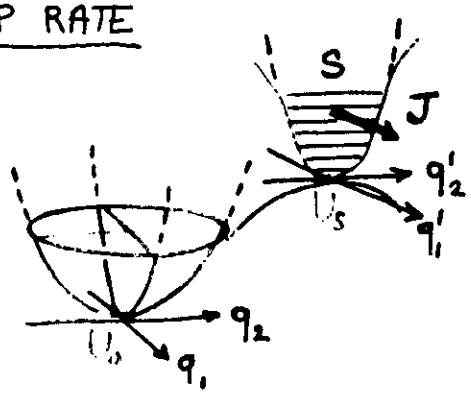
$\therefore \quad D = \Gamma l^2/6 \qquad (\Gamma = \frac{N}{t}$ is jump rate)

Rate Model:

devide configuration space into volumes, γ, around each minimum. Calculate rate from γ through $\gamma\gamma'$ to γ' (assume system randomizes).



EQUILIBRIUM JUMP RATE



Problem:

Given that the well U_0 is occupied, what is the jump flux J.

$$P_n = I_n = \frac{A}{h^{3N}} \int d\vec{q}\, d\vec{p}\; e^{-E(\vec{q},\vec{p})/kT} = A\, e^{-F_n/kT}$$

$$J = \frac{A}{h^{3N}} \int_{S,\dot{q}_1>0} d\vec{q}\, d\vec{p}\; \dot{q}_1\, e^{-E(\vec{q},\vec{p})/kT}$$

$$E_S = U_S + \frac{1}{2}\sum_{j=2}^{3N}\left(\dot{q}_j^2 + \omega_j'^2 q_j'^2\right) + \dot{q}_1^2 \omega_1'^2 \qquad \omega_1'^2 < 0$$

In normal coordinates:

$$E_0 = U_0 + \frac{1}{2}\sum_{j=1}^{3N}\left(\dot{q}_j^2 + \omega_j^2 q_j^2\right)$$

Hence, for harmonic system with randomization

$$J = \frac{1}{h_1}\prod_{j=1}^{3N}\frac{\hbar\omega_j}{kT}\prod_{j=2}^{3N}\left(\frac{\hbar\omega_j'}{kT}\right)^{-1} e^{-(U_S-U_0)/kT}\int_{q_1>0} d\dot{q}_1\, \dot{q}_1\, e^{-\dot{q}_1^2/2kT}$$

or

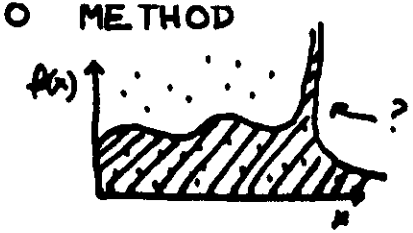
$$J = \left[\prod_{j=1}^{3N}\nu_j \Big/ \prod_{j=2}^{3N}\nu_j'\right] e^{-(U_S-U_0)/kT}$$

VINEYARD SLATER

Accurate anharmonic theory requires sampling near U_0 and on the saddle hyperplane S

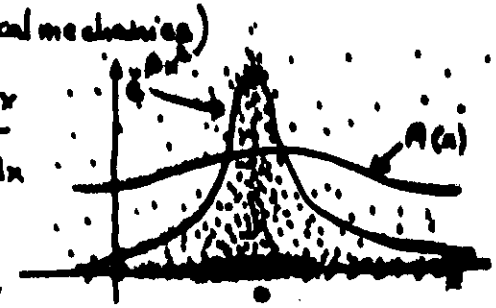
ONE MONTE CARLO METHOD

0. MC to evaluate integrals



1. Metropolis MC (in statistical mechanics)

$$\langle A \rangle = \frac{\int A\, e^{-\beta U(x)}\, dx}{\int e^{-\beta U(x)}\, dx}$$



2. we want $\int e^{-\beta U}\, dx$?

or more precisely $\dfrac{\int e^{-\beta U_2}\, dx}{\int e^{-\beta U_1}\, dx} = \dfrac{Z_2}{Z_1}$

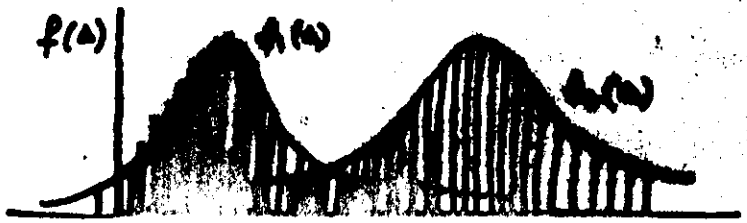
trick

$$\frac{Z_2}{Z_1} = \frac{\int e^{-\beta(U_2-U_1)}\, e^{-\beta U_1}\, dx}{\int e^{-\beta U_1}\, dx} = \langle e^{-\beta(U_2-U_1)} \rangle_1$$

$$= \frac{\int e^{-\beta U_2}\, dx}{\int e^{-\beta(U_1-U_2)}\, e^{-\beta U_2}\, dx} = \frac{1}{\langle e^{\beta(U_2-U_1)} \rangle_2}$$

WELL'S SIMPLE EVOLUTION

problem



3. OVERLAPPING DISTRIBUTIONS METHOD

(VALLEAU-TORRIE, BENNETT ~1975)

$$f_1(\Delta) = \frac{\int \delta(\Delta - U_2 + U_1)\, e^{-\beta U_1} dx}{\int e^{-\beta U_1} dx} = \langle \delta(\Delta - U_2 + U_1) \rangle_1$$

$$\int_{-\infty}^{+\infty} f_1(\Delta)\, d\Delta = 1$$

$$f_1(\Delta) e^{-\beta\Delta} = e^{-\beta\Delta} \int \delta(\Delta - U_2 + U_1)\, e^{-\beta U_1} dx \,/\, Z_1$$

$$= \int \delta(\Delta - U_2 + U_1)\, e^{-\beta(U_2 - U_1)}\, e^{-\beta U_1} dx / Z_1$$

$$= \frac{\int \delta(\Delta - U_2 + U_1)\, e^{-\beta U_2} dx}{\int e^{-\beta U_2} dx} \; Z_2/Z_1$$

$$= f_2(\Delta)\, Z_2/Z_1$$

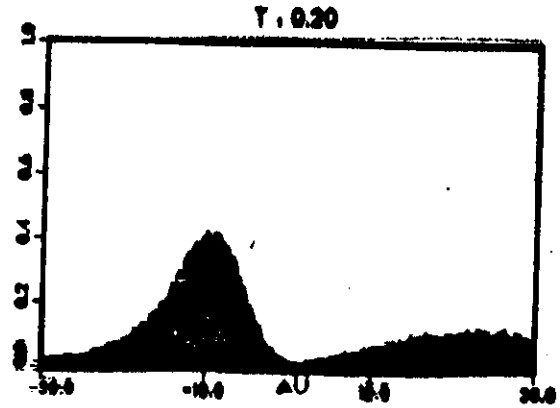
$$\rightarrow \boxed{\frac{Z_2}{Z_1} = \frac{f_1(\Delta)}{f_2(\Delta)}\, e^{-\beta\Delta}}$$

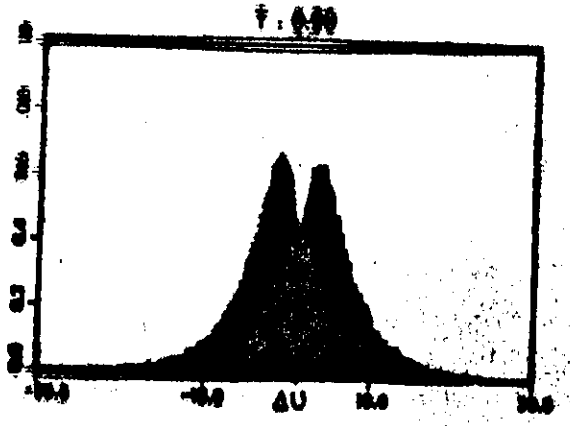
HIGH ACCURACY

ref: C.H. Bennett, J. Comp. Phys. 22, 245 (1976)

review article on Monte Carlo Free Energy Differences methods:
D. Frenkel, in "Molecular Dynamics Simulation of Stat. Mech. Systems", eds. G. Ciccotti and W.G. Hoover, (North-Holland, Amsterdam, 1986)

Monte Carlo: overlapping distribution method





ref.: G De Loreuzi and G. Jacucci,
Phys. Rev B, 33, 1993 (1986)

VACANCY FORMATION IN ARGON

Lennard-Jones
108 particles, pbc
$T_M = 83°K$

T (°K)	0	40	60	80	
U/N	-8.56	-7.49	-6.92	-6.22	err 1/3
ΔU_L	8.42	8.38	8.29	8.09	
ΔU_V	6.45	5.35	4.19	2.75	
ΔU_P	8.56	8.43	8.31	7.64	
ΔF_L	7.41	7.60	7.23	6.89	
ΔF_V	2.45	1.62	1.71	1.37	$+O(\frac{1}{N})$
ΔG_P	6.13	1.40	1.55	1.49	
			MC -6%	MC -10%	
→ ΔH_P	6.18	8.03	8.62	8.54	
			1.21	1.50	← STATIC $_P$
$\Delta V_P/V$	1.06	1.02	1.00	0.92	
			MC 1.21		

1. $\Delta V_P/V \sim 1$ → $C_P \sim C_L$, $C_P \leftarrow C_V$
2. $\Delta U_L(T=0) = U/N$, but as T increases ΔU_L is const
3. $\Delta F_V \cong \Delta G_P$ consistency of results
4. Note: important to remember $P = P_V + P_W$
   where $P_V = -\left(\frac{\partial U_0}{\partial V}\right)_T$, $P_W = -\left(\frac{\partial (F-U_0)}{\partial V}\right)_T$
5. Temperature dep. of h_0 (divacancies not neces.?)

COMPUTER SIMULATION OF POINT DEFECTS.

Giulio De Loreuzi, CNR, Trento

Additional Bibliography:

1. On Point Defects and Diffusion:

   C.P. Flynn
   "Point Defects and Diffusion", Clarendon Press, Oxford (1972)

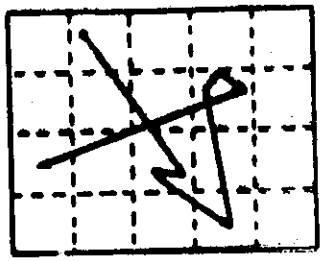
2. On Computer Calculations of Point Defects Properties:

   G. Jacucci
   "Defect Calculations beyond the Harmonic Model",
   in "Diffusion in Crystalline Solids", edited by
   G.E. Murch and A.S. Nowick, Academic Press, New York (1984)

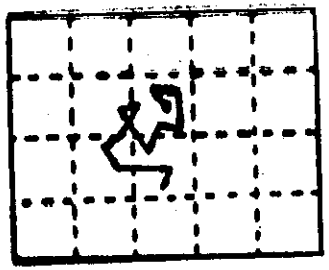
3. On Monte Carlo Free Energy Difference Calculations:

   D. Frenkel, in
   "Molecular Dynamics Simulation of Statistical Mechanical Systems", edited by G. Ciccotti and W. G. Hoover, North-Holland, Amsterdam (1986)

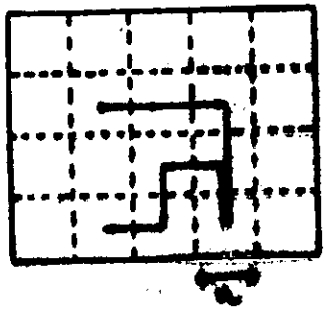
Regimes of diffusion



gas-like $D = \frac{\langle R^2 \rangle}{2t}$



Liquid-like



Solid-like Jumps $D = \frac{a^2}{\lambda} K$

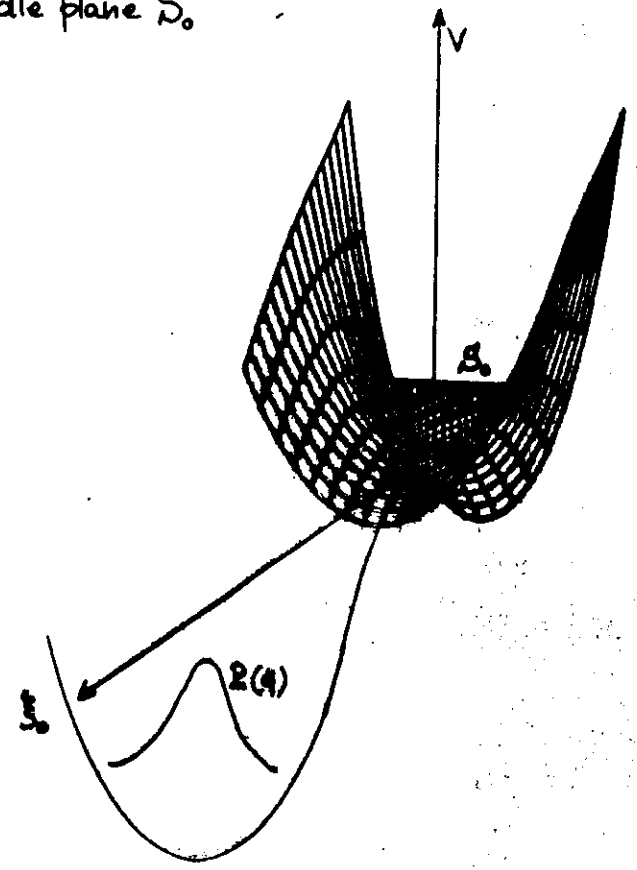
ref : G. Vineyard, J. Phys. Chem. Sol. 3, 121 (1

EQUILIBRIUM JUMP RATE

$$R = \sqrt{\frac{kT}{2\pi}} \frac{\int_{S_0} e^{-\beta U(x)} dx}{\int_{\text{Equil.}} e^{-\beta U(x)} dx}$$

VINEYARD SLATER

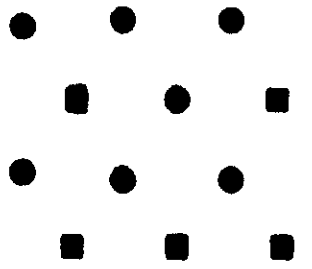
Flux through the saddle plane S_0



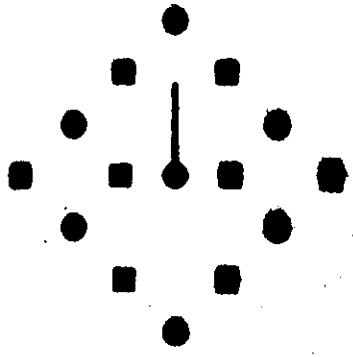
EQUILIBRIUM

VACANCY JUMP in FCC crystal

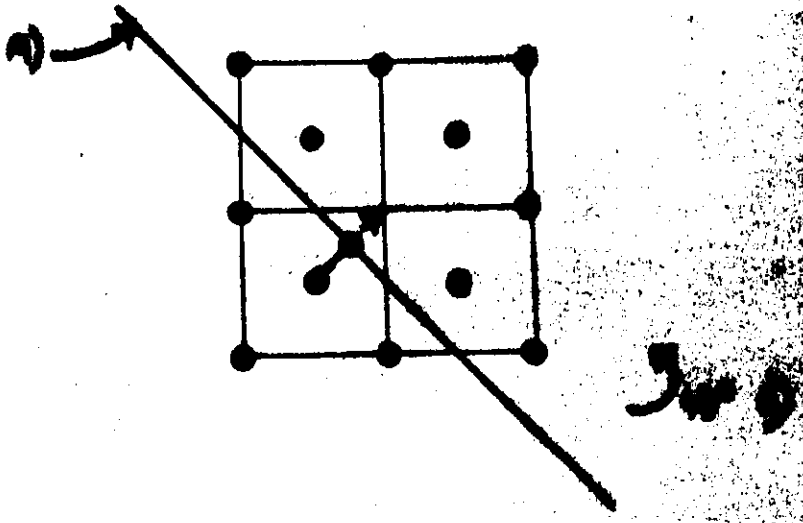
UNSTABLE MODE in SADDLE POINT C.



A) plane normal to the jump

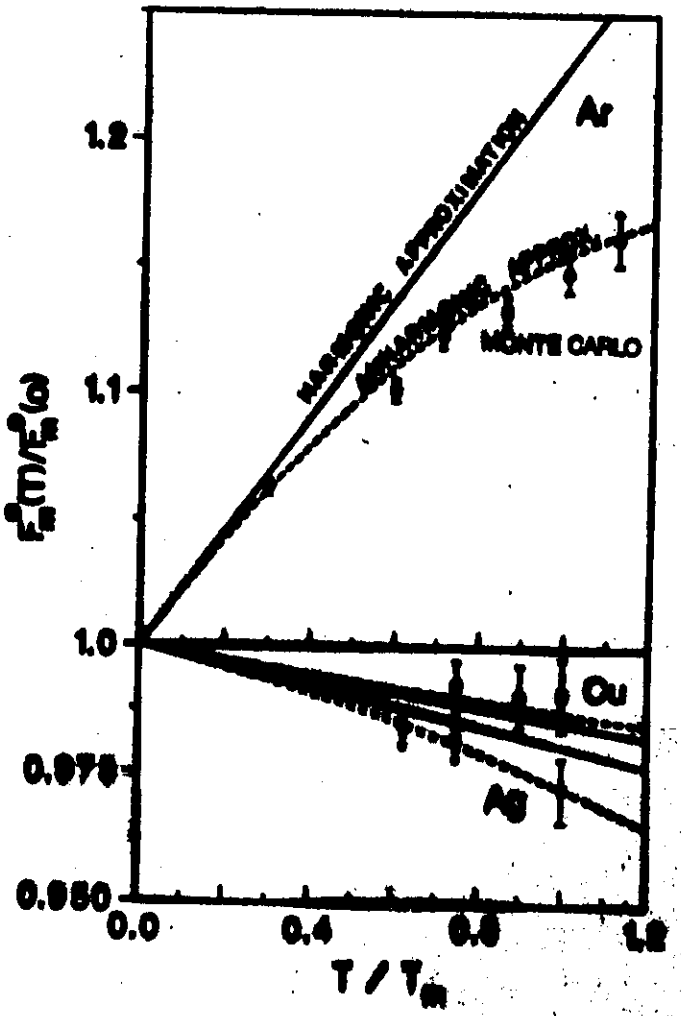


B) plane of the jump



FREE ENERGY DIFFERENCE

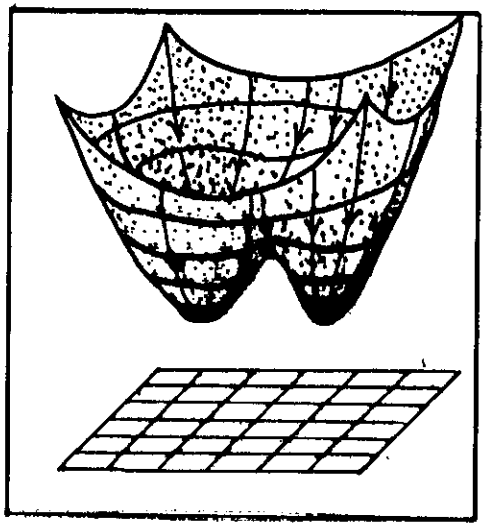
BETWEEN SADDLE PLANE AND EQUILIBRIUM

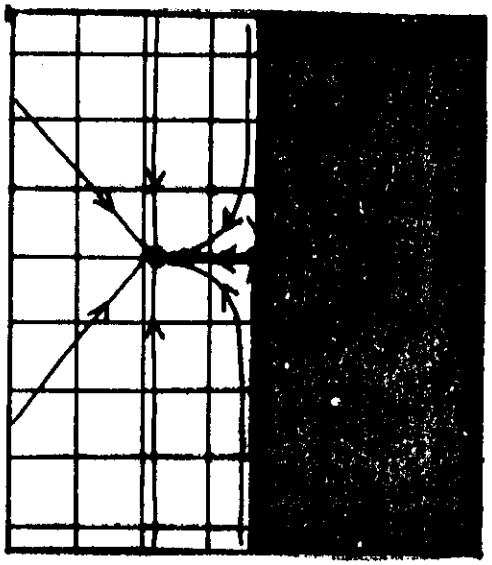


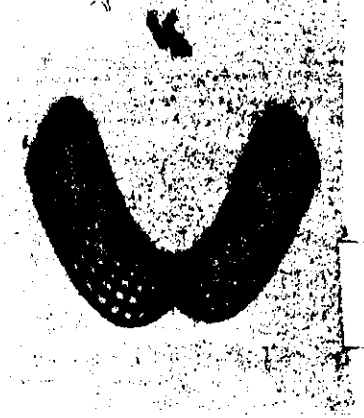
TEMPERATURE DEPENDENCE AT FIXED VOLUME

ref.: DeLorenzi, Jaccucci, Physica submitted to Phys. Rev. B, 1987

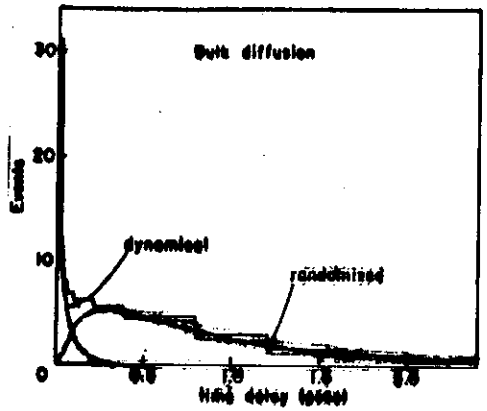
Saddle between two minima



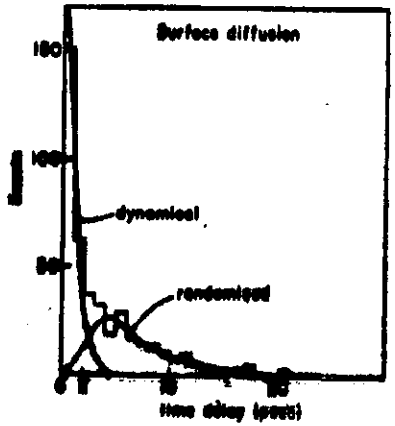




TIME INTERVAL BETWEEN JUMPS



DeFano-Jacucci
Phys. Rev. Lett.
33, 300 (1974)

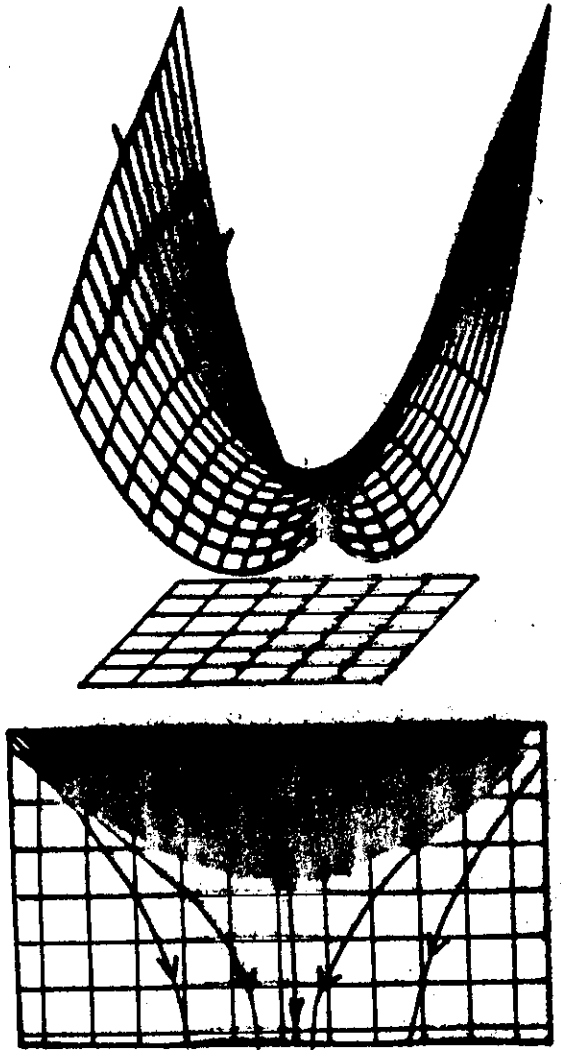


DeLorenzo-Jacucci
Physica
Suppl. Vol. 115, 307(

Figura-Jacucci
Phys. Rev. B, 35
6888 (1987)

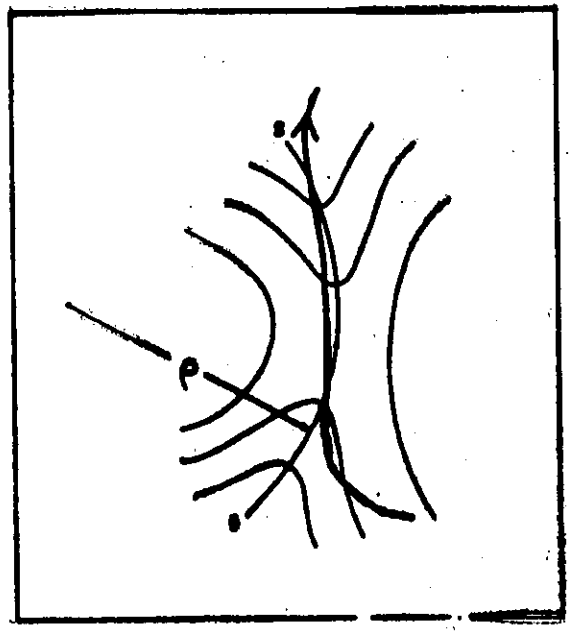
ref: G. DeLorenti, G. Jacucci, C.P. Flynn
Phys. Rev. B, 30, 5430 (1984)

Sella Lennard-Jones



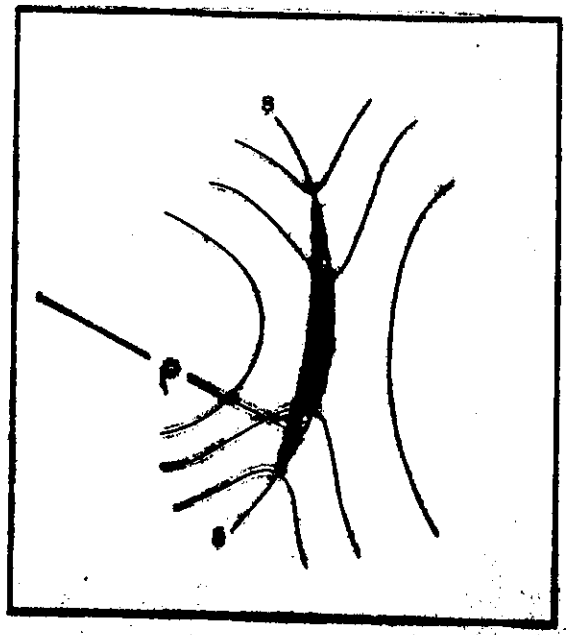
MULTIPLE CROSSINGS

Newtonian trajectory on curved barrier



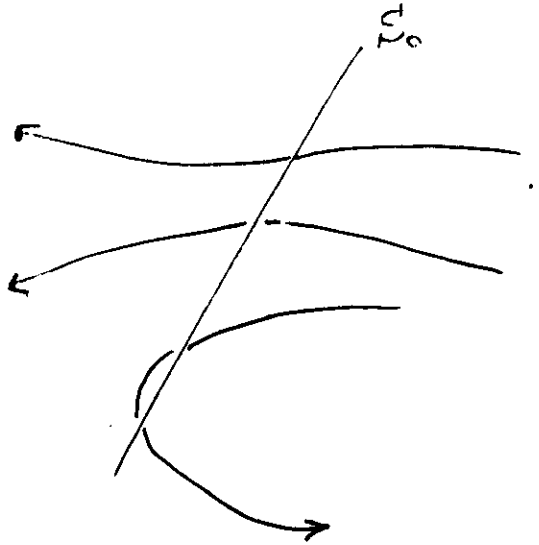
MULTIPLE RECROSSINGS ⟹ ERROR IN RATE

CRITICAL TRAJECTORIES



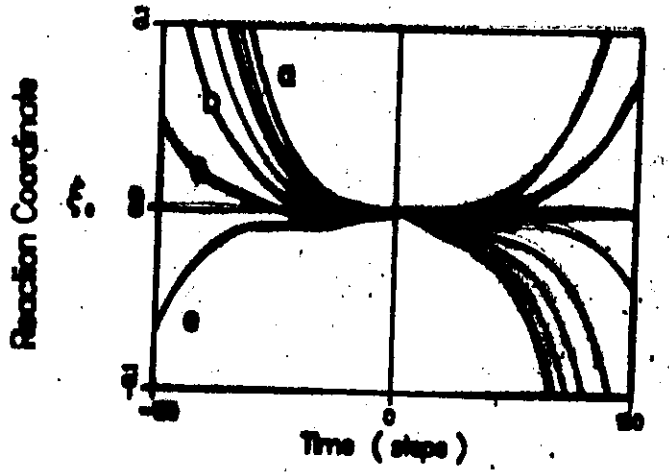
BASIC IDEA:

use Molecular Dynamics to find the fraction of trajectories through S_0 that come back soon (return jumps)

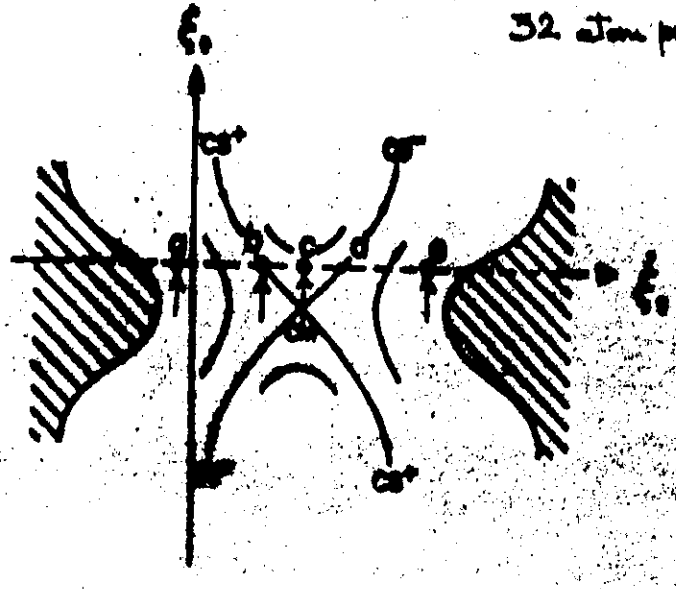


MD Trajectories

ref:
M. Marchese
G. Jacucci
C. P. Flynn
submitted
to Phys. Rev. B
1987

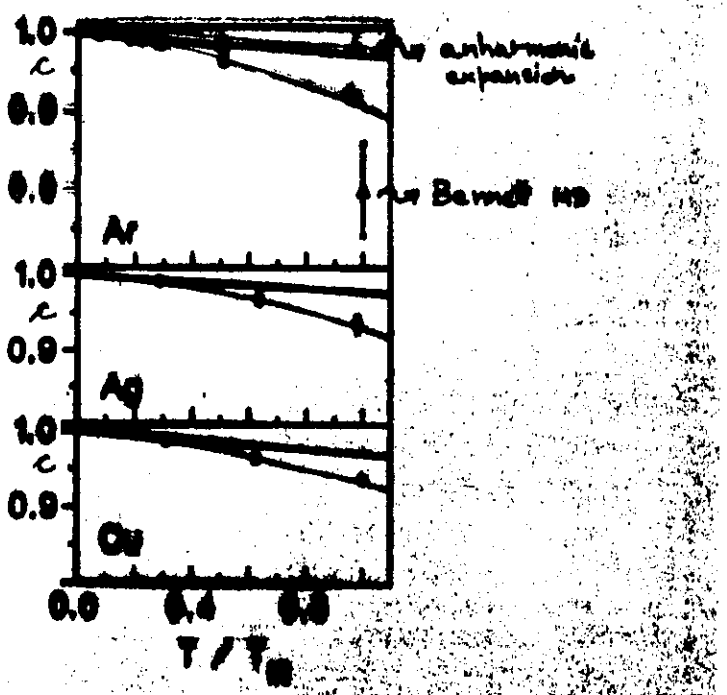


32 atom periodic LJ



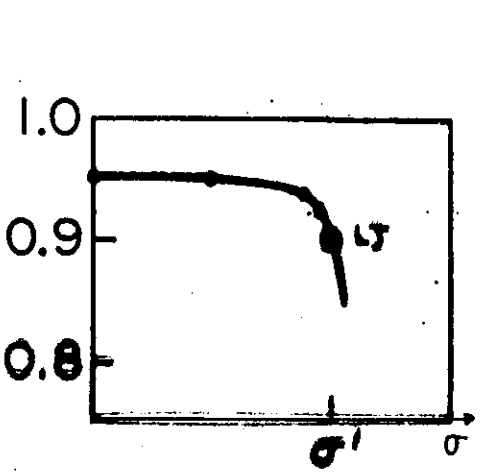
FRACTION OF SUCCESSFULL TRAJECTORIES

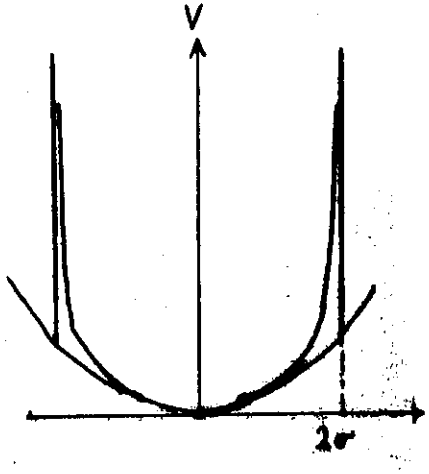
Conversion coefficient $R = c \cdot R_0$

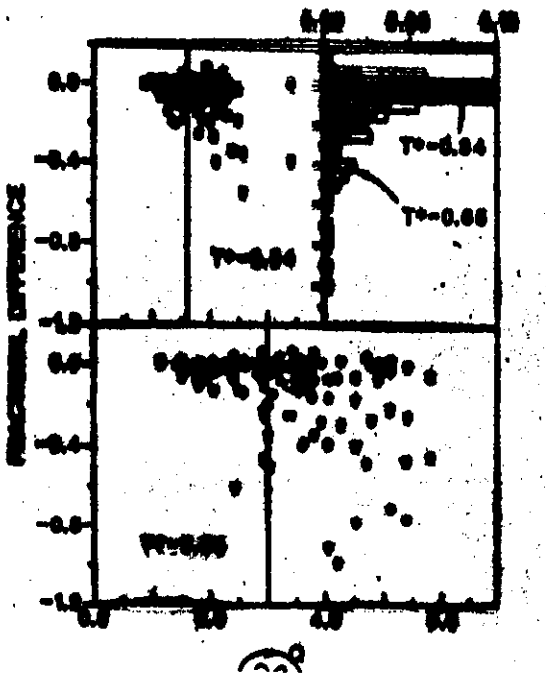


Vineyard theory is excellent, only 10% error but mass dependence is large.

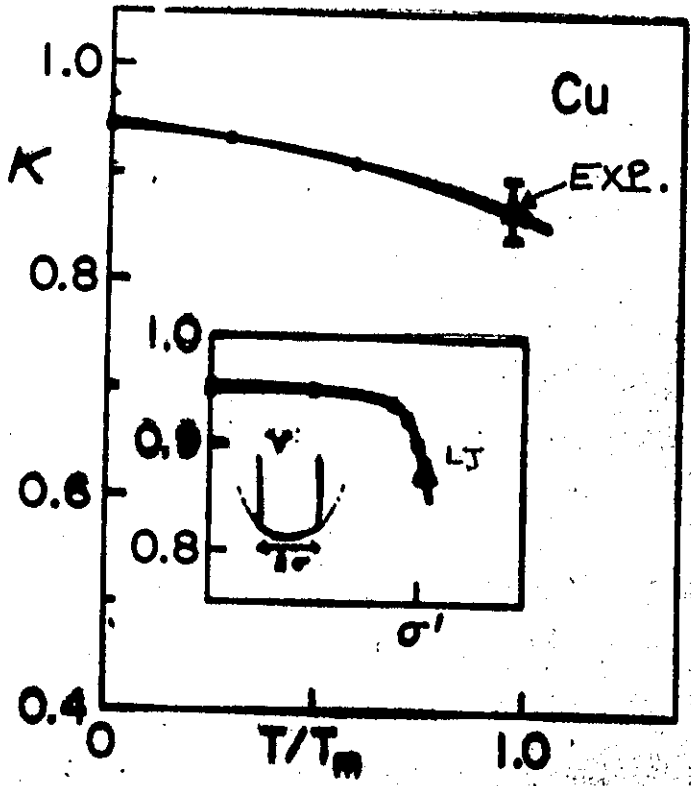
Hard core effects







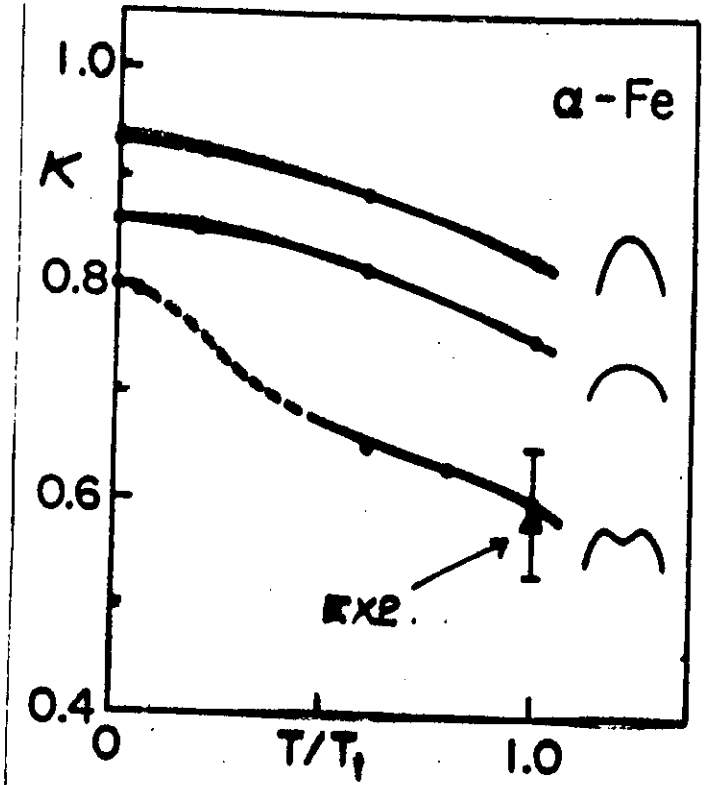
ISOTOPE EFFECT IN FCC



(a)

Marchese, Jacucci; [illegible] 1982

ISOTOPE EFFECT IN BCC



(b)

FINNIS POTENTIAL

good E_M, E_F
still flexibility

Marchese, Jacucci, Flynn
1987