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SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
(25 April - 17 June 1988)

DYNAMICAL AND DISSIPATIVE EFFECTS IN RATE PROCESSES
(Lecture IV)

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THE EFFECT OF FRICTION

Caldeira-Leggett

$\longrightarrow$ Annals of Physics

149, 374 (1983)

– We need to consider the interaction between the BP and the heath bath.

– Heath bath of $\boxed{\text{BOSONS}}$ ($\longrightarrow$ e.g. PHONONS)

Hamiltonian :

$$H = H_p^{(0)} + H_b^{(0)} + H_1$$

$$\begin{cases} H_p^{(0)} = p^2/2M + V(q) \\ H_b^{(0)} = \sum_k \hbar\omega_k b_k^\dagger b_k \\ H_1 = \sum_k \left[g_k(q)\, b_k^\dagger + h.c. \right] \end{cases}$$

HEATH BATH TRANSL. INVARIANT $\longrightarrow g_k(q) = g_k e^{ikq}$

Provided the time scale of the BP motion is sufficiently large as to make $\cos k[q(\tau) - q(\tau')]$ a slow function on the scale ω_k^{-1} ("LARGE MASS LIMIT") we can expand the cosine.

We then obtain the result

$$S_{eff} \cong \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \int_0^{\beta\hbar} d\tau' \; \overbrace{q(\tau)\, R(\tau-\tau')\, q(\tau')}^{\boxed{\text{LINEAR DISSIPATION}}}$$

with $R(\tau-\tau')$ having a FT

$$R(\Omega_\nu) = \frac{1}{\pi} \int_0^\infty d\omega \, \frac{j(\omega)}{\omega} \, \frac{\Omega_\nu^2}{\omega^2 + \Omega_\nu^2}$$

and where we have introduced the

$\boxed{\text{"SPECTRAL DENSITY"}}$

$$j(\omega) = \frac{\pi}{\hbar} \sum_k k^2 |g_k|^2 \, \delta(\omega - \omega_k)$$

~~Assuming~~ Let assume

$$\boxed{\frac{j(\omega)}{\omega} \xrightarrow[\omega \to 0]{} \text{finite value} \equiv M\eta}$$

(TRUE FOR ONE-DIMENSIONAL PHONONS)

The low frequency behaviour of $R(\Omega_\nu)$ in this case is

$$R(\Omega_\nu) \underset{\Omega_\nu \to 0}{\sim} \frac{M\eta}{2}\,|\Omega_\nu|$$

The effective action in the "low frequency range" of $q(\tau)$ becomes

$$S_{eff} \cong \frac{M\eta}{4\pi}\int_0^{\beta\hbar} d\tau \int_0^{\beta\hbar} d\tau' \,\frac{[q(\tau)-q(\tau')]^2}{(\tau-\tau')^2}$$

As shown by Caldeira and Leggett such a form for S_{eff} corresponds to $\boxed{\text{OHMIC DISSIPATION}}$ i.e. is the QM euclidean action of a system which classically is described by a LANGEVIN EQUATION with a frequency independent FRICTION η.

A simple way of verifying this is to calculate the mobility μ of a free BP whose action is S_{eff} besides the kinetic energy term: the result is

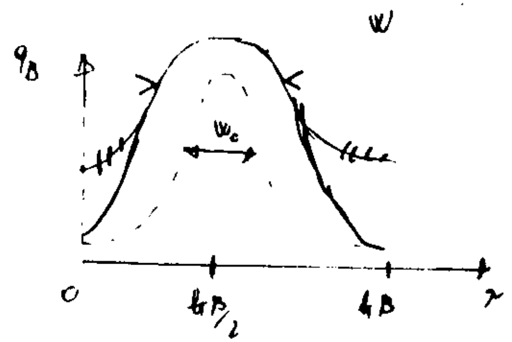
$$\mu(\omega) = \frac{1}{M}\,\frac{1}{i\omega+\eta}$$

which shows that η = FRICTION COEFFICIENT

The BP total action is

$$S[q] = \int_0^{\beta\hbar}\left[\frac{M}{2}\dot q^2 + V(q)\right]d\tau + S_{eff}[q]$$

In the large β limit the $\boxed{\text{BOUNCE}}$ is still a stationary point of S, but it is $\boxed{\text{modified}}$ by the dissipative term (see Caldeira-Leggett)



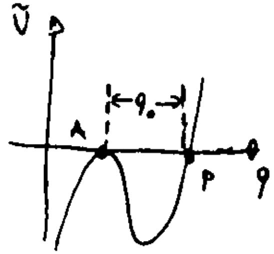
$W_0 \sim \omega_A^{-1}$

$W \sim \begin{cases} \omega_A^{-1} & \eta \ll \omega_A \\ \dfrac{\eta}{\omega_A^2} & \eta \gg \omega_A \end{cases}$

The action of the BOUNCE becomes

$$S_B(\eta) = S_B(0) + M\eta\, q_0^2\, \Phi(\eta)$$

with $\Phi(\eta) \sim 1$



The rate is given by $K \cong f(\eta)\, e^{-S_B(\eta)/\hbar}$

with $f(\eta) \sim c\,(\eta/\omega_0)^{9/2}$

Partition function Z :

PHONONS BATH

$$\boxed{Z = \int_{[q(0)=q(\beta\hbar)]} \mathcal{D}q \; e^{-S_p^{(0)}/\hbar} \; Z_b[q]}$$

with

$$Z_b[q] = \int \prod_k \mathcal{D}b_k^* \mathcal{D}b_k \; e^{-S_b^{(0)}/\hbar} \; e^{-S_1/\hbar}$$

Both $S_b^{(0)}$ and S_1 are bilinear in the b_k^*, b_k's and therefore the integration can be done exactly, to give

$$\ln Z_b[q] = -\frac{1}{\hbar} S_{eff}[q]$$

with

$$\boxed{S_{eff}[q] = \sum_k \int_0^{\beta\hbar} d\tau \int_0^{\beta\hbar} d\tau' \cos k[q(\tau) - q(\tau')] \; F_k(\tau - \tau')}$$

and

$$\Omega_\nu = 2\nu\pi(\beta\hbar)^{-1}$$

$$F(\tau-\tau') = (\beta\hbar)^{-1} \sum_\nu e^{-i\Omega_\nu(\tau-\tau')} \frac{|g_k|^2}{\hbar\omega_k} \frac{\Omega_\nu^2}{\Omega_\nu^2+\omega_k^2} \sim$$

$$\sim e^{-\omega_k|\tau-\tau'|}$$

FINITE TEMPERATURES

$$T << T_c$$

$$k(\eta, T) \sim f(\eta, T) \, e^{-S_B(\eta,T)/\hbar}$$

GRABERT AND WEISS, Z. Phys. B56, 171 (1984)

FIND :

$$S_B(\eta, T) \sim S_B(\eta, 0)\left[1 - \frac{\eta}{\omega_0}\tilde{\Omega}(\eta)\left(\frac{T}{\hbar\omega_0}\right)^2\right]$$

$$f(\eta, T) \sim f(\eta, 0)$$

$$\tilde{\Omega}(\eta) = \frac{\langle q^2 \rangle}{\langle q^2 \rangle_\eta}$$

THERMAL ENHANCEMENT OF RATE :

$$\ln k(T) \sim \ln k(0) + A T^2$$

CROSS-OVER TO THERMAL ACTIVATION

The cross-over temperature, defined as the temperature at which the $\boxed{\text{ZERO-MODE}}$ disappears, is given by

$$T_c(\eta) = \frac{\hbar}{2\pi}\left[-\frac{\eta}{2} + \left(\omega_c^2 + \frac{\eta^2}{4}\right)^{1/2}\right]$$

For $\eta \gg \omega_c$: $T_c \sim \dfrac{\hbar\,\omega_c^2}{2\pi\eta} = \dfrac{\omega_c}{\eta}\,T_c(0)$

Note that $T_c(\eta)$ decreases with η !

$\boxed{\text{LARGE FRICTION}} \rightarrow \boxed{\text{CLASSICAL}}$ BEHAVIOUR AT <u>LOWER</u> TEMPERATURES

For $T \gg T_c(\eta)$ LARKIN AND OVCHINNIKOV (Sov. Phys JEPT <u>59</u>, 420, 1984) find

$$K(T) = \frac{T_c}{\hbar}\,\frac{\omega_A}{\omega_c}\,e^{-V_0/T}\,f(\eta, T) \xrightarrow[T\gg T_c]{}$$

$f \rightarrow 1$ FOR $T \gg T_c$

$$\rightarrow \frac{T_c}{\hbar}\,\frac{\omega_A}{\omega_c}\,e^{-V_0/T}$$ which is KRAMER's

SURFACE CHEMICAL REACTIONS

$\Downarrow$ DIFFUSION IS RATE DETERMINING STEP ?

SURFACE DIFFUSION

$\Downarrow$ LOW COVERAGE

DIFFUSION IN A PERIODIC POTENTIAL

DIFFUSION IN A PERIODIC POTENTIAL

CLASSICAL LIMIT

LARGE η CASE

— Ambegaokar, Halperin PRL 22, 1364 (1969)

— R Festa, EGD PHYSICA 90A, 229 (1978)

FPE:

$$\frac{\partial f}{\partial t} + \frac{p}{M}\frac{\partial f}{\partial q} + \langle F\rangle \frac{\partial f}{\partial p} = \eta \frac{\partial}{\partial p}\left(pf + MT\frac{\partial f}{\partial p}\right)$$

For $\langle F\rangle = 0$ THE FPE IS ALWAYS EQUIVALENT TO THE SIMPLE DIFFUSION EQUATION

$$\frac{\partial n}{\partial t} = D_0 \frac{\partial^2 n}{\partial q^2} \quad \text{WITH} \quad D_0 = \frac{T}{M\eta}$$

(a)

FOR $\langle F\rangle \neq 0$, AND PROVIDED η IS LARGE

$$\left[\eta^2 \gg \frac{2T}{M}\left(\frac{\langle F'\rangle}{\langle F\rangle}\right)^2\right]$$

$(\eta \gg \omega)$

WE KNOW THAT

FOKKER PLANCK EQUATION

$\downarrow$

$\boxed{\text{SMOLUCHOWSKI EQUATION}}$:

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial q} D_0\left(\frac{\partial n}{\partial q} - \frac{1}{T}\langle F\rangle n\right) \quad (1)$$

$$D_0 = \frac{T}{M\eta}$$

$\downarrow$

$$D = \frac{1}{2} \lim_{t\to\infty} \frac{\partial}{\partial t}\langle q^2\rangle_t = ?$$

Setting $\boxed{\tilde{n} = e^{V/2T}\, n(q,t)}$ eq. (1) becomes

$$\frac{\partial \tilde{n}}{\partial t} = -\hat{S}\,\tilde{n} \; ; \quad \hat{S} = \left(\frac{\partial}{\partial q} + \frac{F}{2T}\right) D_0 \left(-\frac{\partial}{\partial q} + \frac{F}{2T}\right)$$

(b)

$\hat{S}$ DEPENDS PERIODICALLY ON Q, SO THAT, BY **BLOCH THEOREM** THE EIGENSTATES OF $\hat{S}$

$$\boxed{\hat{S}\,\varphi_k^{(\alpha)} = \lambda_k^{(\alpha)}\,\varphi_k^{(\alpha)}}$$

WILL BE OF THE FORM

$$\varphi_k^{\alpha}(q) = e^{ikq}\,\chi_k^{(\alpha)}(q)$$

"BAND INDEX" ("RBZ" SCHEME)

PERIODIC FUNCTION OF q

In terms of the $\varphi_k^{(\alpha)}$'s :

$$\boxed{\tilde{n}(q,t) = \sum_{k\alpha} c_k^{(\alpha)}\,e^{-\lambda_k^{(\alpha)} t}}$$

DIFFUSION IS A "LARGE t" PHENOMENON $\longrightarrow$ "D IS DETERMINED BY "THE SMALLEST $\lambda_k^{(\alpha)}$'s"

$$\Downarrow$$

LOWEST BAND ($\alpha = 1$)

$$D = \frac{1}{2}\frac{\partial^2}{\partial k^2}\lambda_k^{(1)}\Big|_{k=0}$$

For q-independent $\eta \to D_0 = T/M\eta$; if η q-independent $\to \lambda_k^{(\alpha)} = \frac{T}{M\eta}\Lambda_k^{(\alpha)} \to$

$$\to D = \frac{T}{\eta}(M^*)^{-1}$$

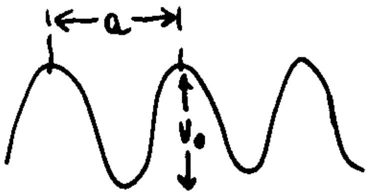
$$\boxed{(M^*)^{-1} = M^{-1}\,\frac{1}{2}\frac{\partial^2}{\partial k^2}\Lambda_k^{(1)}\Big|_{k=0}}$$

USING "$\underset{\sim}{k}\cdot\underset{\sim}{p}$" EXPANSION:

WE FOUND, IN ONE DIMENSION

$$D^{-1} = \langle D_0^{-1} e^{V/T} \rangle \langle e^{-V/T} \rangle \qquad (2)$$

WITH $\langle f(q) \rangle = \frac{1}{a}\int_0^a dx\, f(x)$



POTENTIAL "LATTICE CONSTANT"

From (2):

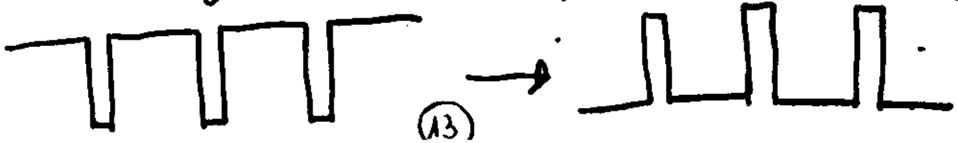
(a) $\boxed{D \le D_0}$

$T \ll V_0$

(c) $D \sim D_0 e^{-\frac{V_0}{T}} \sim \frac{1}{\eta} e^{-V_0/T}$

(b) For q-independent D_0:

"Reversing the potential, D is UNCHANGED!



(13)

SMALL η ($\eta \ll \omega$)

NOZIÈRES AND ICHE, J Phys. 40, 225 (1979)

FIND:

a) $\boxed{\frac{T}{V_0}\omega \ll \eta < \omega}$ $\longrightarrow$ $D \sim a^2 \omega e^{-V_0/T} \sim D_{ART}$

($\Delta \gg T$)

$\Delta \sim \eta \frac{V_0}{\omega}$

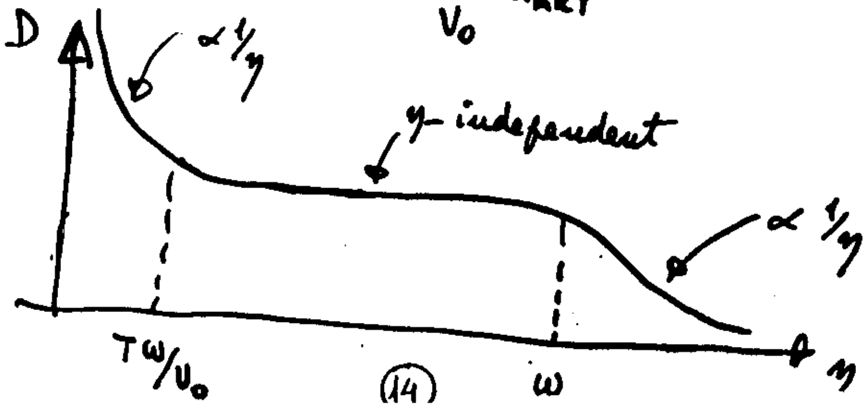
$D \sim k_{ART} \cdot a^2$

(RANDOM WALK WITH k_{ART} STEPS OF LENGTH PER UNIT TIME)

b) $\boxed{\eta \ll \frac{T}{V_0}\omega}$ $\longrightarrow$ $D \sim k\ell^2 \sim \frac{a^2\omega^2}{\eta} e^{-V_0/T} = \frac{\omega}{\eta} D_{ART}$

($\Delta \ll T$) $\longrightarrow$ $\ell = \frac{T}{\Delta} a$

$k = \frac{T\eta}{V_0} k_{ART}$



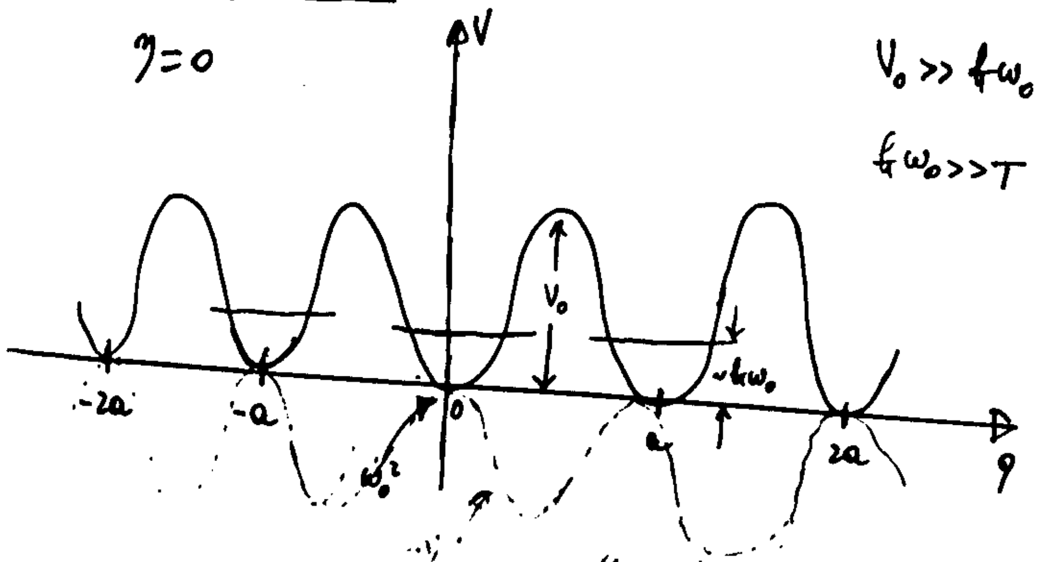
(14)

QUANTUM CASE

$\eta = 0$

$V_0 \gg \hbar\omega_0$

$\hbar\omega_0 \gg T$

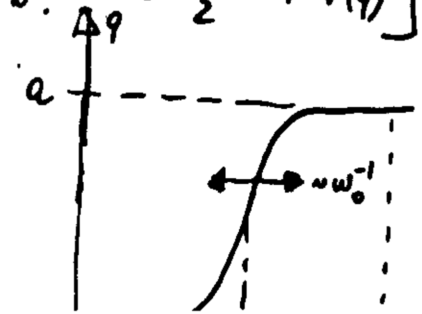


TIGHT BINDING → "INSTANTONS"

(see S. COLEMAN, ERICE LECTURES 1978 - PLENUM PRESS 1979)

$$S^{(0)}[q] = \int_0^{\beta\hbar} d\tau \left[\frac{M\dot{q}^2}{2} + V(q) \right] \longrightarrow$$

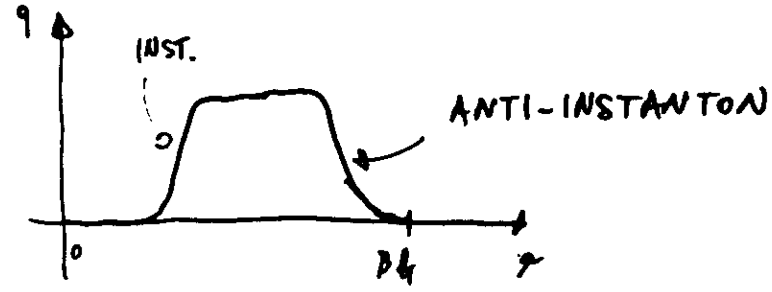
$\longrightarrow$



"INSTANTON"

(FINITE ACTION

STRINGS OF INSTANTONS ARE ALSO APPROXIMATE STATIONARY POINTS



$q(0) = q(\beta\hbar) \Longrightarrow$ EQUAL NUMBER OF INSTANTONS AND ANTI-INSTANTONS IN EACH STRING!

$$Z = \sum_{\text{"strings"}} Z_s \longrightarrow e^{-\frac{\beta\omega}{2}} \sum_{k=-\pi/a}^{\pi/a} e^{\beta\Delta\cos ka}$$

THE EFFECT OF FRICTION

DISSIPATION $\longrightarrow$ MICROSCOPIC DESCRIPTION OF INTERACTION WITH BATH

$\downarrow$

HEATH BATH OF — ELECTRONS
— PHONONS

ELECTRONS BATH

$$H = H_0^{el} + H_0^{p} + H_1$$

$$H_0^{el} = \sum_k \varepsilon_k c_k^+ c_k$$

$$H_0^{p} = p^2/2M + V(q)$$

$$H_1 = \sum_{kk'} V_{kk'} e^{i(k-k')q} c_k^+ c_{k'}$$

UNIFORM EL. GAS

BY A CANONICAL TRANSFORMATION ($\longrightarrow$ POLARON PROBLEM) WE OBTAIN

(M. SASSETTI, F NAPOLI, E.G. to be published)

$$\tilde{H} = e^{iS} H e^{-iS} = \frac{1}{2M}\left(p + \sum_k k c_k^+ c_k\right)^2 + V(q) + \sum_k \varepsilon_k c_k^+ c_k + \sum_{kk'} V_{kk'} c_k^+ c_{k'}$$

"INTEGRATING OUT" THE ELECTRONS

$$S[q] = S^0[q] + S_{eff}[q]$$

LINEAR OHMIC DISSIPATION WITH FRICTION η (CALDEIRA-LEGGETT)

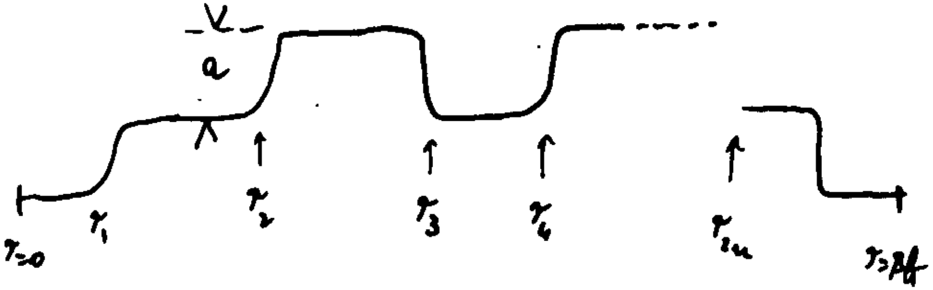
$$S_{eff}[q] \cong M\eta \int_0^{\beta\hbar} d\tau \int_0^{\beta\hbar} d\tau'\, q(\tau) \left[\frac{\pi}{2\beta^2} \frac{1}{\sin^2 \pi \frac{(\tau-\tau')}{\beta\hbar}}\right] q(\tau')$$

WITH

$$M\eta = \int_0^\infty dt \, \langle \hat{\mathcal{F}}(0)\, \hat{\mathcal{F}}(t) \rangle_{ad}$$

"BOOTSTRAP" RESULT !

EVALUATION OF $S[q]$ ON STRINGS OF INSTANTONS :



$$S[q_{2n}] = 2n\, S^{(inst)} + S_{eff}^{(2n)}$$

$$S_{eff}^{(2n)}/\hbar = \underbrace{\frac{4\eta}{\pi}\frac{a^2}{\hbar}}_{g} \sum_{i,j=1}^{2n} e_i e_j \ln \frac{\beta\hbar}{\pi\tau_0}\left|\sin\frac{\pi}{\beta\hbar}(\tau_i-\tau_j)\right|$$

LOGARITHMIC INTERACTION BETWEEN INSTANTONS

"COULOMB GAS" OF INSTANTONS $\rightarrow$

$\rightarrow$ $g < 2$ "PLASMA" $\rightarrow$ "DIFFUSIVE REGIME"

STATIC MOBILITY

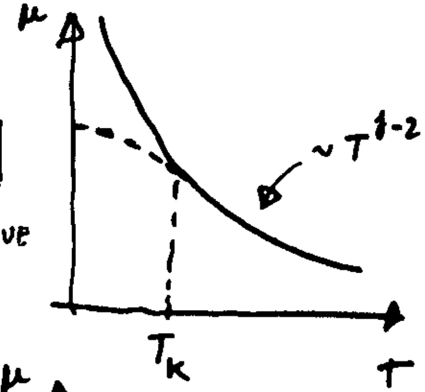
$$\mu(T) = \frac{2\pi a^2}{\hbar} y^2 \frac{\Gamma(g/2)}{\Gamma(g)} \left(\frac{2\pi T}{\hbar\omega}\right)^{g-2} \; ; \; y = \frac{\Delta}{\hbar\omega}$$

(cfr ASHLANGUL, POTTER, SAINT JAMES, J. Phys. 47, 1671, (1985))

$\rightarrow$ For $g<2$ the previous expression is correct ONLY FOR $\boxed{T > T_k \sim \hbar\omega\, y^{2/(2-g)}}$

$\boxed{0<g<2}$

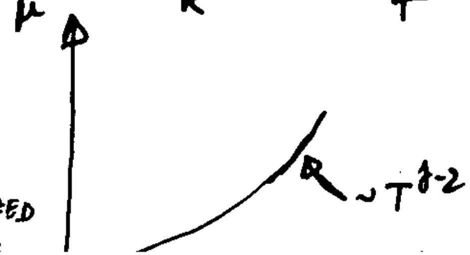
"DIFFUSIVE REGIME"



$D = T\mu$

$g>2$

"LOCALIZED REGIME"



THE $\boxed{\gamma=2}$ CROSS-OVER CORRESPONDS

TO A CRITICAL FRICTION

$$M\eta_c = \frac{2\pi\hbar}{a^2}$$

CAN η REACH SUCH A VALUE ?

IN CASE OF A <u>PHONONS</u> BATH YES

" " AN <u>ELECTRONS</u> BATH ?

MAY BE only FOR HIGHLY DEGENERATE STATES

IN CASE OF DIFFUSION OF μ^+ IN COPPER KADON et al [Phys Lett <u>109 A</u>, 61, (1985)]

FIND $\boxed{\gamma \sim 0.64}$