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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

(Lectures I, II & III)

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1. BROWNIAN MOTION IN A FIELD OF FORCE

Consider a BROWNIAN PARTICLE (BP), i.e. a particle of mass M moving in a medium, assumed in thermal equilibrium at temperature $T = \beta^{-1}$. The BP is acted upon by an external field of force $K(q) = -\frac{\partial V}{\partial q}$, in addition to the irregular force $F(t)$ due to the medium

$$\dot{p} = K(q) + F(t)$$

$$\dot{q} = \frac{p}{M}$$

According to LANGEVIN, and providing M is large, the quantity

$$R(t) = F(t) + \eta\, p(t)$$

represents a RANDOM GAUSSIAN VARIABLE. The correlation time of R is usually very short, so that we can assume that

$$\langle R(t_1)\, R(t_2) \rangle = 2G\, \delta(t_1 - t_2)$$

i.e. $R(t)$ has a white spectrum.

Relation between η and G

Consider a time interval τ sufficiently short on the BP time scale, but sufficiently long on the medium time scale. The quantity

$$A(\tau) = \int_t^{t+\tau} R(t')\, dt'$$

is a random variable with gaussian distribution

$$W_\tau(A) = \frac{1}{(4\pi G \tau)^{1/2}}\, e^{-\frac{A^2}{4G\tau}}$$

Consider now the variable

$$B(\tau) = \int_t^{t+\tau} F(t')\, dt' = A(\tau) - \eta \int_t^{t+\tau} p(t')\, dt' \,.$$

Using the time-scales hypothesis

$$B(\tau) \simeq A(\tau) - \eta p \tau$$

and the d.f. for B will be

$$\varphi_\tau(B,p) = W_\tau(B+\eta p) =$$

$$= \frac{1}{(4\pi G\tau)^{1/2}} e^{-\frac{1}{4G\tau}(B+\eta p)^2}$$

We then obtain the MOMENTS of B

$$\langle B \rangle = -\eta p \tau$$

$$\langle B^2 \rangle = 2G\tau$$

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$$\langle B^{2n} \rangle = O(\tau^n) \qquad n \geq 1$$

We notice now that B represents simply the change Δp of the BP momentum during the interval τ

$$B = \Delta p \quad \Rightarrow \quad \langle \Delta(p^2) \rangle = 2p\langle B \rangle + \langle B^2 \rangle =$$

$$= -2\eta p^2 \tau + 2G\tau \quad ?$$

The last result must hold in particular when the BP is in thermal equilibrium with the medium (i.e. for $p^2 = MT$, $\langle \Delta(p^2) \rangle = 0$), so that we obtain

$$2G\tau = 2\eta p^2 \tau = 2MT\eta$$

$$G = M\eta T$$

i.e. a very simple relation between the friction coefficient η and the strength G of the random force-force correlation.

FOKKER - PLANCK EQUATION

The FP equation is a transport equation for the probability density $f(p, q, t)$ of finding at time t the BP at point (p, q) in phase space.

To derive it, let again τ be a time interval short on the BP time scale, but long on the "heath-bath" time scale. We know that during τ the momentum B received by the BP from the bath is a random quantity, whose distribution is $\varphi_\tau(B, p)$: from this it follows

$$f(p + K\tau,\ q + \frac{p}{m}\tau,\ t+\tau) \cong$$

$$\cong \int_{-\infty}^{+\infty} dB\ \varphi_\tau(B, p-B)\, f(p-B, q, \tau)$$

To first order in τ:

$$\tau \left[\frac{\partial f}{\partial t} + \frac{p}{m}\frac{\partial f}{\partial q} + K\frac{\partial f}{\partial p} \right] = \varphi_\tau(B, p-B)\, f(p-B, q, \tau) - \langle B \rangle \frac{\partial f}{\partial p} + \frac{1}{2}\langle B^2 \rangle \frac{\partial^2 f}{\partial p^2}$$

Recalling that

$$-\langle B \rangle = \eta\, p\, \tau$$

$$\langle B^2 \rangle = 2M\eta T \tau$$

we obtain

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

which is called "FOKKER-PLANCK" equation.

We stress that the FP equation holds provided the BP motion and the thermal bath fluctuations have quite different time scales.

The FP equation is not easy to solve analytically in his general form, so that it is useful to see what form it takes in the two limiting cases of "large" and "small" values of the friction η.

LARGE FRICTION LIMIT

SMOLUCHOWSKI EQUATION

Integrating over p the FP equation along the phase space straight line

$$q = M\gamma\,(q_0 - q)$$

we easily obtain the (still exact) equation

$$\frac{\partial}{\partial t}\int f(p,q,t)\,dp = -\frac{1}{M\gamma}\int_{\left(q=q_0-\frac{p}{M\gamma}\right)}\frac{\partial}{\partial q}\left[K(q)\,f(p,q,t) - T\frac{\partial f}{\partial q}\right]dp$$

In the large friction limit f will tend very rapidly to become a Maxwell distribution $e^{-\frac{p^2}{2MT}}$ locally at every q, since γ is proportional to the diffusion coefficient in p-space ($D_p = M\gamma T$). Thus for sufficiently large γ the scale of variation $\Delta p \sim (2MT)^{1/2}$ of f with respect to p will become much smaller than the scale of variation with respect to $M\gamma q$, which is $\sim$

$$\Delta q \sim M\gamma\,|K(q)/\ldots|$$

This condition will be fulfilled provided

$$\Delta p \ll \Delta q \qquad \text{or}$$

$$\gamma \gg \left(\frac{2T}{M}\right)^{1/2}\left|\frac{K'(q)}{K(q)}\right|$$

Another way of stating such a condition is that the distance that a thermally drifting particle (with speed $\left(\frac{2T}{M}\right)^{1/2}$) traverses in a time γ^{-1} must be very short compared with a distance $\sim\left|\frac{K(q)}{K'(q)}\right|$ over which $K(q)$ varies appreciably (OVER DAMPED MOTION). If the large γ condition is satisfied we can approximate the above equation as

$$\frac{\partial}{\partial t}\int f(p,q_0,t)\,dp \cong -\frac{1}{M\gamma}\frac{\partial}{\partial q_0}\left[K(q_0)\int f(p,q_0,t)\,dp + - T\frac{\partial}{\partial q_0}\int f(p,q_0,t)\,dp\right],$$

which holds approximately at each q_0 and t. Noting that $\int f(p,q_0,t)\,dp = n(q_0,t)$ represents the (probability) [illegible]

$$\frac{\partial n(q,t)}{\partial t} = \frac{\partial}{\partial q}\left(\frac{T}{H\eta}\right)\left[\frac{\partial n}{\partial q} - \frac{k(q)}{T}\, n\right]$$

This equation is called "Smoluchowski equation" (SE), and has the form of a diffusion equation in configuration space. Comparing with the continuity equation $\frac{\partial n}{\partial t} = -\frac{\partial j}{\partial q}$ we see that the current j, according to SE is given by

$$j = -D\left(\frac{\partial n}{\partial q} - \frac{1}{T}\, k(q)\, n\right)$$

where

$$D = \frac{T}{H\eta}$$

represents the diffusion coefficient.
Note that at thermal equilibrium it is $j = 0$, and from the above expression for j it then follows

$$\frac{n(q_2)}{n(q_1)} = e^{\frac{1}{T}\int_{q_1}^{q_2} k(q)\,dq},$$

i.e. the Boltzmann distribution is realized. 0

SMALL FRICTION LIMIT

When the condition $\eta \ll \omega$ is satisfied, ω being a typical oscillation frequency of the BP, the energy of the BP suffers only a little change during an oscillation period (UNDERDAMPED MOTION). In this case the FP equation can be approximately reduced to a diffusion equation along the energy (or better ACTION) coordinate.
To achieve this let first rescale the (p, q) variables so that they both have dimensions of $(\text{action})^{1/2}$ (i.e. $p \to \frac{p}{(H\eta)^{1/2}}$, $q \to q(H\eta)^{1/2}$).
Second, let perform a canonical transformation from (p, q) variables to "action and angle" variables

$$(p, q) \longrightarrow (A, \varphi)$$

where the "action" is given by

$$A(p, q) = \oint p\, dq \equiv A(E)$$

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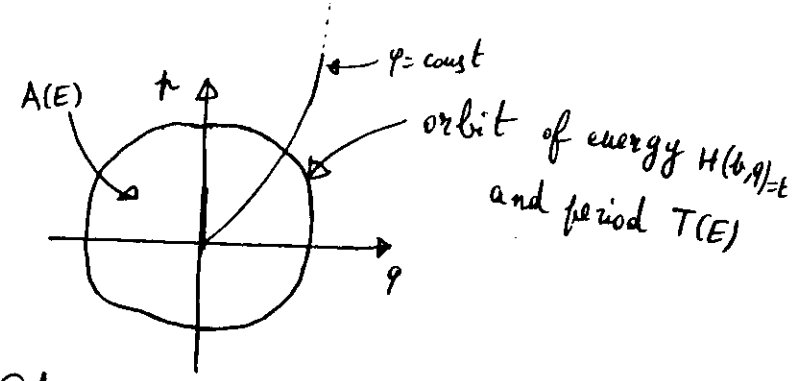
Note that:

- $A(E)$ is the action integral of an orbit with energy E described by the BP IN ABSENCE of dissipation ($\eta = 0$):



$$\frac{\partial A}{\partial E} = T(E) \equiv 2\pi\,\omega^{-1}(E)$$

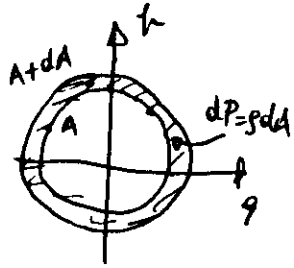
- The curves $\varphi = \text{const}$ are orthogonal trajectories to $A = \text{const}$:

$$\begin{cases} \dfrac{\partial \varphi}{\partial p} = -\lambda \dfrac{\partial A}{\partial q} = -\omega^{-1}\lambda \dfrac{\partial H}{\partial q} \\ \dfrac{\partial \varphi}{\partial q} = \lambda \dfrac{\partial A}{\partial p} = \omega^{-1}\lambda \dfrac{\partial H}{\partial p} \end{cases} \rightarrow \oint_{(A=\text{const})} d\varphi = 1$$

From the condition $[\varphi, A] = 1 \rightarrow \lambda = \omega^2 \left[\left|\frac{\partial H}{\partial p}\right|^2 + \left|\frac{\partial H}{\partial q}\right|^2\right]^{-1}$

Provided $\eta \ll \omega(E)$ the Brownian motion can be visualized as a slow change in time of the (probability) density along the A-coordinate, given by

$$S(A,t) = \oint_{(A=\text{const})} f(A,\varphi,t)\, d\varphi$$



Writing the FP equation in terms of the (A, φ) variables, integrating over φ and using the periodicity condition $f(A, \varphi+1, t) = f(A, \varphi, t)$ one obtains the approximate equation for S

$$\frac{\partial S}{\partial t} \cong \eta\left[S + J_1(A)\frac{\partial S}{\partial A} + J_2(A)\frac{\partial^2 S}{\partial A^2}\right]$$

where

$$J_1(A) = A + T\,\omega^{-1}$$

$$J_2(A) = T\,\omega^{-1}\,A \quad ;$$

using $\omega^{-1}\frac{\partial}{\partial A} = \frac{\partial}{\partial E}$ the previous equation becomes

$$\frac{\partial S}{\partial t} = \eta \frac{\partial}{\partial A}\left(AS + TA\frac{\partial S}{\partial E}\right)$$

which represents a diffusion equation along the A-coordinate. The corresponding current j_A is given by

$$j_A = -\eta\left(AS + TA\frac{\partial S}{\partial E}\right)$$

At equilibrium it is $j_A = 0$, so that

$$\frac{\partial S}{\partial E} = -\frac{1}{T}S \Rightarrow S \equiv S(E) \propto e^{-E/T}$$

i.e. we obviously obtain Boltzmann's distribution.

2. BROWNIAN MOTION MODEL OF CHEMICAL REACTIONS

RATE OF ESCAPE OVER BARRIERS

- CLASSICAL THEORY - (H.A. KRAMERS, 1940)

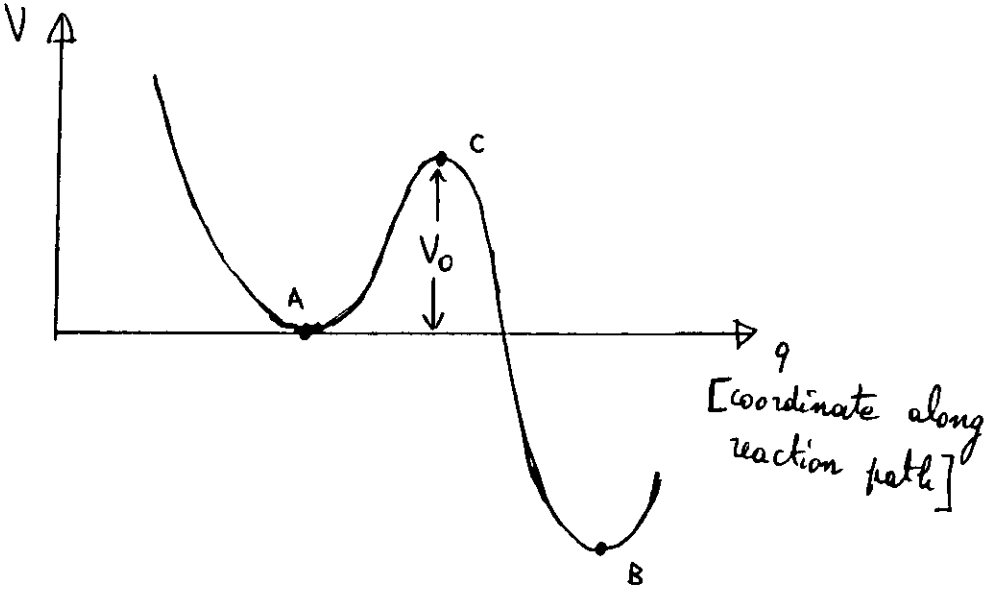
CHEMICAL REACTION rates are usually thermally activated processes, in which the rate obeys an "ARRHENIUS LAW" of the form

$$K = \frac{\omega}{2\pi} e^{-\frac{V_0}{T}}$$

where: V_0 is the height of the potential energy (or free energy) barrier which separates the initial state of the process (REAGENTS) from the final state (PRODUCTS);

$\frac{\omega}{2\pi}$ is the so-called "attempt" frequency (number of successful attempts per unit time to overpass the barrie

Assuming the reaction to be described by the time variation of a single coordinate in the configuration space of reagents, we can reduce it to a one-dimensional process.



While the Boltzmann factor $e^{-V_0/T}$ in Arrhenius law is an equilibrium quantity, the attempt frequency $f = \frac{\omega}{2\pi}$ has in principle to be determined from non-equilibrium considerations.

The simplest theory for the pre-factor f is EYRING's so-called ABSOLUTE RATE THEORY (or "transition state theory") in which the reagents in the initial state at A are assumed in thermal equilibrium, and the prefactor f is estimated in a purely kinematic way by simply counting the number of reagent in the Maxwellian tail about A with sufficient kinetic energy to surmount the barrier. One then finds very easily

$$f = f_A = \frac{\omega_A}{2\pi}$$

where f_A is the oscillation frequency near A. The rate within the absolute rate theory (ART) is therefore

$$K_{ART} = \frac{\omega_A}{2\pi} e^{-\frac{V_0}{T}}$$

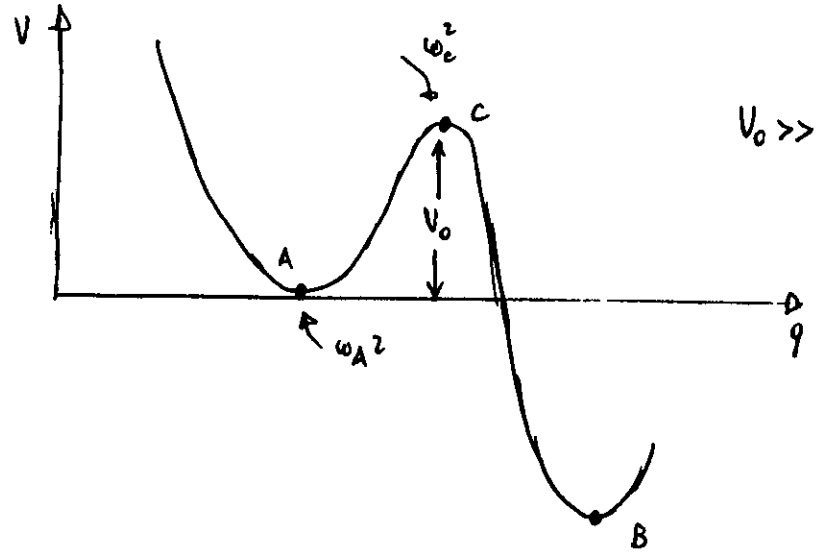
In the BROWNIAN MOTION model the representative point of the reagents along the reaction path is treated as a Brownian particle (BP), interacting with the heath bath which is in contact with the reagents. In the case of HETEROGENEOUS CATALYSIS the heath bath is of course the solid surface on which the reaction takes place.

The calculation of the REACTION RATE amounts then to calculate the rate of escape of a "particle" from well A over the potential barrier C.

On a purely classical ground, and assuming the Brownian motion hypothesis to be correct (i.e. very different time scales of BP motion and heath bath fluctuations), such a process can be studied by means of the Fokker-Planck equation (FPE)

In the LARGE FRICTION limit ($\eta >> \omega^2_{A,C}$)

We know that the FPE reduces to the SE.



$$SE: \quad \frac{\partial n}{\partial t} = \frac{\partial}{\partial q}\left(\frac{T}{M\eta}\right)\left[\frac{\partial u}{\partial q} - \frac{k(q)}{T} n\right]$$

Assuming a near-Boltzmann distribution near A, and practically ~~zero~~ zero density at B a quasi-stationary diffusion current j will flow from A toward B:

$$j = -\frac{T}{M\eta}\left[\frac{\partial n}{\partial q} - \frac{k(q)}{T} n\right] \cong \text{const}$$

Such equation can easily be integrated, to give

$$j = \frac{T}{H\eta}\ \frac{n_A e^{V_A/T} - n_B e^{V_B/T}}{\int_A^B e^{V/T}\,dq} \sim \frac{T}{H\eta}\ \frac{n_A e^{V_A/T}}{\int_A^B e^{V/T}\,dq}$$

On the other hand, the number N_A of particles in well A will be approximately

$$N_A \cong n_A e^{V_A/T} \int_{(\text{well A})} e^{-V(q)/T}\,dq \cong$$

$$\cong n_A \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\frac{H\omega_A^2 q^2}{T}}\,dq = \frac{n_A}{\omega_A}\left(\frac{2\pi T}{H}\right)^{1/2},$$

and the rate will be given by

$$K = \frac{1}{N_A}\left(-\frac{dN_A}{dt}\right) = \frac{j}{N_A} \cong \frac{\omega_A}{\eta}\left(\frac{T}{2\pi H}\right)^{1/2} \frac{e^{V_A/T}}{\int_A^B e^{V/T}\,dq} \cong$$

$$\cong \frac{\omega_A}{\eta}\left(\frac{T}{2\pi H}\right)^{1/2} \frac{e^{-V_c/T}}{\int_{-\infty}^{+\infty} e^{-\frac{1}{2}H\omega_c^2 q^2/T}\,dq} =$$

$$= \frac{\omega_A}{2\pi}\ \frac{\omega_c}{\eta}\ e^{-V_0/T}$$

$$K \cong \frac{\omega_c}{\eta}\ \frac{\omega_A}{2\pi}\ e^{-V_c/T} = \frac{\omega_c}{\eta}\ K_{AB}$$

From the relation

$$j \cong \frac{T}{H\eta}\ \frac{n_A e^{V_A/T}}{\int_A^B e^{V/T}\,dq} \cong \frac{T}{H\eta}\ \frac{n_P e^{V_P/T}}{\int_P^B e^{V/T}\,dq}$$

which holds for an arbitrary point P, it follows

$$\frac{n_P}{n_A} \cong e^{-\frac{(V_P - V_A)}{T}}\ \frac{\int_P^B e^{V/T}\,dq}{\int_A^B e^{V/T}\,dq}$$

When P is considerably to the left of C it is $\int_P^B e^{V/T}\,dq \sim \int_A^B e^{V/T}\,dq$, so that in P there is still practically a Boltzmann distribution, while for P considerably to the right $n_P \sim 0$.

For $P \equiv C$ we have $\int_P^B e^{V/T}\,dq \sim \frac{1}{2}\int_A^B e^{V/T}\,dq$ so that $n_c/n_A \cong \frac{1}{2}\, e^{-\frac{(V_P - V_A)}{T}}$, i.e. in P one has half of the equilibrium density. The region around C where the density changes from ~ equilibrium to ~ zero is a narrow slice $\delta \sim (T, 1/2$ [illegible]

In the SMALL FRICTION limit ($\eta \ll \omega_A$) we know that the FPE reduces to

$$\frac{\partial \rho}{\partial t} = - \frac{\partial j}{\partial A}$$

with

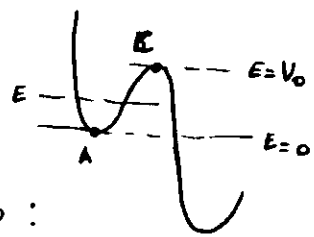
$$j = - \eta \left(A \rho + T A \frac{\partial \rho}{\partial E} \right) \cong \text{const}$$

where we assumed again a quasi-stationary process.

We write the last equation as

$$- \frac{1}{\eta A T} j = \frac{\partial \rho}{\partial E} + \frac{1}{T} \rho = e^{-E/T} \frac{\partial}{\partial E} \left(\rho e^{E/T} \right),$$

which can be integrated from a value of E corresponding to an orbit near A, up to $E = V_0$:



$$j = T \eta \; \frac{\rho(E) e^{E/T} - \rho_E e^{V_0/T}}{\int_E^{V_0} \frac{1}{A} e^{E'/T} dE'} \cong$$

$$\cong T \eta \; \frac{\rho(E) e^{E/T}}{\int_A^{V_0} \frac{1}{A} e^{E'/T} dE'} \quad \text{since } \rho_c \sim 0$$

The integral in the denominator is dominated by $E' \sim V_0$

$$\int_E^{V_0} \frac{1}{A} e^{E'/T} dE' \sim e^{V_0/T} \frac{1}{A_c} \int_{-\infty}^{0} e^{E'/T} dE' =$$

$$= e^{V_0/T} \frac{T}{A_c}$$

and we obtain

$$j \cong \eta A_c e^{-V_0/T} \rho(E) e^{E/T} \sim \eta A_c e^{-V_0/T}$$

since near A we have a Boltzmann distribution.

On the other hand the number of particles in well A is approximately

$$N_A \sim \int_A^C \rho \, dA = \int_0^{V_0} \rho(E) \, \omega^{-1}(E) \, dE \cong$$

$$\cong \omega_A^{-1} \int_0^{\infty} e^{-E/T} dE = T \omega_A^{-1}$$

Thus we get a rate

$$K = \frac{j}{N_A} \cong \eta \frac{A_c \omega_A}{T} e^{-V_0/T} \gtrsim \eta \frac{V_0}{T} e^{-V_0/T}$$

TWO η - REGIMES :

$$\eta \gg \omega_c \longrightarrow K \cong \frac{\omega_A \omega_c}{2\pi\eta} e^{-V_0/T}$$

(RATE DECREASING WITH η)

$$\eta \ll \omega_A \longrightarrow K \sim \eta \frac{V_0}{T} e^{-V_0/T}$$

(RATE INCREASING WITH η)

In the INTERMEDIATE η-REGIME we expect the ART result to be valid

$$\downarrow$$

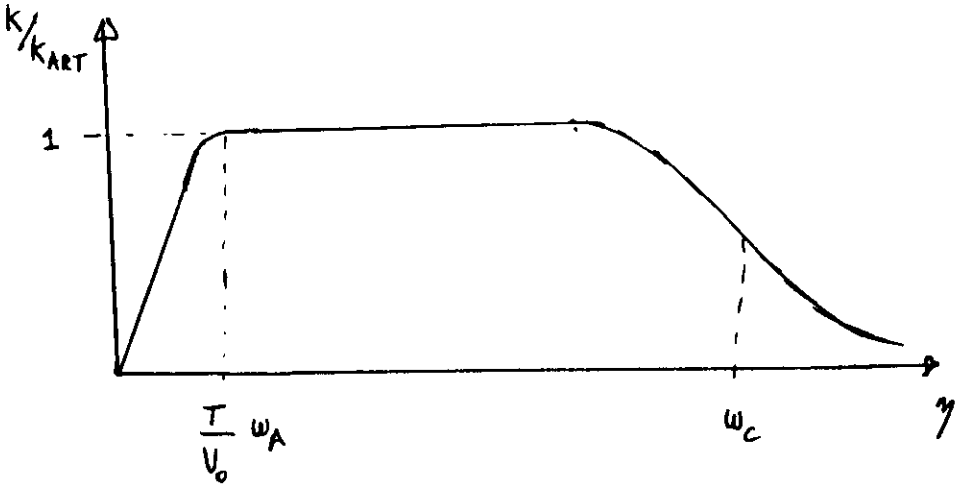
$$K = K_{ART} = \frac{\omega_A}{2\pi} e^{-\frac{V_0}{T}}$$

By a detailed balance argument (see below) one knows that $K \leq K_{ART}$ always, so that the precise range of validity of the low friction regime must be $\eta < \frac{T}{V_0} \omega_A$.

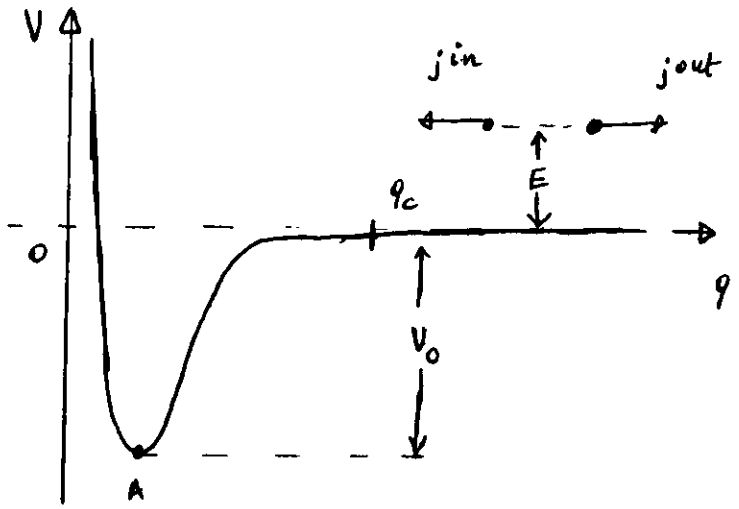
In the range $\eta > \frac{T}{V_0} \frac{\omega_A}{2\pi}$ Kramers derives a more general expression for K

$$K = \frac{\omega_A}{2\pi\omega_c} \left[-\eta/2 + \left(\eta^2/4 + \omega_c^2 \right)^{1/2} \right] e^{-V_0/T}$$

which gives the ART result for $\eta \ll \omega_c$ and the previous large η result for $\eta \gg \omega_c$.



Relation between DESORPTION RATE and STICKING



Let j^{out} be the FLOW of particles which leave the well A per unit time:

$$j^{out} = K N_A$$

According to ART this FLOW is given by

$$j^{out}_{ART} = \frac{1}{M} \int_0^\infty dp\, p\, f_{eq}(p, q=q_c) = K_{ART} N_A$$

At THERMAL equilibrium between adsorbed particles and gas particles there is an INGOING FLOW

$$j^{in} = \frac{1}{M} \int_0^\infty dp\, p\, f_{eq}(p, q=q_c)\, S(p)$$

where

$S(p) \equiv$ "STICKING" probability for an ingoing particle with momentum p

and of course it must be

$$j^{in} = j^{out}$$

But we have seen that

$$j^{out} = K N_A = K_{ART} \left(\frac{K}{K_{ART}}\right) N_A =$$

$$= \frac{K}{K_{ART}}\, j^{out}_{ART}$$

i.e.

$$\frac{K}{K_{ART}} = \frac{j^{out}}{j^{out}} = \frac{\int_0^\infty dp\, p\, f_{eq}(p, q_c)\, S(p)}{\int_0^\infty \ldots}$$

We obtain

$$\frac{k}{k_{ART}} = \frac{\int_0^\infty dh\, h\, f_{eq}(h, q_c)\, S(h)}{\int_0^\infty dh\, h\, f_{eq}(h, q_c)} = \frac{\int_0^\infty dE\, e^{-E/T}\, S(E)}{\int_0^\infty dE\, e^{-E/T}}$$

where $E = v^2/2H$ is the kinetic energy at $q = q_c$.

We have found

$$\frac{k}{k_{ART}} = \bar{S} \leq 1$$

where $\bar{S}$ is the AVERAGE STICKING PROBABILITY for particles having a maxwellian distribution with temperature T equal to that of the adsorbed particles

$$\bar{S} = \frac{\int_0^\infty dE\, e^{-E/T}\, S(E)}{\int_0^\infty dE\, e^{-E/T}} \leq 1$$

What can we say about $S(E)$?

At small friction $\eta \ll \omega_A$ an incoming particle of energy E after a round trip starting and arriving at q_c will be approximately

$$\Delta = \eta \oint H v^2 dt \cong \eta \oint h\, dq = \eta A(E) \qquad (E = \text{const})$$

and so, by definition of STICKING

$$S(E) = \begin{cases} 1 & E < \Delta \\ 0 & E > \Delta \end{cases}$$

The average sticking $\bar{S}$ will be

$$\bar{S} = \frac{\int_0^\infty dE\, e^{-E/T}\, S(E)}{\int_0^\infty dE\, e^{-E/T}} \cong \frac{\int_0^{\Delta_0} dE\, e^{-\beta E}}{\int_0^\infty dE\, e^{-\beta E}} =$$

$$= 1 - e^{-\eta \Delta_0 / T} \qquad \text{with } \Delta_0 = \eta A(0) \sim \eta\, v_0/\omega_A$$

What can we say about $S(E)$?

At small friction $\eta \ll \omega_A$ the energy LOST by an incoming particle of energy E, after a round trip starting and arriving at q_c, will be approximately

$$\Delta = \eta \oint M v^2 dt \cong \eta \oint_{(E=\text{const})} p\, dq = \eta\, A(E)$$

and so, by definition of STICKING

$$S(E) = \begin{cases} 1 & E < \Delta \\ 0 & E > \Delta \end{cases}$$

The average sticking $\bar{S}$ will be

$$\bar{S} = \frac{\int_0^\infty dE\, e^{-E/T}\, S(E)}{\int_0^\infty dE\, e^{-E/T}} \cong \frac{\int_0^{\Delta_0} dE\, e^{-E/T}}{\int_0^\infty dE\, e^{-E/T}} = 1 - e^{-\Delta_0/T}$$

with $\Delta_0 \equiv \eta A(0) \sim \eta \frac{V_0}{\omega_A}$

We obtain

$$\bar{S} \cong 1 - e^{-\Delta_0/T} \cong 1 - e^{-\frac{\eta V_0}{\omega_A T}}$$

Note that $\bar{S} \xrightarrow[T \to 0]{} 1$!

From the general result $\frac{k}{k_{ART}} = \bar{S}$ we obtain

$$\frac{k}{k_{ART}} \cong 1 - e^{-\frac{\eta V_0}{\omega_A T}}$$

which for $\eta \ll \omega_A \frac{T}{V_0}$ reduces to

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

which is Kramer's result.

The above result suggests that

$$\frac{k}{k_{ART}} \sim 1 - e^{-\frac{\eta V_0}{\omega_A T}} \quad \text{for } \omega_A \frac{T}{V_0} < \eta < \omega_A$$

CALCULATION OF γ

↓

EVALUATION OF K

(ART OR NOT ?)

Consider a chemical reaction taking place on a metal surface. The reactant atoms will be chemisorbed on the surface, and within the BORN-OPPENHEIMER scheme (BO) they will move from one minimum to another of the BO potential energy hypersurface, corresponding to different chemical compounds.

Neglecting the phonons degrees of freedom, such a motion can only take place through a NON ADIABATIC coupling with the electrons of the metal (→ HEATH BATH OF ELECTRONS)

BORN/OPP

ver 2 of H

– According to the point of view Kumar, Schmich, Suhl and G d'A (KSSG) (PR B11, 2122, 1975), let assume that the ad-atoms motion can be treated classically, and that the masses are large enough, so that such a motion and the heath bath fluctuations have very different time scales. The FPE description will then apply, with a FRICTION COEFFICIENT η describing the NON ADIABATIC (or DISSIPATIVE) coupling with the ELECTRONS.

– How do we calculate the friction ?

A possible way is the so-called "BOOTSTRAP" procedure of KSSG : let start from the FPE for the system's representative point (→ "AD-ATOM") along the reaction path :

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

where q is the reaction coordinate, and

$$V(q) = -T \ln Z_{el}[q]$$

is the ADIABATIC potential energy (or FREE ENERGY) arising from the interaction between the electrons and the "ad-atom", or "Brownian particle" (BP) at fixed position q. Here

$$Z_{el}[q] = \operatorname*{Tr}_{del} e^{-\beta H_{ad}(q)}$$

is the partition function of the adiabatic hamiltonian

$$H_{ad}(q) = H_{el}^{(0)} + H_1(q)$$

which describes the electrons and their interaction with the BP held fixed at q. Note that the mass M in the FPE is in general a q-dependent effective mass along the reaction ..10

The "BOOTSTRAP" logic rests on the assumption of the validity of the FPE, and consists in comparing certain RESPONSE FUNCTIONS calculated from the FPE with their exact KUBO expressions.

Let imagine that a small external force

$$F_1(t) = F_1 e^{-i\omega t}$$

is applied to the BP. We can then calculate from the FPE the DENSITY n_1, the CURRENT j_1 and the KINETIC ENERGY DENSITY K_1 responses induced by F_1. We then find

$$M(\gamma - i\omega) j_1(q) = F_1 n_{eq}(q) - \frac{\partial V}{\partial q} n_1(q) - 2\frac{\partial k_1}{\partial q}$$

where $n_{eq}(q) \sim e^{-V(q)/T}$ is the equilibrium density. The QM operators corresponding to the previous variables are related by an exact Heisenberg equation

$$M \frac{\partial \hat{j}}{\partial t} + 2\frac{\partial \hat{k}}{\partial} - \hat{F}\hat{n} = 0$$

Remarks :

- Both the thermal average

$$\langle \dots \rangle = Z_{ad}^{-1}[q]\, Tr\{ e^{-\beta H_{ad}(q)} \dots \}$$

and the time-dependence of $\hat{f}_{ad}(t)$

$$\hat{f}_{ad}(t) = e^{i\hat{H}_{ad}t} \hat{f} e^{-i\hat{H}_{ad}t}$$

are defined with the BP held fixed at q, i.e. are taken with respect to the adiabatic hamiltonian.

- The friction η_ω is in general frequency-dependent. However, provided the time scale of the BP motion is long enough with respect to the typical electronic relaxation times, η_ω can be replaced by its zero-frequency limit.

A similar equation holds for the Fourier-transforms of their Kubo responses:

$$-i\omega M j_1 = F_1 n_{eq} + (\hat{F}\hat{n})_1 - 2\frac{\partial k_1}{\partial q}$$

Comparing with the previous result from FPE

$$M(\eta - i\omega) j_1 = F_1 n_{eq} - \frac{\partial V}{\partial q} n_1 - 2\frac{\partial k_1}{\partial q}$$

we obtain

$$M\eta j_1 = n_1 \frac{\partial V}{\partial q} - (\hat{F}\hat{n})_1$$

i.e. a relation which gives η in terms of the exact KUBO responses n_1, j_1 and $(\hat{F}\hat{n})_1$. Evaluation of η in the limit $M \to \infty$ gives

$$M\eta_\omega(q) = \frac{1}{T} Re \int_0^\infty dt\, e^{i\omega t} \langle \hat{\mathcal{F}}\, \hat{\mathcal{F}}_{ad}(t) \rangle_{ad}$$

where

$$\hat{\mathcal{F}} = \hat{F}\{r_{el}, q\} - \langle \hat{F} \rangle_{ad}$$

is the fluctuating part of the microscopic force $\hat{F}$ by which the BP is acted [illegible]

EVALUATION OF η

$$M\eta_{ij} = \frac{1}{T} \lim_{\omega \to 0} Re \int_0^\infty e^{i\omega t} \langle \hat{\mathcal{F}}_i\, \hat{\mathcal{F}}_{ad_j}(t) \rangle_{ad}$$

The fluctuating force $\hat{\mathcal{F}}_i$ will be in general

$$\hat{\mathcal{F}}_i = -\nabla_i \int d\underset{\sim}{r}\, V(\underset{\sim}{r} - \underset{\sim}{R})\, \delta\hat{n}(\underset{\sim}{r})$$

where

$$\delta\hat{n} = \hat{n} - \langle \hat{n} \rangle_{ad}$$

is the electron density fluctuation.

The expression for η_{ij} is also

$$M\eta_{ij} = \lim_{\underset{\sim}{R} \to \underset{\sim}{R}'} \nabla_i \nabla_j' \int d\underset{\sim}{r}\, d\underset{\sim}{r}'\, V(\underset{\sim}{r} - \underset{\sim}{R})\, V(\underset{\sim}{r}' - \underset{\sim}{R}') \cdot \lim_{\omega \to 0} \left[-\frac{1}{\omega} Im\, \chi(\underset{\sim}{r}\, \underset{\sim}{r}' \omega) \right.$$

where

$$\chi(\underset{\sim}{r}\, \underset{\sim}{r}' \omega) = -\frac{i}{\hbar} \int_0^\infty dt\, e^{i\omega t} \langle [\delta\hat{n}(\underset{\sim}{r}, t), \delta\hat{n}(\underset{\sim}{r}', 0)] \rangle_{ad}$$

is the DENSITY RESPONCE of the [illegible] 2D

In the case of a CHARGED BP in a homogeneous electron gas, and evaluating χ at ZERO ORDER in the coupling of the electrons with the BP the friction η becomes

$$M\eta = \frac{4\pi e^2}{3} \sum_{\underset{\sim}{q}} \lim_{\omega \to 0} \left[-\frac{1}{\omega} \varepsilon^{-1}(\underset{\sim}{q}\,\omega) \right]$$

where $\varepsilon(\underset{\sim}{q}\,\omega)$ is the dielectric function of the electron gas.

With $\varepsilon = \varepsilon_{RPA}$ we obtain

$$\eta \cong \frac{4}{3\pi} \frac{m}{M} \frac{e^2}{2\hbar a_0} F(k_F a_0)$$

where $a_0 \equiv$ Bohr radius and $F(k_F a_0) \sim 1$ for reasonable k_F. The order of magnitude of η is then

$$\eta \sim \frac{m}{M} \frac{e^2}{2\hbar a_0}$$

In the case of NON INTERACTING electrons η can be evaluated to all orders in the coupling between the electrons and the BP.

For a homogeneous electron gas and a spherically symmetric potential V one finds

$$\eta = \frac{8}{3\pi} \frac{m}{M} \frac{E_F}{\hbar} \sum_{\ell} (\ell+1) \sin^2(\delta_\ell - \delta_{\ell-1})$$

where the phase shifts are taken at the Fermi level. Comparing with the expression for the IMPURITY RESISTIVITY ρ caused by n_I "heavy particles" per unit volume, we obtain

$$n_I M \eta = n e^2 \rho$$

Results of similar form were obtained by W Schaich (Surf Sci 49, 221, 1975) also in the case of an ad-atom near a

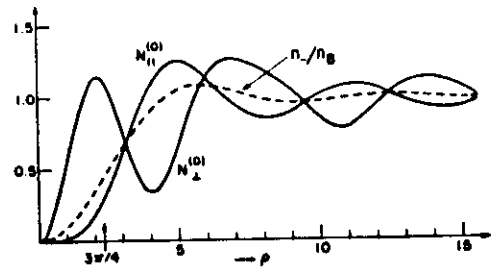


Fig. 1. The spatial dependence of the friction parameter in a low order response calculation, eq. (16), is plotted versus $\rho = k_F|R - R^{(0)}|$. Also shown by the dashed line is the variation of the electronic charge density, n_-, normalized by its bulk value. The location $\rho = 3\pi/4$ is the edge of the neutralizing positive background charge.

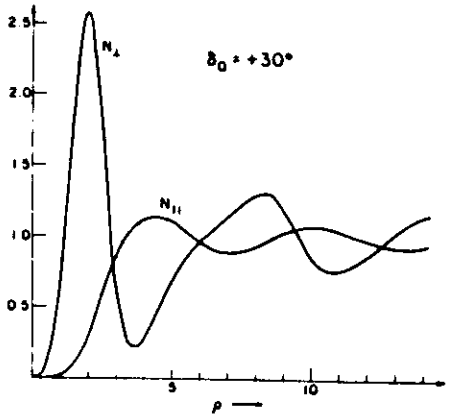


Fig. 2. The spatial variation of the exact friction parameter, eqs. (25), (A.1)–(A.10), for Fermi level s wave phase shift equal to +30° is plotted versus $\rho = k_F|R - R^{(0)}|$.

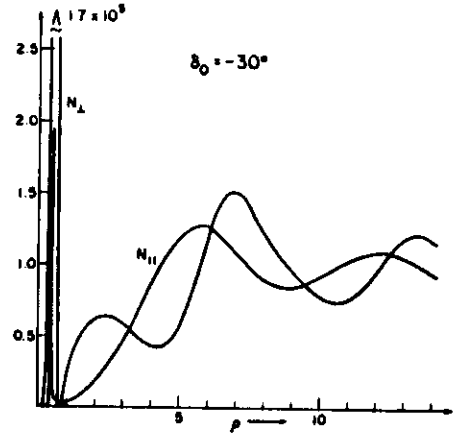
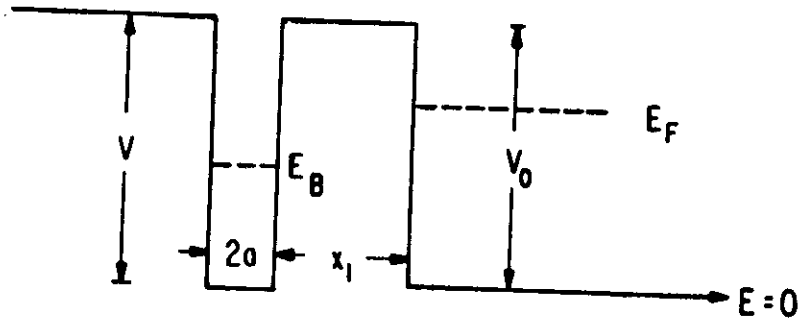


Fig. 3. The spatial variation of the exact friction parameter, eqs. (25), (A.1)–(A.10), for Fermi level s-wave phase shift equal to −30° is plotted versus $\rho = k_F|R - R^{(0)}|$.



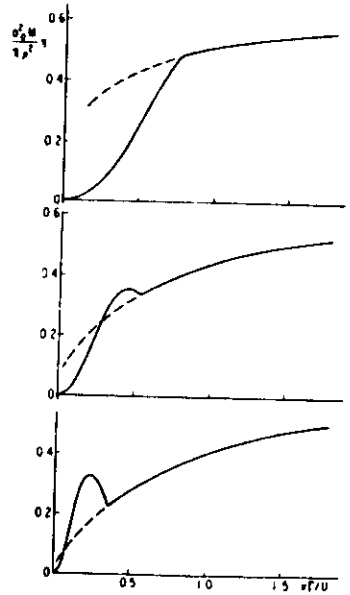


FIG. 1. η versus $\epsilon\Gamma/U$ with $(\epsilon_a - \epsilon_F)/U = -0.2$ (or .8), -0.1 (or -0.9), and -0.05 (or -0.95).

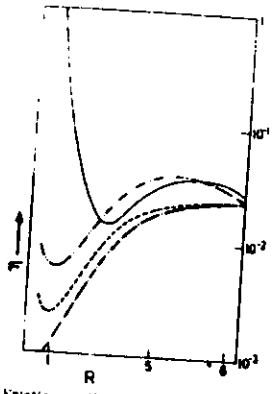


FIG. 4. Friction coefficient η vs nuclear separation R. The atomic level lies 0.5 below the Fermi energy and the coupling constant $\Gamma = 0.05$. The solid line corresponds to η^{L}_{Mol}, the dashed line to $\eta^{L}_{\Gamma=\infty}$, the dash-dot line

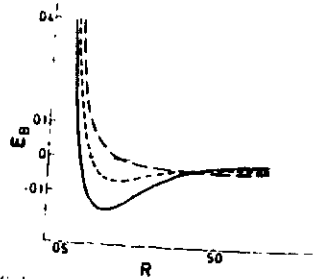


FIG. 5. Binding energy E_B (measured in Hartree) vs nuclear separation R (in Bohr radius units), for the case when the atomic level ϵ_a is 0.5 below the Fermi level. The coupling Γ of the localized states to the metal states is 0.001 (solid line), 0.05 (dashed line), and 0.1 (dash-dot line).

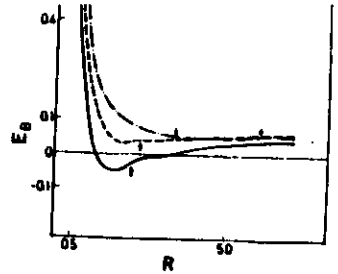


FIG. 7. Binding energy E_B vs nuclear separation R for the case when the atomic level ϵ_a lies 0.05 *above* the Fermi energy. The solid line corresponds to $\Gamma = 0.001$, the dashed line to $\Gamma = 0.05$, and the dash-dot line to $\Gamma = 0.1$. The arrows indicate where the magnetic solutions appear and disappear.

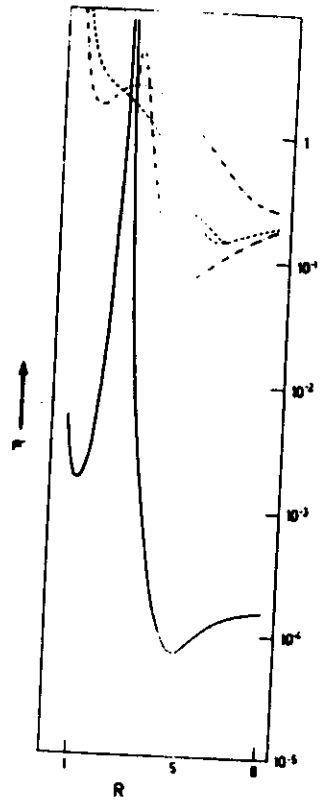
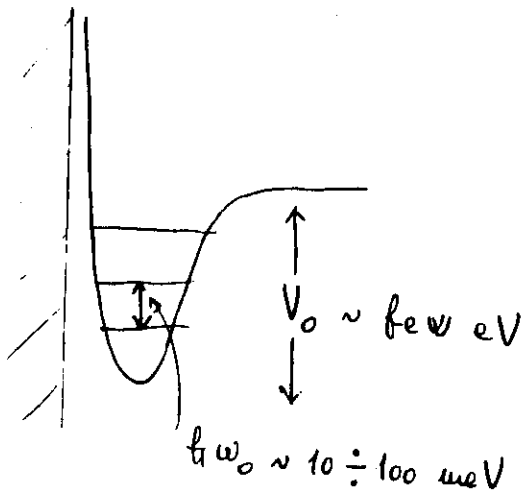


FIG. 8. Friction coefficient η^{L}_{Mol} vs nuclear separation R, when the atomic level lies 0.05 above the Fermi energy. The solid line corresponds to $\Gamma = 0.001$, the dash-double-dot line to $\Gamma = 0.05$, and the dashed line to $\Gamma = 0.1$. For $\Gamma = 0.001$ only the magnetic solution has been plotted. For $\Gamma = 0.05$ the value of η for the stable magnetic solution shoots up at $R \approx 2.5$, while for $\Gamma = 0.1$ the magnetic value lies first below the unstable nonmagnetic value of η ($3.5 \lesssim R \lesssim 5$) and later above ($5 \lesssim R \lesssim 6$).

3. RATE OF ESCAPE OVER (AND ACROSS) BARRIERS

QUANTUM CASE

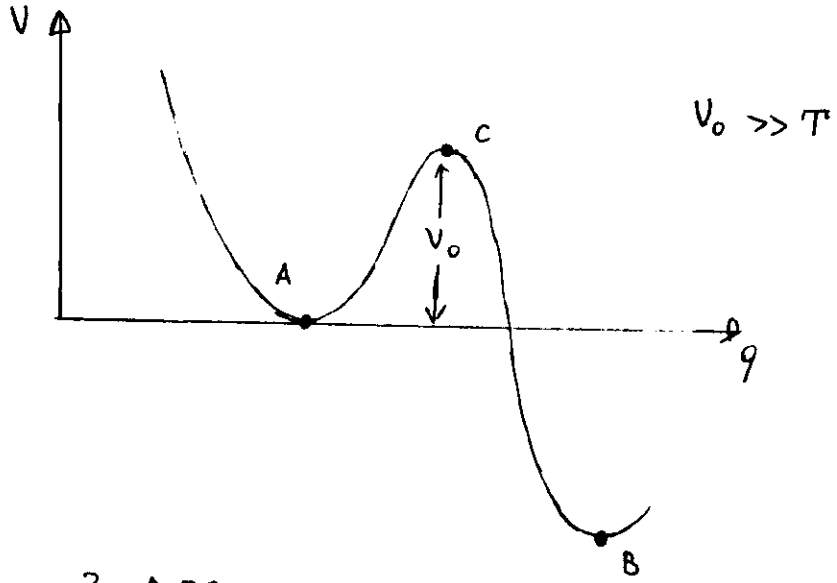
In a typical chemisorption well



the level spacing is usually in the range $10 \div 10^2$ meV which correspond to $10^2 \div 10^3$ °K, depending on the ad-atom mass.

QUANTUM EFFECTS become important at temperatures $T \lesssim \hbar\omega_0$, so that they could in principle be very important even at [illegible]

It is then worthwhile to reconsider the problem of ESCAPE FROM A POTENTIAL WELL from the QM point of view. This will lead us also to a QUANTUM MECHANICAL definition of the FRICTION COEFFICIENT.



3 REGIMES :

1) $T \ll \hbar\omega_{A,C}$ QUANTUM TUNNELING

2) $T \gg \hbar\omega_{A,C}$ CLASSICAL THERMAL ACTIVATION

3) $T \sim \hbar\omega_{A,C}$ QUANT...

UNDAMPED CASE ($\gamma = 0$)

1) TUNNELING REGIME ($T \ll \hbar\omega_{A,C}$)

($\gamma = 0$)

As in the classical case let consider a situation with near thermal equilibrium in well A, and ~ zero density in well B.

Only few low lying levels of well A will have chance to be occupied, because $T \ll \hbar\omega_A$. Each of these levels however is a "METASTABLE" or "QUASI-STATIONARY" state (see LANDAU-LIFSHITZ, "Quantum mechanics", § 134) with FINITE LIFE-TIME $\hbar\Gamma_n^{-1}$ and COMPLEX ENERGY

$$z_n = E_n - i\frac{\Gamma_n}{2}$$

The probability $P(t)$ to find the particle at time t in well A will be

$$P(t) = \sum_n e^{-\beta E_n} \int_{(\text{well } A)} dq\, |\varphi_n(q,t)|^2 , \qquad \beta = \frac{1}{T}$$

so that

$$-\frac{dP}{dt} = -\sum_n e^{-\beta E_n} \int_{(\text{well } A)} dq \left[\varphi_n^* \dot{\varphi}_n + \varphi_n \dot{\varphi}_n^* \right] =$$

$$= \frac{1}{\hbar} \sum_n e^{-\beta E_n} \Gamma_n \int_{(\text{well } A)} dq\, |\varphi_n(q,t)|^2$$

Normalizing to 1 the φ_n's in the well A we obtain for the rate K

$$K = -\frac{1}{P(t)}\frac{dP}{dt} = \frac{1}{\hbar}\frac{\sum_n e^{-\beta E_n}\Gamma_n}{\sum_n e^{-\beta E_n}} \cong$$

$$\cong \frac{1}{\hbar}\left[\Gamma_0 + \sum_{n>0} e^{-\beta(E_n - E_0)} (\Gamma_0 - \Gamma_n) \right]$$

On the other hand, introducing a COMPLEX PARTITION FUNCTION

$$Z = \mathrm{Tr}\, e^{-\beta H} = \sum_n e^{-\beta E_n} e^{i\beta\Gamma_n/2}$$

the corresponding FREE ENERGY will be

$$F = -\frac{1}{\beta} \ln Z \cong E_0 - i\frac{\Gamma_0}{2} + \sum_{n>0} e^{-\beta(E_n - E_0)} \left[1 - i\frac{\beta}{2}(\Gamma_n - \Gamma_0) \right]$$

(We have used $\beta(E_n - E_0) \gg 1$ and

Comparing the expression for K and F we obtain

$$K \cong -\frac{2}{\hbar} I_m F$$

To calculate $F = -\beta^{-1} \ln Z$ ($\to K$ given by the above equation) we write Z as a PATH INTEGRAL (see e.g. FEYNHAN-HIBBS, "QM AND PATH INTEGRALS")

$$Z = \int \mathcal{D}q \; e^{-\frac{1}{\hbar} S[q]}$$

$$[q(0) = q(\beta\hbar)]$$

where $\mathcal{D}q$ denotes functional integration over all "paths" $q = q(\tau)$, where τ is the "imaginary time" variable $0 \le \tau \le \beta\hbar$. $S[q]$ is the EUCLIDEAN ACTION defined as

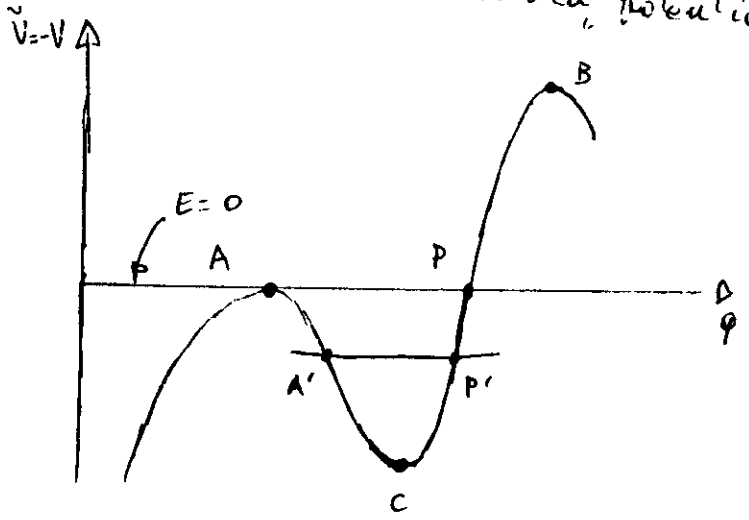
$$S[q] = -\int_0^{\beta\hbar} d\tau \; L[t = -i\tau]$$

where $L(t) = \frac{m}{2}\dot{q}^2 - V(q)$ is the Lagrangian in the usual (i.e. the [illegible]

We can write $S[q]$ in the form

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

which corresponds to the classical action of a "particle" in the "inverted" potential $\tilde{V} = -V$



In the SEMICLASSICAL LIMIT $\frac{S}{\hbar} \to \infty$ the integral for Z is dominated by the STATIONARY POINTS of S, which are the classical "paths". They are subjected to both the conditions

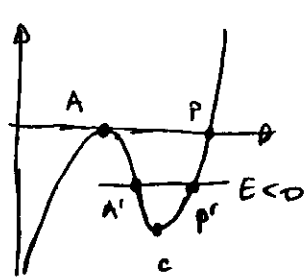
$$q(0) = q(\beta\hbar) \quad ; \quad \dot{q}(0) = \dot{q}(\beta\hbar)$$

Therefore these paths can only be CLOSED "ORBITS".

In absence of the "well" around c the only possible paths would be

$$q = q_A = \text{const}$$

$$q = q_c = \text{const}$$

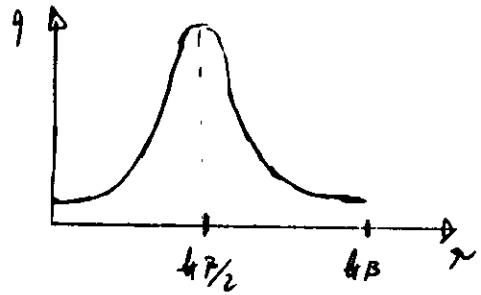


In presence of the minimum at c there is another, non-trivial path, in which the particle starts from A at $\tau = 0$, it rolls the "valley" across c and inverts its motion (it "BOUNCES") at the classical turning point P, finally returning at A. This path is called "BOUNCE" (→ Callan - Coleman PR D16, 1762, 1977).

Such a "bounce" takes an infinite "time" in his trip, and so it satisfies the b.c. $q(0) = q(\beta\hbar)$ only for $\beta \to \infty$.

For finite $\beta\hbar$ the appropriate path is the orbit with turning points A'P', and energy $E < 0$ such that the period $T(E)$ is equal to $\beta\hbar$.

Shape of the BOUNCE:



For "QUADRATIC PLUS CUBIC POTENTIAL"

$$V(q) = a(k^2 q^2 - k^3 q^3)$$

and $\beta\hbar \to \infty$ the BOUNCE has the analytical form:

$$q_B(\tau) = \frac{q_0}{\cosh^2 \frac{\omega_A}{2}(\tau - \hbar\beta/2)} \; ; \; q_0 = q_P - q_A$$

FL

In the "saddle point approximation" the partition function Z will be equal to

$$Z \cong Z_A + Z_{BOUNCE}$$

with

$$Z_A \equiv Z_{OSC} \longleftarrow \text{p.f. of an harmonic oscillator of frequency } \omega_A$$

and

$$Z_{B_{BOUNCE}} = e^{-S_B/\hbar} I_B ,$$

where $S_B = \int_0^{B\hbar} \left[\frac{m}{2} \dot{q}_B^2 + V(q_B) \right] d\tau$

is the action of the BOUNCE, and I_B is the contribution of the fluctuations around the BOUNCE

$$I_B = \int \mathcal{D}y \; e^{-m/2\hbar \int_0^{B\hbar} d\tau \, y(\tau) \mathcal{L}_B y(\tau)}$$

$$[y(0) = y(B\hbar)]$$

where $\mathcal{L}_B$ is the operator associated to the second variation of S_M : $\mathcal{L}_B = -\frac{d^2}{} + \frac{1}{} V''[q_0(\tau)]$

Expanding $y(\tau)$ with respect to the eigenvectors x_n of $\mathcal{L}_B$ we reduce the fluctuations integral I_B to a gaussian form

$$I_B \propto (\det \mathcal{L}_B)^{-1/2}$$

What about the SPECTRUM of $\mathcal{L}_B$?

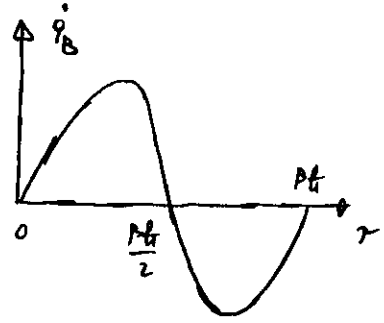
First :

- $\mathcal{L}_B$ has certainly an eigenstate x_1 with eigenvalue zero ("ZERO-MODE"), because

$$\mathcal{L}_B \dot{q}_B(\tau) = 0$$

where $\dot{q}_B$ is the BOUNCE VELOCITY.

Second :



$\dot{q}_B$ HAS A ZERO

x_1 HAS A NODE

THERE IS AN EIGENSTATE x_0 WITH NEGATIVE EIGEN

So, our gaussian integral is not in good shape, because among the factors of $\det \mathcal{L}_B$ one is ZERO and another is NEGATIVE !

What does that mean ?

The ZERO-MODE $\lambda_1 = 0$ means that along the functional "direction" x_1 the action is flat, and we cannot use the SPA : in fact, moving along x_1 simply corresponds to a TIME TRANSLATION of the BOUNCE (the bounce is periodic, so that nothing changes if we change the time origin)
This nuisance can be remedied by the so-called FADDEEV-POPOV technique (for a simpler version see Callan-Coleman paper), which allows to do the x_1-integration separately from the others.

The result is

$$(\det \mathcal{L}_B)^{-1/2} \longrightarrow \left(\frac{W_B}{2\pi\hbar}\right)^{1/2} \beta\hbar \; (\det' \mathcal{L}_B)^{-1/2}$$

where

$$W_B = \oint_{(\text{BOUNCE})} p\, dq = H \oint \dot{q}_B^2 \, d\tau$$

and $\det' \mathcal{L}_B$ means that the zero-eigenvalue is omitted.

The NEGATIVE MODE $\lambda_0 < 0$ means that along the x_0-direction the action has not a minimum, but a maximum, which means that the BOUNCE is a SADDLE POINT of the action.
This is not surprising, because after all we were looking for an imaginary part of Z!

In fact, as shown by Langer, Ann. Phys 54, 258 (1969)

the complex partition function must be interpreted as the analytical continuation of the f.f. for a system with a stable potential ($\lambda_0 > 0$) to that of a system with a metastable one ($\lambda_0 < 0$).

The situation is

$$Z_{BOUNCE} = e^{-S_B/\hbar} I_B$$

NOMINALLY DIVERGENT

ANALYT. CONT FROM $\lambda_0 > 0$

→ see AFFLECK, PRL 46 388 (1981) IMAGINARY QUANTITY

The final result for I_B, obtained by doing properly both the zero-mode integration and the analytical continuation is

$$I_B = \frac{i}{2} \beta \left| \frac{dT}{dE} \right|^{-1/2}_{E=E_B} \left(\frac{\hbar}{2\pi} \right)^{1/2}$$

59

where $T(E)$ is the period of a classical orbit of

On the other hand Z is given by

$$Z \simeq Z_A + Z_{BOUNCE}$$

with

$$Z_A = Z_{OSC} = \left[2 \sinh \left(\beta \hbar \frac{\omega_A}{2} \right) \right]^{-1}$$

We finally obtain for the rate the expression

$$K = -\frac{2}{\hbar} \cdot Im\, F = \frac{2}{\beta\hbar} Im \ln Z \simeq \frac{2}{\beta\hbar} Im \left(\frac{Z_{BOUNCE}}{Z_{OSC}} \right) =$$

$$= \frac{1}{Z_{OSC}} \left| 2\pi\hbar \frac{dT}{dE} \right|^{-1/2}_{E=E_B} e^{-S_B/\hbar}$$

i.e.

$$K = f\, e^{-S_B/\hbar}$$

For the "QUADRATIC PLUS CUBIC POTENTIAL," and for $\beta\hbar \to \infty$ one finds

$$S_B = \frac{36}{5} \frac{V_0}{\omega_0}$$

$$\omega_0 \equiv \omega_A = \omega_C$$

60

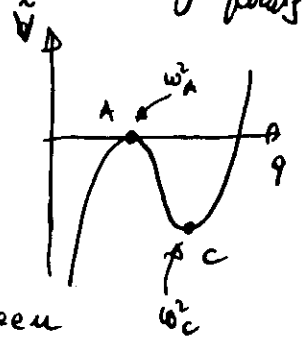
$$f = (\ldots)^{1/2} \ldots$$

2. QUANTUM AND CLASSICAL THERMAL ACTIVATION

The BOUNCE exists only in the low TEMPERATURE REGIME $\beta > \frac{2\pi}{\hbar\omega_c} = \beta_c$ $\left(T < \frac{\hbar\omega_c}{2\pi}\right)$

because for $\beta < \frac{2\pi}{\hbar\omega_c}$ no orbit can satisfy anymore the condition $T(E) = \beta\hbar$.

For $\beta < \beta_c$ only the trivial stationary points $q = q_A$ and $q = q_c$ exist.



Moreover, as shown by LANGER, in this case the relation between the RATE and Im F becomes

$$K = -\frac{\beta}{\beta_c}\frac{2}{\hbar}\,\mathrm{Im}\,F$$

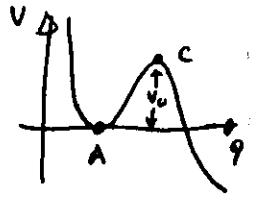
In this case the operator associated to the "curvature" of the action at $q = q_c$ is

$$\mathcal{L}_c = -\frac{\partial^2}{\partial\tau^2} - \omega_c^2$$

It has no ZERO-MODE, but still a negative mode

$$\lambda_0 = -\omega_c^2$$

The result for the rate is



$$K \simeq \frac{\omega_c}{2\pi}\,\frac{\sinh\left(\beta\hbar\omega_A\right)}{\sin\left(\beta\hbar\frac{\omega_c}{2}\right)}\,e^{-\beta V_0} \qquad T > T_c = \frac{\hbar\omega_c}{2\pi}$$

For $T \gg \hbar\omega_A, \hbar\omega_c$ the rate becomes

$$K \underset{\beta\to\infty}{\longrightarrow} \frac{\omega_A}{2\pi}\,e^{-\beta V_0} \equiv K_{ART}$$

THE EFFECT OF FRICTION

Caldeira - Leggett

Annals of Physics

149, 374 (1983)

- We need to consider the interaction between the BP and the heath bath.
- Heath bath of BOSONS (→ 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 → $g_k(q) = g_k e^{ikq}$

Partition function Z:

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

$[q(0) = q(\beta\hbar)]$

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

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

and

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

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

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

LINEAR DISSIPATION

$$S_{eff} \cong \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \int_0^{\beta\hbar} d\tau' \; q(\tau) R(\tau - \tau') q(\tau')$$

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

$$R(\Omega_0) = \frac{1}{\pi} \int_0^{\infty} d\omega \; \frac{j(\omega)}{\omega} \; \frac{\Omega_0^2}{\omega^2 + \Omega_0^2}$$

and where we have introduced the "SPECTRAL DENSITY"

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

Let assume

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

The low frequency behaviour of $R(\Omega_0)$ in this case is

$$R(\Omega_0) \underset{\Omega_0 \to 0}{\sim} \frac{M\eta}{2} |\Omega_0|$$

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 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.

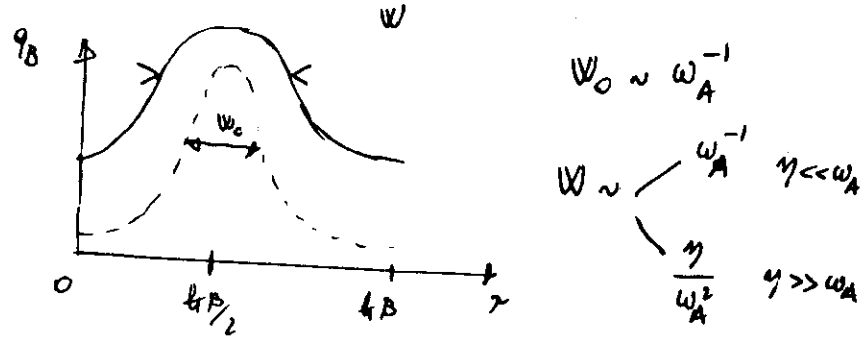
A simple way of verifying this is to calculate the mobility μ of a free BP whose action is S_{eff}, besides the kinetic energy term: the result is

$$\mu(\omega) = \frac{1}{M} \frac{1}{i\omega + \eta}$$ which shows that $\eta \equiv$ FRICTION

The BP total action is

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

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



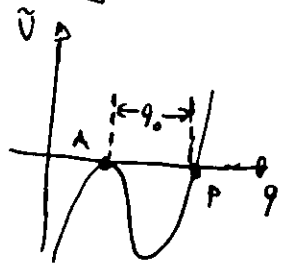
$$W_0 \sim \omega_A^{-1}$$

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

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 $K \simeq f(\eta)\, e^{-S_B(\eta)/\hbar}$

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

FINITE TEMPERATURES

$T \ll T_c$

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

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

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

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

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

THERMAL ENHANCEMENT OF RATE:

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

CROSS-OVER TO THERMAL ACTIVATION

The cross-over temperature, defined as the temperature at which the 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 $\eta \gg \omega_c$: $T_c \sim \frac{\hbar\omega_c^2}{2\pi\eta} = \frac{\omega_c}{\eta} T_c(0)$

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

LARGE FRICTION $\longrightarrow$ CLASSICAL BEHAVIOUR AT LOWER TEMPERATURES

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

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

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