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

SURFACE DIFFUSION

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BASICS ①

Tracer D^*

single particle $\langle \Delta X \rangle = 0$

$$\langle (\Delta X)^2 \rangle \equiv \langle (X(t) - X(0))^2 \rangle = a^2 N$$

N = # steps of length $\underline{a}$ in t (random walk)

In 2 dimensions, since motion along x, y considered independent

$$\langle (\Delta r)^2 \rangle \equiv \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle = a_x^2 N_x + a_y^2 N_y$$

$$= a^2 N_{tot}(t) \quad \text{if } a_x = a_y$$

$$\therefore \langle (\Delta r)^2 \rangle = a^2 \nu_{eff}\, t \quad \text{if } \nu_{eff} t = N(t)$$

we define D^* as

$$\langle (\Delta r)^2 \rangle = 4 D^* t$$

or $\underline{D^* = \frac{1}{4} a^2 \nu_{eff}}$; $\nu_{eff} \sim \nu e^{-E/kT}$

$$\underline{D^* = \frac{1}{4} a^2 \nu e^{-E/kT}}$$

①

The "chemical" D ②

we assume that a diffusion current density $\vec{j}$ = atoms/sec per unit (in length) is given by

(1) $\underline{\vec{j} = -D \nabla_r \rho}$ $\qquad \rho$ = concentration (or density) atoms/cm^2

constitutive equation

we also have from continuity

(2) $\mathrm{div}\, \vec{j} = -\dfrac{\partial \rho}{\partial t}$

or $\vec{\nabla} \cdot \vec{j} = -\dfrac{\partial \rho}{\partial t}$

(1) + (2) $\Rightarrow$

$$\frac{\partial \rho}{\partial t} = D \vec{\nabla} \cdot \vec{\nabla} \rho = D \nabla^2 \rho$$

$$\underline{D \nabla^2 \rho = \frac{\partial \rho}{\partial t}} \qquad \text{"Fick's Law"}$$

②

For anisotropic D ③

$$\begin{pmatrix} D_{xx} & D_{xy} \\ D_{yx} & D_{yy} \end{pmatrix} \begin{pmatrix} \frac{\partial \rho}{\partial x} \\ \frac{\partial \rho}{\partial y} \end{pmatrix} = \begin{pmatrix} J_x \\ J_y \end{pmatrix}$$

$$\vec{J}_x = \vec{\imath}\left(D_{xx} \frac{\partial \rho}{\partial x} + D_{xy} \frac{\partial \rho}{\partial y} \right)$$

$$\vec{J}_y = \vec{\jmath}\left(D_{yy} \frac{\partial \rho}{\partial y} + D_{yx} \frac{\partial \rho}{\partial x} \right)$$

$\Downarrow$

$$\vec{\nabla}\cdot\vec{J} = D_{xx} \frac{\partial^2 \rho}{\partial x^2} + D_{yy} \frac{\partial^2 \rho}{\partial y^2} + 2D_{xy} \frac{\partial^2 \rho}{\partial y \partial x} = \frac{\partial \rho}{\partial t}$$

since $D_{xy} = D_{yx}$ from symmetry

we can always find principal axes which make

$$D = \begin{pmatrix} \bar{D}_{xx} & 0 \\ 0 & \bar{D}_{yy} \end{pmatrix}$$

and then $\underline{\dfrac{\partial \rho}{\partial t} = \bar{D}_{xx} \dfrac{\partial^2 \rho}{\partial x^2} + \bar{D}_{yy} \dfrac{\partial^2 \rho}{\partial y^2}}$

③

D and D* in terms of velocity–velocity correlation functions ①

D^* as we have seen is given by

$$4D^* t = \langle r^2 \rangle \qquad \text{choosing } r(0,0) = 0$$

$$\langle r^2 \rangle = \left\langle \left(\int_0^t v(t')\,dt' \right)^2 \right\rangle$$

$$= \left\langle \int_0^t v(t'')\,dt'' \int_0^t v(t')\,dt' \right\rangle$$

$$= \int dt'\,dt'' \,\langle v(t') v(t'') \rangle$$

$\Downarrow$ (see Reif)

$$2\int_0^t ds\,(t-s)\langle v(0) v(s) \rangle$$

where $s = t' - t''$

as $t \to \infty$

$$D^* = \frac{1}{2}\left(\lim_{t\to\infty} \frac{(t-s)}{t} \int_0^\infty ds\,\langle v(0) v(s) \rangle \right)$$

$$\overset{(4)}{=} \frac{1}{2} \int_0^\infty ds\,\langle v(0) v(s) \rangle$$

or

$$D^* = \frac{1}{2N} \sum_{i=1}^{N} \int v_i(0)\, v_i(t)\, dt$$

Note this involves a single particle velocity-velocity correlation function. This is essentially $\frac{1}{4} a^2 \nu_{eff}$:

If $v(0)$, $v(t)$ are correlated only over $\frac{1}{2}$ effective vibrational period $\frac{1}{\nu_{eff}}$

$$\langle v_i(0)\, v_i(t) \rangle \sim \tfrac{1}{2}(a\,\nu_{eff} \cdot a\,\nu_{eff})$$

$$\text{or } \tfrac{1}{2} a^2 \nu_{eff}^2$$

$$\text{and } \int v\, t = \tfrac{1}{2} a^2 \nu^2 . t = \tfrac{1}{\nu}$$

$$= \tfrac{1}{2} a^2 \nu^2 \, \tfrac{1}{\nu}$$

$$= \tfrac{1}{2} a^2 \nu_{eff}$$

$$\text{or } D^* = \tfrac{1}{4} a^2 \nu_{eff}$$

What is the analogue of $\int dt \langle v_i(0) v_i(t) \rangle$ for $D_{chemical}$? It can be shown starting from

$$S(k,\omega) = 2 k k T \rho^2 \frac{Dk^2}{\omega^2 + (Dk^2)^2}$$

that

$$D = \frac{1}{2kTK\rho^2} \lim_{\omega \to 0} \lim_{k \to 0} \left(\frac{\omega^2}{k^2} S(k,\omega) \right)$$

and from this after a lot of messiness that

$$D = \frac{1}{2kT\rho^2 K \cdot A} \int_0^\infty dt \langle \vec{J}(0)\, \vec{J}(t) \rangle$$

where $\vec{J} = \sum_{i=1}^{N} v_i(t)$

$$\text{i.e. } D = \frac{1}{2A \underbrace{S_0}_{\langle (\delta N)^2 \rangle}} \int_0^\infty \Big\langle \sum_{i=1}^{N} v_i(0) \sum_{j=1}^{N} v_j(t) \Big\rangle dt$$

i.e. D involves cross correlations of velocities

First note that $D \propto \frac{1}{2\langle(\delta N)^2\rangle}$

i.e. $D \propto \frac{1}{\text{compressibility}}$

if the latter diverges at a phase transition $D \to 0$

Also D not simply related to D^*

Write $D = \frac{1}{2\langle(\delta N)^2\rangle}\left(\int_0^\infty dt \sum_i v_i(0) v_i(t) + \int \sum_{i \neq j} v_i(0) v_j(t)\, dt\right)$

Then

$$\frac{D}{D^*} = \frac{1}{\langle(\delta N)^2\rangle}\left[N + \frac{\int_0^\infty \langle \sum_{i\neq j} v_i(0) v_j(t)\rangle dt}{\int_0^\infty \langle v_i(0) v_i(t)\rangle dt}\right]$$

and only if there is no cross correlation ($v_i(0)$ totally independent of $v_j(t)$)

is $\frac{D}{D^*} = \frac{\langle N\rangle}{\langle(\delta N)^2\rangle}$

This last relation can also be written

$$\frac{D}{D^*} = \frac{\partial(\mu/kT)}{\partial \ln p}$$ as we know (or will know)

and is called the Darken Equation

"Jump Rate D"

Empirically (Ehrlich & Reed, Surf. Sci 102, 588 (1981)) have defined

$$D_J = \tfrac{1}{4} a^2 \Gamma(\theta) \langle N\rangle / \langle(\delta N)^2\rangle$$

$$= \tfrac{1}{4} a^2 \Gamma(\theta) \frac{\partial(\mu/kT)}{\partial \ln\theta}$$

obviously this is related to Darken eqn. since it amounts to assuming its validity once ν_{eff} is replaced by a θ dependent jump rate $\Gamma(\theta)$

(4)

Some Results for Lattice Gases (simple)

$$\frac{\langle(\delta N)^2\rangle}{\langle N\rangle} = \frac{1-\theta}{1+2\eta\theta(1-\theta)}$$

θ = fractional coverage $\eta = \varepsilon/RT$

n.n. interaction energy

$\therefore$ for $\theta \sim 0$ or $\theta \sim 1$

(or $\varepsilon = 0$

$$\frac{(\delta N)^2}{\langle N\rangle} = 1-\theta \qquad \text{(also from } \mu\text{)}$$

$$\mu = \mu_0 + RT\ln\theta \quad \text{at (low } \theta\text{)}$$

$$D^* = D^*(\theta=0)\,(1-\theta)$$

$D \neq f(\theta)$ but $D^*(\theta=0) \equiv D^*_0$

The above satisfies Darken eqn. of course

(11)

Miscellaneous Results

Einstein Relation

For charged particles (or assume a charge q for Gedankenexperiments)

Assume an electrical potential gradient $-\nabla V = F$

Then electric current density (flux

$$\vec{J}_F = M\rho F q$$

at equilibrium (or better steady state) this is balanced by diffusion flux

$$\vec{J}_D = -D\,\nabla_x \rho$$

$$\rho(x) = \rho_0\, e^{-Fqx/RT} \quad \text{for any Boltzmann statistics system}$$

$$\therefore \frac{\partial\rho}{\partial x} = \rho(x)\left(-\frac{Fq}{RT}\right)$$

and $\vec{J}_D = -\vec{J}_F \Rightarrow \dfrac{D\rho F q}{RT} = M\rho F q$

$$\boxed{\frac{D}{kT} = M}$$

$\vec{J}_D$ in terms of chem. pot. μ

$$\vec{J}_D = -D \frac{\partial \rho}{\partial x}$$

For ideal component

$$\mu = \mu_0 + kT \ln \rho$$

$$\therefore \vec{J} = -D \frac{\rho}{kT} \nabla_x \mu$$

$$\underline{\underline{= - M \rho \nabla \mu}}$$

we assume this holds generally also for non-ideal systems and also when $\nabla \mu$ include effects on μ, such as electric fields, curvature, etc.

D and Density Correlation Functions

Basic notion is Onsager's hypothesis a spontaneous fluctuation from equilibrium decays by macroscopic laws <u>if</u> we are in long wave length limit (hydro-dynamic regime). Thus

$$\frac{\partial \delta\rho}{\partial t} = D \nabla^2 \delta\rho$$

where $\delta\rho$ is a density fluctuation

$$\delta\rho \equiv \rho(r,t) - \bar{\rho}$$

multiply both sides by $\delta\rho(r=0, t=0) \equiv \delta\rho(0,0)$. Note that this is <u>not</u> a function of r or t

we define $S(r-r', t) = \langle \delta\rho(r',0)\, \delta\rho(r,t) \rangle$

since we assume S depends only on $r-r'$ (being an ensemble average).

NOTE S is just a dynamical structure factor

For perfect crystal ($T = 0°K$)

$$S(r, r' t) = S(r, r'; 0) = S(r - r')$$

$$= \sum e^{i\vec{k}|\vec{r}-\vec{r}'|} = \text{set of delta functions at lattice points}$$

for disordered system

$$\lim_{t\to\infty} S(r - r'; t) = 0$$

$$\lim_{|r-r'|\to\infty} S(r - r'; t) = 0$$

finite, const t

since we then have

$$\langle (\delta\rho(r, 0)\, \delta\rho(r'; t)) \rangle$$

$$= \langle \delta\rho(r, 0) \rangle \langle \delta\rho(r'; t) \rangle$$

$$= 0 . 0$$

we can let $r' = 0$ if we wish

Then

$$\left\langle \delta\rho(0)\, \frac{\partial}{\partial t} \rho(r, t) \right\rangle = \frac{\partial}{\partial t} S(r, t) = D \nabla^2 S$$

since we can move $\delta\rho(0,0)$ to either side of $\frac{\partial}{\partial t}$ or ∇_r^2

Once again

$$\frac{\partial \langle \delta\rho(0,0)\, \delta\rho(r, t) \rangle}{\partial t} = D \nabla_r^2 \langle \delta\rho(0,0)\, \delta\rho(r, t) \rangle$$

1) $$\frac{\partial S(r,t)}{\partial t} = D \nabla^2 S(r, t)$$

Now take F.T. w.r. respect to r by defining

2) $$S(k, t) = \int_{-\infty}^{\infty} d^2 r'\, e^{-ikr'} S(r'; t)$$

3) $$S(r, t) = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} d^2 k'\, e^{ik' r} S(k', t)$$

substitute (3) in (1)

$$\frac{\partial}{\partial t} \int_{-\infty}^{\infty} d^2 k'\, e^{ik' r} S(k', t) = \int d^2 k'\, e^{ik' r} \frac{\partial S(k', t)}{\partial t}$$

$$D\nabla_r^2 \int d^3k'\, e^{ik'r} S(k',t) = -Dk^2 \int d^3k'\, e^{ik'r} S(k',t)$$

$\therefore$ integrands are equal and

$$\frac{\partial S(k,t)}{\partial t} = -k^2 D\, S(k,t)$$

or $$\underline{\underline{S(k,t) = e^{-k^2Dt} S(k, t=0)}}$$

It is also useful to find $S(k,\omega)$ i.e. a structure factor in terms of wave vector $\vec{k}$ and energy ($\hbar\omega = E$) since this is an observable in scattering experiments, the unit $\propto$ differential cross section $\underline{\sigma(\omega,k)}$ where $\underline{\omega = \text{energy transfer}}$

To find $S(k,\omega)$ we must use a trick since we cannot evaluate

$$\int_{-\infty}^{\infty} dt'\, e^{-i\omega t'} S(k,t')$$

directly. Let us find the Laplace transform of $S(k,t)$

$\tilde{S}(k,z)$ where $z = \omega + i\varepsilon$ $\quad \varepsilon = 0^+$

$$\tilde{S}(k,z) = \int_0^{t=\infty} e^{izt'} S(k,t')\,dt'$$

$$= \int_0^{\infty} e^{izt'} e^{-k^2Dt'} S(k,t=0)\,dt'$$

$$= \frac{i}{z+iDk^2} S(k,0)$$

since positive ε leads to $\int = 0$ at $t' = \infty$.

Let us at once assume that $S(k,0)$ can be replaced by $\underset{k\to 0}{S}(k,0) = S(0,0) \equiv S_0$.

So $$\tilde{S}(k,z) = \frac{i\, S_0}{z+iDk^2}$$

Next we define $S(k,\omega)$ by

$$\text{F.T.} \begin{cases} S(k,\omega) = \int_{-\infty}^{\infty} e^{i\omega t} S(k,t')\,dt' \\ S(k,t) = \frac{1}{2\pi}\int d\omega'\, S(k,\omega')\, e^{-i\omega' t} \end{cases}$$

So
$$\tilde S(k, \omega+i\varepsilon) = \int_0^\infty dt\, e^{i(\omega+i\varepsilon)t}\, S(k,t)$$
$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega'\, S(k,\omega') \int_0^\infty dt\, e^{(i\omega-\varepsilon-i\omega')t}$$
$$= \frac{1}{2\pi i}\int_{-\infty}^{\infty} d\omega' \frac{S(k,\omega')}{(\omega'-\omega)-i\varepsilon}$$

Now $\frac{1}{x-i\varepsilon} = \frac{1}{x-i\varepsilon}\cdot\frac{x+i\varepsilon}{x+i\varepsilon} = \frac{x}{x^2+\varepsilon^2} + \frac{i\varepsilon}{x^2+\varepsilon^2}$

$$= P\left(\frac{1}{x}\right) + i\pi\delta(x)$$

($x = \omega'-\omega$ here)

$$\therefore\ \tilde S(k,\omega+i\varepsilon) = \underbrace{\frac12 S(k,\omega)}_{\mathrm{I}} + \underbrace{\frac{1}{2\pi i} P\int \frac{d\omega'\, S(k,\omega')}{\omega'-\omega}}_{\mathrm{II}}$$

$S(k,\omega)$ must be real

$$\therefore\ \tilde S(k,z)+\tilde S(k,z)^* = 2\,\mathrm{Re}\,\tilde S(k,z) = S(k,\omega)$$

since $P\int$ is real and multiplied by $\frac{-i}{2\pi}$
∴ II is pure imaginary

$$\therefore\ S(k,\omega) = 2\,\mathrm{Re}\,\frac{i\,S_0}{z+iDk^2}$$

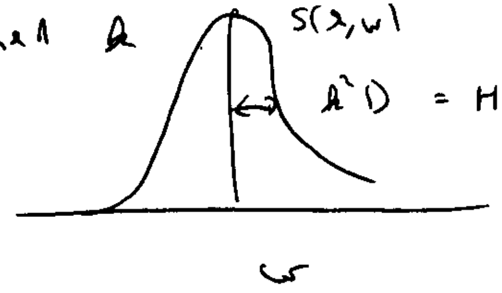
Here z can be set equal to ω since $i\varepsilon$ not important

$$\therefore\ S(k,\omega) = 2S_0\, \frac{k^2 D}{\omega^2+(k^2D)^2}$$

We shall soon see that
$$S_0 = \rho^2 kT K$$
K = compres

so
$$S(k,\omega) = \left(2\rho^2 kTK\right)\frac{k^2D}{\omega^2+(k^2D)^2}$$

Thus D could be found from a scattering expt (for small ω by examining $S(k,\omega)$ as func of ω for fixed k



Note in passing

For incoherent neutron scattering (meaning that spins off which this part of Γ refers to are uncorrelated)

$$\Gamma_s(k,\omega) \Rightarrow \frac{k^2 D^*}{\omega^2 + (k^2 D^*)^2}$$

i.e. faster D^*

Back to space correlations

We had

$$S(x,t) = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} d^2 k' \, e^{ik'x} S(k,t)$$

we now wish to find $f_n(t)$

$$f_n(t) \equiv \langle \delta n(0)\, \delta n(t) \rangle_A \quad (\text{or } \langle \delta N(0)\, \delta N(t) \rangle_A$$

where N or n = # of particles in a probed area A

$$f_n(t) = \langle \int d^2 r \, \delta\rho(r,0) \int d^2 r' \, \delta\rho(r',t) \rangle$$

$$= \int d^2 r \, d^2 r' \langle \delta\rho(r,0)\, \delta\rho(r',t) \rangle$$

$$= \int d^2 r \, d^2 r' \, S(r-r',t)$$

$$= \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} d^2 k' \int_A d^2 r \int_A d^2 r' \, e^{ik' \cdot |r-r'| t} \, e^{-k^2 D t} S_0$$

where we have called $x = r - r'$

The integral over $\vec{k}$ is straightforward and we find

$$f_n(t) = S_0 \int_A d^2 r \int_A d^2 r' \frac{e^{-x^2/4Dt}}{4\pi D t}$$

or

$$f_n(t) = \frac{(\delta N)^2}{A} \int d^2 r \int d^2 r' \frac{e^{-|r-r'|^2/4Dt}}{4\pi D t}$$

This form, $f_n(t)$ is the basis of the field emission fluctuation method. We discuss it in some more detail.

Note first that

$$\rho(r,r';t) = \frac{e^{-|r-r'|^2/4Dt}}{4\pi Dt} = \delta(r-r';t=0)$$

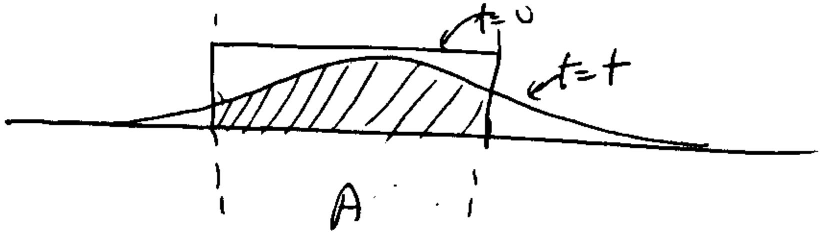
and also that this is a solution of $D\nabla^2\rho = \frac{\partial \rho}{\partial t}$ w. initial condition $\rho = \delta(r-r';t=0)$. Thus $f_n(t)$ has interpretation:

Place δ function at $\vec{r}$, let it evolve in time and measure what is left in A. (This would be correl. function if fluctuation were at $\vec{r}'$) by integrating w. respect to r' over A. But we must <u>average</u> over position of delta function: This is

$$\frac{1}{A}\int d^2 r$$

Finally strength of fluctuation must be properly chosen, so final result is $f_n(t)$ as we have derived it.

Meaning: Use a uniform fluctuation of strength $\langle(\delta n)^2\rangle$ in A, let it evolve in t



integrate over A $\Rightarrow f_n(t)$. Note that $D\nabla^2\rho = \frac{\partial \rho}{\partial t}$ is linear

∴ superposition of solutions ⇒ solution

∴ $\sum \delta(r-r';t) \Rightarrow$ soln

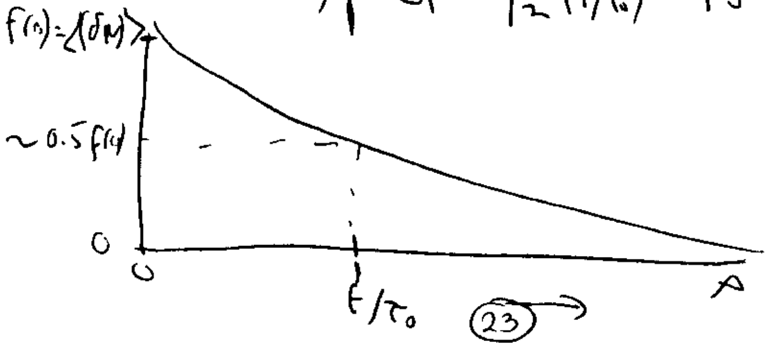
Note that second moment of

$$\rho(r';t) = \frac{e^{-|r-r'|^2/4Dt}}{4\pi D t}$$ centered at r= at t=0

i.e. $$\int_0^\infty r^2 \rho(r;t)\, dr = \langle r^2 \rangle = 4Dt$$

(looks like tracer $D^* = \frac{\langle r^2 \rangle}{4t}$)

Thus we can define a relaxation time $\tau_0 = \frac{r_0}{4D}$ when we look at $f_n(t)$ in a circular region of radius r_0. It is clear that $x = r/r_0$ $x' = r'/r_0$ converts $f_n(t)$ into $f_n(t/\tau_0)$, and we would expect $f_2(t/\tau_0)$ to look like



(23)

Mean Square Fluctuations

Let N = # of particles in region A of open system

$$\langle N \rangle = \frac{\mathrm{Tr}\, e^{-\beta(H-\mu N)} N}{\mathrm{Tr}\, e^{-\beta(H-\mu N)}} = \frac{\mathrm{Tr}\, e^{\alpha N - \beta H} N}{\mathrm{Tr}\, e^{\alpha N - \beta H}}$$

$\beta \equiv \frac{1}{k_B T}$ let $\alpha = \beta\mu$ μ = chem pot

$$\frac{\partial \langle N \rangle}{\partial \alpha} = \frac{\mathrm{Tr}\, e^{\alpha N - \beta H} N^2}{Z} - \frac{\left(\mathrm{Tr}\, e^{\alpha N - \beta H} N\right)^2}{Z^2}$$

$Z \equiv$ part function $\equiv \mathrm{Tr}\, e^{-\beta(H-\mu N)}$

$$\therefore \frac{\partial \langle N \rangle}{\partial \alpha} = \langle N^2 \rangle - \langle N \rangle^2 = \langle (\delta N)^2 \rangle$$

$$\therefore \frac{\partial N}{\partial (\mu/kT)} = \langle (\delta N)^2 \rangle$$

or $$\frac{\langle (\delta N)^2 \rangle}{\langle N \rangle} = \frac{1}{\langle N \rangle} \frac{\partial N}{\partial \mu/kT}$$

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so $\dfrac{(\delta N)^2}{\langle N\rangle} = \left[\dfrac{\partial\mu/kT}{\partial \ln N}\right]^{-1}$

since $\rho = \dfrac{N}{A}$ $\quad d\ln\rho = d\ln N$
$\quad d\ln\theta = d\ln N$

A constant

$$\frac{(\delta N)^2}{\langle N\rangle} = \left[\frac{\partial\mu/(kT)}{\partial\ln\rho}\right]^{-1} \sim \left[\frac{\partial\mu/kT}{\partial\ln\theta}\right]^{-1}$$

Relations between $(\delta N)^2$, compressibility

and $\underset{k\to 0}{S}(k,0)$

we saw that

$$\langle(\delta N)^2\rangle = \frac{\partial\langle N\rangle}{\partial\alpha}$$

Also $\langle N\rangle = \dfrac{\partial\ln Z}{\partial\alpha}$

since $Z = \mathrm{Tr}\, e^{-\beta H+\alpha N}$

$$\frac{\partial Z}{\partial\alpha} = \mathrm{Tr}\left(N e^{-\beta H+\alpha N}\right)$$

and $\langle N\rangle = \dfrac{\partial\ln Z}{\partial\alpha}$ (25) follows from def.

③

$\therefore d\langle N\rangle$

$$\therefore \langle(\delta N)^2\rangle = \frac{\partial\langle N\rangle}{\partial\alpha} = \frac{\partial^2 Z}{\partial\alpha^2}$$

Also

$\beta^{-1}\ln Z = P_{\cdot}A$ (in 2 dimensi

$$\therefore \beta^{-2}\left(\frac{\partial^2\ln Z}{\partial\mu^2}\right)_{A,T} \equiv \langle(\delta N)^2\rangle$$

$$= \beta^{-1}\frac{\partial^2 P}{\partial\mu^2}A$$

$$\therefore \langle(\delta N)^2\rangle = \beta^{-1}\left(\frac{\partial^2 P}{\partial\mu^2}\right)_{A,T}$$

$$d\mu = \left(\frac{\partial\mu}{\partial P}\right)_T dP + \left(\frac{\partial\mu}{\partial T}\right)_P dT$$

$$= \frac{A}{N}\,dP - \frac{S}{N}\,dT$$

$$\therefore \left(\frac{\partial P}{\partial\mu}\right)_T = \frac{N}{A}$$

$$\frac{\partial^2 p}{\partial \mu^2} = \frac{\partial (N/A)}{\partial \mu} = \frac{\partial (N/A)}{\partial p}\frac{\partial p}{\partial \mu}$$

$$= \frac{\partial (A/N)}{\partial (N/A)}\frac{\partial (A/N)}{\partial p}\frac{\partial p}{\partial \mu}$$

$$= -\left(\frac{N}{A}\right)^2 \frac{N}{A}\frac{1}{N}\frac{\partial A}{\partial p}$$

$$= +\left(\frac{N^2}{A}\right) - \frac{1}{A}\frac{\partial A}{\partial p}$$

$$-\frac{1}{A}\left(\frac{\partial A}{\partial p}\right)_T \equiv K_T \quad \text{isothermal compressibility}$$

$$\therefore \frac{\partial^2 p}{\partial \mu^2} = \frac{N^2}{A} K$$

and $\langle(\delta N)^2\rangle = \beta^{-1}\frac{N^2}{A}K$

or $\dfrac{\langle(\delta N)^2\rangle}{N} = kT\left(\dfrac{N}{A}\right)K$

$\langle(\delta N)^2\rangle$ and $S_{k\to 0}(k,0)$

Note first that

$$\langle(\delta N)^2\rangle = \left\langle\left(\int(\rho(r,0)-\bar\rho)\,d^2r\right)^2\right\rangle$$

$$= \left\langle\left(\int d^2r\,\delta\rho(r,0)\right)^2\right\rangle$$

$$= \left\langle\int d^2r\,\delta\rho(r,0)\int d^2r'\,\delta\rho(r',0)\right\rangle$$

$$= \int d^2r\int d^2r'\,\langle\delta\rho(r,0)\,\delta\rho(r',0)\rangle$$

By definition

$$S(r,r',0) = \langle\delta\rho(r,0)\,\delta\rho(r',0)\rangle$$

also S depends only on $r-r'$

$$\therefore S(r-r',0) = \langle\delta\rho(r,0)\,\delta\rho(r',0)\rangle$$

and $\langle(\delta N)^2\rangle = \int d^2r\,d^2r'\,S(r-r',0)$

Introduce $\frac{1}{2}(r+r') = R$

$r - r' = x$

$$\langle(\delta N)^2\rangle = \int_A d^2R \int_A d^2x\; S(x,0)$$

$$= A \int_A d^2x\; S(x,0)$$

we also have

$$S(x,t) = \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} d^2k\; e^{ik\cdot x}\, S(k,t)$$

$$S(k,t) = \int_{-\infty}^{\infty} d^2x\; e^{-ikx}\, S(x,t)$$

$$\therefore \lim_{k\to 0} S(k,0) = \lim_{k\to 0}\int_{-\infty}^{\infty} d^2x\; e^{-ikx}\, S(x,0)$$

$$= \int_{-\infty}^{\infty} d^2x\; S(x,0)$$

$$= \frac{\langle(\delta N)^2\rangle}{A}$$

$$\therefore \frac{(\delta N)^2}{A} = \frac{N}{A}\,\frac{N}{A}\,kT\,K_T = S(0,0)$$

$$S(0,0) = \left(\frac{N}{A}\right)^2 kT\,K_T$$

$$\frac{A.S(0,0)}{N} = \frac{\langle(\delta N)^2\rangle}{N}$$

$$A.S(0,0) = \left(\frac{\partial \mu/kT}{\partial \ln N}\right)^{-1}$$

$$A.S(0,0) = \langle(\delta N)^2\rangle$$

equivalent forms

Summary of Important Relations

D^* (trace D) $= \dfrac{\langle r^2\rangle}{4t} \approx \frac{1}{4} a^2 \nu e^{-E/kT}$

$$= \frac{1}{2}\int_0^\infty dt \langle v_i(0) v_i(t)\rangle$$

D defined by $\vec{J} = -D \,\mathrm{grad}\,\rho$ (ρ = density)

$$D = \frac{1}{2kT\rho^2 K A}\int_0^\infty \Big\langle \sum_{i=1}^N v_i(0) \sum_{j=1}^N v_j(t)\Big\rangle dt$$

D sometimes written $D_0 e^{-E/kT}$

D_0, E have no simple meanings in interacting systems except as $\theta \to 0$

$$\frac{D}{D^*} \longrightarrow \frac{\langle N\rangle}{\langle(\delta N)^2\rangle} \quad \text{(Darken eqn.)}$$

$$\frac{D}{kT} = M \qquad M = \text{mobility}$$

$$S(r-r';t) \equiv \langle \delta\rho(r,0)\,\delta\rho(r';t)\rangle$$

$$= \left(\frac{1}{2\pi}\right)^2 \int_{-\infty}^{\infty} d^2k\, e^{i\vec{k}\cdot|r-r'|}\, S(k,t)$$

$$S(k,t) = e^{-k^2 Dt}\, S(k,t=0)$$

$$\lim_{k\to 0} S(k,0) \equiv S_0 = \langle(\delta N)^2\rangle / A$$

$$\frac{\langle(\delta N)^2\rangle}{\langle N\rangle} = \rho kT K \qquad K = -\frac{1}{A}\left(\frac{\partial A}{\partial \rho_2}\right)_T = \text{compressibility}$$

$$\frac{\langle(\delta N)^2\rangle}{N} = \left[\frac{\partial(\mu/kT)}{\partial \ln N}\right]^{-1} \qquad \mu = \text{chem. pot.}$$

$$S(k,\omega) \cong 2 S_0 \frac{k^2 D}{\omega^2 + (k^2 D)^2}$$

$$f_n(t) = \frac{\langle\delta N\rangle^2}{A}\int d^2r \int d^2r'\, S(r-r';t)$$

$$= \frac{\langle(\delta N)^2\rangle}{A}\int d^2r \int d^2r'\, \frac{e^{-|r-r'|^2/4Dt}}{4\pi Dt}$$

References for Diffusion

Theory General

D. Forster, Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions, Benjamin, Cummings, Reading, Mass. (1975).

G. Mazenko in Surface Mobilities on Solid Materials, Vu Thien Binh, ed. Plenum Press, New York (1983).

F. Reif, Fundamentals of Statistical and Thermal Physics, McGraw Hill, New York (1965).

FIM Work (summary)

D.W. Bassett in Surface Mobilities on Solid Materials, Vu Thien Binh, ed. Plenum Press, New York (1983) and references therein.
G. Ehrlich and K. Stolt, Ann. Rev. Phys. Chem. 31, 603 (1980).

Field Emission (Shadowing and Fluctuation)

R. Gomer in Surface Mobilities on Solid Materials, Vu Thien Binh, ed. Plenum Press, New York (1983), see also detailed Fluctuation List.

LID

S.M. George in Diffusion at Interfaces, Springer, New York, Heidelberg (1988).

E.G. Seebauer, A.C.T. Kong, L.D. Schmidt, J. Chem. Phys. 88, 6597 (1988) and references therein.

Profiles from Work Function Changes

R. Butz and H. Wagner, Surf. Sci. 63, 448 (1977).

Yu. S. Vedula, A.T. Loburets, and A.G. Naumovets, Sov. JETP 50, 391 (1979).

Simulations

S.M. Valone, A.F. Voter, and J.D. Doll, Surf. Sci. 155, 687 (1985).

X.-P. Jiang and H. Metiu, J. Chem. Phys. 88, 1891 (1988).

M. Tringides and R. Gomer, Surf. Sci. 145, 121 (1984).

M. Tringides and R. Gomer, Surf. Sci. 166, 419 (1986).

M. Tringides and R. Gomer, Surf. Sci. 166, 440 (1986).

STM, Possible Application to Diffusion

R. Gomer, App. Phys. A39, 1 (1986).

Fluctuation Method

R. Gomer, Surf. Sci. 38, 373 (1973). [Elementary Theory]

B. Bell, R. Gomer, and H. Reiss, Surf. Sci. 55, 494 (1976). [Mean Square Fluctuations]

J.-R. Chen and R. Gomer, Surf. Sci. 79, 413 (1979). [O/W(110)]

J.-R Chen and R. Gomer, Surf. Sci. 81, 589 (1979). [CO/W(110)]

J.-R. Chen and R. Gomer, Surf. Sci. 94, 456 (1980). [Xe/W(110)]

J.R. Banavar and R. Gomer, Surf. Sci. 97, L345 (1980). [boundary conditions]

G. Mazenko, J.R. Banavar and R. Gomer, Surf. Sci. 107, 459 (1981). [theory, rigorous]

R. DiFoggio and R. Gomer, Phys. Rev. B25, 3490 (1982). [^{1}H, ^{2}H/W(110)]

D.R. Bowman, R. Gomer, K. Muttalib and M. Tringides, Surf. Sci. 138, 581 (1984). [anisotropy, theory]

S.C. Wang and R. Gomer, Surf. Sci. Lett. 141, L304 (1984). [^{1}H diff. into W(110)]

C. Dharmadhikari and R. Gomer, Surf. Sci. 143, 223 (1984). [^{1}H, ^{2}H/W(111)]

M. Tringides and R. Gomer, Surf. Sci. 155, 254 (1985). [^{1}H, ^{2}H, O/W(110) anisotropy]

S.C. Wang and R. Gomer, J. Chem. Phys. 83, 4193 (1985). [^{1}H, ^{2}H, ^{3}H/W(110)]

M. Tringides and R. Gomer, J. Chem. Phys. 84, 4049 (1986). [O, W/W(211) anisotropy]

R. Gomer and A. Auerbach, Surf. Sci. 167, 493 (1986). [effect of resolution]