



# *Condensed Matter Physics*

## *Diffusion*

*István Groma*

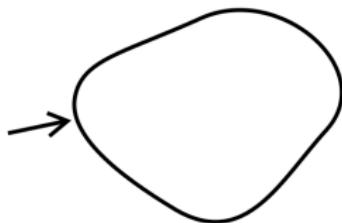
*ELTE*

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## Standard diffusion

Conservation of mass



$$\frac{\partial c}{\partial t} + \operatorname{div} \vec{j} = 0 \quad \vec{j} = c \cdot \vec{v}$$

Fick II.

$$\vec{j} = -D \nabla c$$

Gives

$$\frac{\partial c}{\partial t} - \operatorname{div}(D(c) \nabla c) = 0$$

We take

$$\boxed{\frac{\partial c}{\partial t} - D \Delta c = 0}$$



## Periodic perturbation

1D problem

$$\frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial x^2} = 0$$

Let us take

$$c(x, t) = A(t) \sin(kx)$$

after substituting

$$\dot{A}(t) \sin(kx) + Dk^2 A(t) \sin(kx) = 0$$

gives

$$\dot{A}(t) = -Dk^2 A(t)$$

The solution is

$$\Rightarrow A(t) = A_0 e^{-Dk^2 t}$$

Any perturbation dies out!

## Functional derivative

$$F[c + \delta c] = F[c] + \int \frac{\delta F}{\delta c} \delta c dV$$

If

$$F = \int f(c) dr^3$$

then

$$F[c + \delta c] - F[c] = \int \left. \frac{df}{dc} \right|_c \delta c dr^3$$

leading to

$$\frac{\delta F}{\delta c} = \frac{df}{dc}$$

If

$$\int \frac{1}{2} (\nabla c)^2 dr^3$$

$$\int \left\{ \frac{1}{2} (\nabla(c + \delta c))^2 - \frac{1}{2} (\nabla c)^2 \right\} dr^3 = \int \{ \nabla c \nabla \delta c \} dr^3 + \frac{1}{2} (\nabla \delta c)^2 \approx \int \nabla c \nabla \delta c dr^3$$



## Functional derivative

We have  $\nabla \delta c$   
with partial integration

$$\int \nabla c \nabla \delta c dr^3 = - \int \nabla(\nabla c) \delta c dr^3 + \oint (\nabla c \delta c) dA$$

We do not vary on the surface, so

$$\frac{\delta F}{\delta c} = -\nabla(\nabla c) = -\Delta c$$



## Generalized diffusion

### Thermodynamics

$$\vec{j} = -M \text{grad} \mu$$

For the simple case

$$G = \int g(c) d^3r$$

Since

$$\frac{\delta G}{\delta c} = \frac{dg}{dc} = \mu$$

We conclude

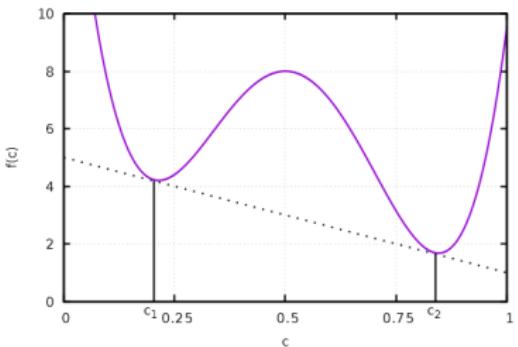
$$\frac{\partial c}{\partial t} - \text{div} M(c) \text{grad} \frac{\delta G}{\delta c} = 0$$

If

$$g_0(c) = \frac{\alpha}{2}(c - c_0)^2$$

we get beck Fick II.

## Spinodal decomposition



In a range the second derivative

$$D = M \frac{d\mu}{dc} = M \frac{d^2 g_0}{dc^2}$$

is negative, i.e. perturbations blow up!

Surface tension!

Energy of a precipitation

$$E = \frac{4\pi}{3} r^3 \varepsilon_0 + 4\pi r^2 \alpha \quad (1)$$

where  $\varepsilon_0$  and  $\alpha$  have different dimension

## Spinodal decomposition

$$\frac{\alpha}{\varepsilon_0} = I \quad \left[ \frac{\alpha}{\varepsilon_0} \right] = m$$

with a characteristic length  $I$ .

Chan and Hilliard suggested the form

$$G = \int \left( g_0(c) + \frac{\beta}{2}(\nabla c)^2 \right) d^3r$$

leading to

$$\boxed{\frac{\partial c}{\partial t} - M\Delta \left( \frac{dg_0}{dc} \right) + M\beta\Delta^2 c = 0}$$

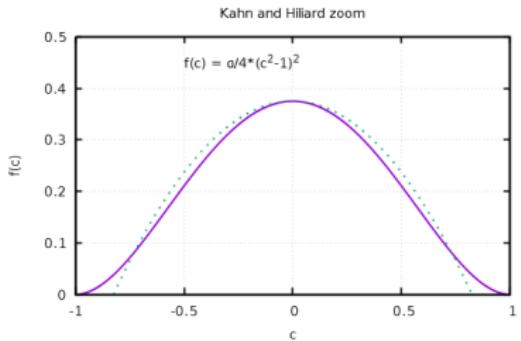
They used

$$f(c) = \frac{\alpha}{4}(c^2 - 1)^2$$

i.e.

$$G = \iiint \left[ \frac{A}{2}(c^2 - 1)^2 + \frac{\beta}{A}(\nabla c)^2 \right] dr^3$$

# Spinodal decomposition



$$\frac{\partial c}{\partial t} + \operatorname{div} \vec{j} = 0 \quad \vec{j} = -M \nabla \frac{\delta G}{\delta c}$$

$$\frac{\delta G}{\delta c} = 2a(c^2 - 1)c - \beta \Delta c$$

$$\frac{\partial c}{\partial t} - \Delta \{2aM(c^2 - 1)c\} + M\beta\Delta^2 c = 0$$



## Spinodal decomposition

Close to the maximum of  $g_0(c)$

$$\frac{\partial c}{\partial t} + 2aM\Delta c + M\beta\Delta^2 c = 0$$

Again

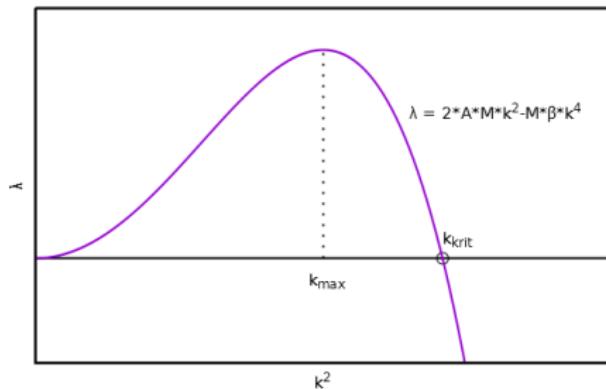
$$c(x, t) = A(t) \sin(kx)$$

After substituting it

$$\dot{A} \sin(kx) - 2AMk^2\Theta(t) \sin(kx) + M\beta k^4 A(t) \sin(kx) = 0$$

$$\dot{A} = \underbrace{(2AMk^2 - M\beta k^4)}_{:=\lambda} A(t)$$

## Spinodal decomposition



$$A(t) = A_0 e^{\lambda t}$$

So

$$c(x, t) = A_0 e^{\lambda t} \sin(kx)$$

Maximum growing rate is at  $k_{\max}$ . We have a length scale selection