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room 316, New Horizons

Gaussian chain, "blobs", excluded-volume problem ($\to$ lectures of 2011)

Electrostatics in Soft Matter

1. Maxwell equations and basics electrostatics

System of point charges in vacuum

particle # i, valency z_i, elementary charge e (>0)

$\rightarrow$ particle charge $z_i e$, position $\vec{r}_i$

microscopic expression for charge density

$$\rho(\vec{r}) = \sum_i z_i e \, \delta(\vec{r} - \vec{r}_i),$$ for concentration

of ionic species a: $c_a(\vec{r}) = \sum_{i \in a} \delta(\vec{r} - \vec{r}_i)$

Current density:

$$\vec{j}(\vec{r}) = \sum_i z_i e \, \dot{\vec{r}}_i \, \delta(\vec{r} - \vec{r}_i)$$

$$\Rightarrow \frac{\partial}{\partial t} \rho(\vec{r}) = \frac{\partial}{\partial t} \sum_i z_i e \, \delta(\vec{r} - \vec{r}_i) =$$

$$= \sum_i z_i e \left[- \frac{\partial}{\partial \vec{r}} \delta(\vec{r} - \vec{r}_i) \right] \dot{\vec{r}}_i = - \frac{\partial}{\partial \vec{r}} \cdot \vec{j}$$

$$\Rightarrow \boxed{\frac{\partial}{\partial t} \rho + \vec{\nabla} \cdot \vec{j} = 0}$$

Continuity eq.
(conservation of charge)

electric field $\vec{E}$, magnetic field $\vec{H}$

ε_0 : dielectric const. of vacuum

c : speed of light

Lorentz force on a particle:

$$\vec{F}_L = e z_i \left[\vec{E} + \frac{1}{\varepsilon_0 c^2} \dot{\vec{r}}_i \times \vec{H} \right]$$

Maxwell equations:

$$\vec{\nabla}\cdot\vec{E} = \frac{1}{\varepsilon_0}\rho \qquad \vec{\nabla}\times\vec{E} = -\frac{1}{\varepsilon_0 c^2}\frac{\partial}{\partial t}\vec{H}$$

$$\vec{\nabla}\cdot\vec{H} = 0 \qquad \vec{\nabla}\times\vec{H} = \vec{j} + \varepsilon_0\frac{\partial}{\partial t}\vec{E}$$

Soft-matter systems: $\dot{\vec{r}}_i \ll c$

$\Updownarrow$ quasi-static approximation $\boxed{c \to \infty}$

magnetic field decouples

$$\vec{F}_L = z_i e \vec{E} \quad , \quad \vec{\nabla} \cdot \vec{E} = \frac{1}{\varepsilon_0} \rho \quad , \quad \vec{\nabla} \times \vec{E} = 0$$

$\Rightarrow$ exists a potential ϕ : $\quad \vec{E} = -\vec{\nabla} \phi$

$$\leadsto \vec{\nabla} \times \vec{E} = - \vec{\nabla} \times \vec{\nabla} \phi = 0$$

$\Rightarrow$ Poisson equation : $\boxed{\boxed{-\vec{\nabla}^2 \phi = \frac{1}{\varepsilon_0} \rho}}$

Consider a charge density localized in space, or decays quickly, as $r \to \infty$

$\phi(\vec{r}) \to 0$ for $r \to \infty$ normalization of ϕ

Green's function : <u>Ansatz</u>

$$\phi(\vec{r}) = \frac{1}{\varepsilon_0} \int d^3\vec{r}\,' \, G(\vec{r}-\vec{r}\,') \, \rho(\vec{r}\,')$$

Green's function

translational invariance

$$\frac{1}{\varepsilon_0}\rho(\vec{r}) = -\vec{\nabla}_r^2 \phi(\vec{r}) = \frac{1}{\varepsilon_0}\int d^3\vec{r}\,' \rho(\vec{r}\,')\left[-\vec{\nabla}_r^2 G(\vec{r}-\vec{r}\,')\right]$$

$$\overset{!}{=} \frac{1}{\varepsilon_0} \int d^3\vec{r}\,' \, \delta(\vec{r}-\vec{r}\,') \rho(\vec{r}\,')$$

$$\Rightarrow -\vec{\nabla}_r^2 G(\vec{r}-\vec{r}\,') = \delta(\vec{r}-\vec{r}\,')$$

$$\Rightarrow \boxed{-\vec{\nabla}^2 G(\vec{r}) = \delta(\vec{r})}$$

$\kappa > 0$

generalize to $\left[-\vec{\nabla}^2 + \kappa^2\right] G(\vec{r}) = \delta(\vec{r})$

(Coulomb case recovered for $\kappa = 0$). Fourier transform

$$G(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3\vec{k}\, \tilde{G}(\vec{k}) \exp[i\vec{k}\cdot\vec{r}]$$

$$\delta(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3\vec{k} \exp[i\vec{k}\cdot\vec{r}]$$

$$-\vec{\nabla}^2 G(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3k \; \tilde{G}(\vec{k}) \; \vec{k}^2 e^{i\vec{k}\vec{r}}$$

$$\rightsquigarrow \left[\vec{k}^2 + \kappa^2\right] \tilde{G}(\vec{k}) = 1 \qquad \tilde{G}(\vec{k}) = \frac{1}{k^2 + \kappa^2}$$

$$G(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3\vec{k} \; \frac{1}{k^2+\kappa^2} \; \exp(i\vec{k}\cdot\vec{r})$$

coordinate system in $\vec{k}$-space: $\hat{e}_z \propto \vec{r}$

spherical coordin. " " k, θ, φ

$$G(\vec{r}) = \frac{1}{(2\pi)^3} \int_0^\infty dk\, k^2 \int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\varphi\, \frac{1}{k^2+\kappa^2} \exp[ikr\cos\theta]$$

$$\int_{-1}^{1} du\, e^{ikru} = \frac{e^{ikru}}{ikr}\Bigg|_{u=-1}^{u=1} = \frac{e^{ikr} - e^{-ikr}}{ikr} =$$

$$= \frac{2i\sin(kr)}{ikr} = 2\,\frac{\sin(kr)}{kr}$$

$kr = x$

$$G(\vec{r}) = \frac{1}{2\pi^2} \int_0^\infty dk\, k^2 \frac{1}{k^2+\kappa^2} \frac{\sin(kr)}{kr} = \text{Wolfram Alpha}$$

$$= \frac{1}{2\pi^2 r} \int_0^\infty dx\, \frac{x^2}{x^2 + (\kappa r)^2} \frac{\sin x}{x} = \frac{1}{2\pi^2 r} \frac{\pi}{2} e^{-\kappa r}$$

$\leadsto G(r) = \frac{1}{4\pi r} e^{-\kappa r}$ Yukawa potential

Coulomb limit: $\kappa \to 0$

$G(r) = \frac{1}{4\pi r}$ Coulomb potential

$\leadsto \rho(\vec{r})$ generates the potential

$$\boxed{\phi(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \int d^3\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}}$$

$$-\frac{\partial}{\partial x}\left(\frac{1}{r}\right) = -\frac{\partial}{\partial x}\left(x^2+y^2+z^2\right)^{-1/2} = +\frac{1}{2}\left(x^2+y^2+z^2\right)^{-3/2} 2x$$

$$r = \left(x^2+y^2+z^2\right)^{1/2} \qquad\qquad = x \cdot \frac{1}{r^3}$$

$$-\vec{\nabla}\left(\frac{1}{r}\right) = \frac{\vec{r}}{r^3} = \frac{\hat{r}}{r^2} \qquad \hat{r} = \frac{\vec{r}}{r} \quad \text{unit vector}$$

$$\boxed{\vec{E}(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\int d^3\vec{r}\,' \,\frac{\rho(\vec{r}\,')\left(\vec{r}-\vec{r}\,'\right)}{\left|\vec{r}-\vec{r}\,'\right|^3}}$$

go back to the particle picture

$$\rho(\vec{r}) = \sum_j z_j e \, \delta(\vec{r}-\vec{r}_j)$$

$$\Rightarrow E(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \sum_j z_j e \frac{\vec{r}-\vec{r}_j}{|\vec{r}-\vec{r}_j|^3}$$

at the position of a charge i

$$\vec{E}(\vec{r}_i) = \frac{1}{4\pi\varepsilon_0} \sum_{j(\neq i)} z_j e \frac{\vec{r}_i-\vec{r}_j}{|\vec{r}_i-\vec{r}_j|^3}$$

remove unphysical self-interaction!

force on particle i

$$\vec{F}_i = \frac{1}{4\pi\varepsilon_0} \sum_{j(\neq i)} z_i z_j e^2 \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^3} =$$

$$= \frac{1}{4\pi\varepsilon_0} \sum_{j(\neq i)} z_i z_j e^2 \left(-\vec{\nabla}_i\right) \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

define $u_{ij} := \dfrac{z_i z_j}{4\pi\varepsilon_0} \dfrac{e^2}{|\vec{r}_i - \vec{r}_j|}$ $\Rightarrow$ $\vec{F}_i = -\vec{\nabla}_i \left[\sum_{j(\neq i)} u_{ij}\right]$

Ansatz: $U = \sum_{k<l} u_{kl}$ each pair only once

$$-\vec{\nabla}_i U = -\sum_{k<l} \vec{\nabla}_i u_{kl} = -\sum_{l(>i)} \vec{\nabla}_i u_{il} - \sum_{k(<i)} \vec{\nabla}_i u_{ki}$$

$$= -\sum_{j(\neq i)} \vec{\nabla}_i u_{ij} \quad \text{OK} \quad \Leftrightarrow \quad \boxed{\vec{F}_i = -\vec{\nabla}_i U}$$

alternative:

$$\boxed{U = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \sum_{i\neq j} \frac{z_i z_j}{|\vec{r}_i - \vec{r}_j|}}$$ electrostatic energy

continuum:

$$\boxed{U = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\int d^3\vec{r}\int d^3\vec{r}\,'\,\frac{\rho(\vec{r})\,\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}}$$

$$\phi(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\int d^3\vec{r}\,'\,\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

furthermore:

$$\rho(\vec{r}) = \varepsilon_0\,\vec{\nabla}\cdot\vec{E}$$

$$\leadsto \boxed{U = \frac{1}{2}\int d^3\vec{r}\,\rho(\vec{r})\,\phi(\vec{r})}$$

$$\Rightarrow \; U = \frac{1}{2} \int d^3\vec{r} \left(\varepsilon_0 \vec{\nabla} \cdot \vec{E} \right) \phi(\vec{r}) =$$

partial integration

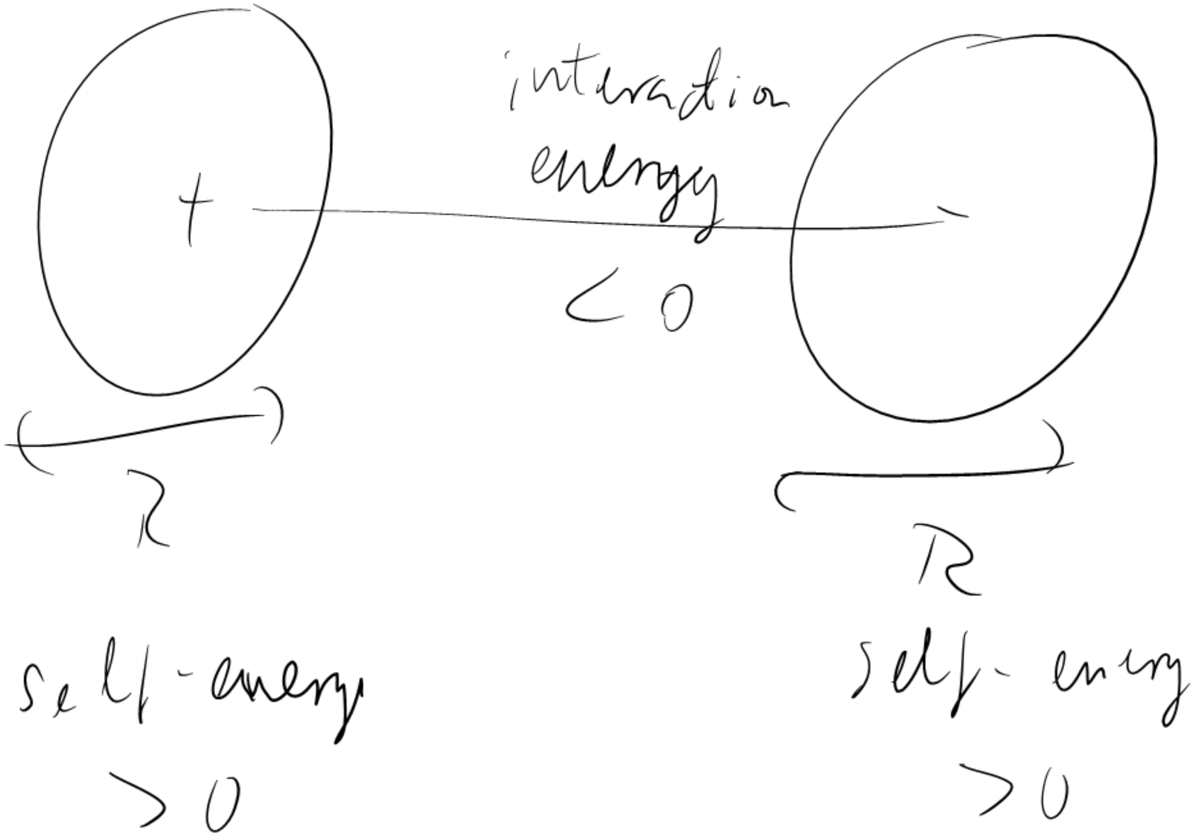
$$= -\frac{1}{2} \int d^3 r \; \varepsilon_0 \vec{E} \left(\vec{\nabla} \phi \right) =$$

$$= \boxed{+\frac{\varepsilon_0}{2} \int d^3 r \; \vec{E}^2 = U}$$

$$\boxed{U \geq 0}$$

What about

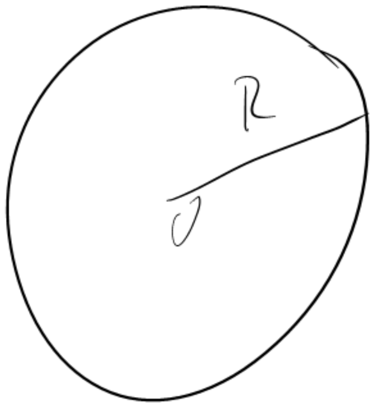
expect
$U < 0$
(binding energy)



From now on: electrostatics in matter:

$\varepsilon_0 \to \varepsilon$

2. Charged droplets



ball, charge Q, radius R

charge density $\rho = \dfrac{Q}{\frac{4\pi}{3} R^3}$

$U = ??$

$$-\vec{\nabla}^2 \phi = \frac{1}{\varepsilon} \rho = \text{const.} \qquad \phi = \phi(r)$$

$$\vec{\nabla}^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \text{angle-dependent terms}$$

$$\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \phi = -\frac{1}{\varepsilon} \rho r^2 \Rightarrow r^2 \frac{\partial}{\partial r} \phi = -\frac{1}{\varepsilon} \rho \frac{r^3}{3} + A$$

$$\frac{\partial}{\partial r} \phi = -\frac{1}{\varepsilon} \rho \frac{r}{3} + \frac{A}{r^2}$$

at $r = 0$;

ϕ regular, $\frac{\partial}{\partial r} \phi$ regular

$\Rightarrow A = 0$

$$\boxed{\phi = -\frac{1}{\varepsilon} \rho \frac{r^2}{6} + B}$$

$$\boxed{-\frac{1}{\varepsilon} \rho \frac{R^2}{6} + B \overset{!}{=} \frac{Q}{4\pi \varepsilon R}}$$