

§ 4 拉普拉斯方程 分离变量法

$$\nabla^2 \varphi = 0$$

1、此类边值问题的特点：

- ① 区域内不出现自由电荷；
- ② 区域内的电势满足方程：

$$\nabla^2 \varphi = 0$$

——方程称为拉普拉斯（Laplace）方程

$$\nabla^2 \varphi = 0$$

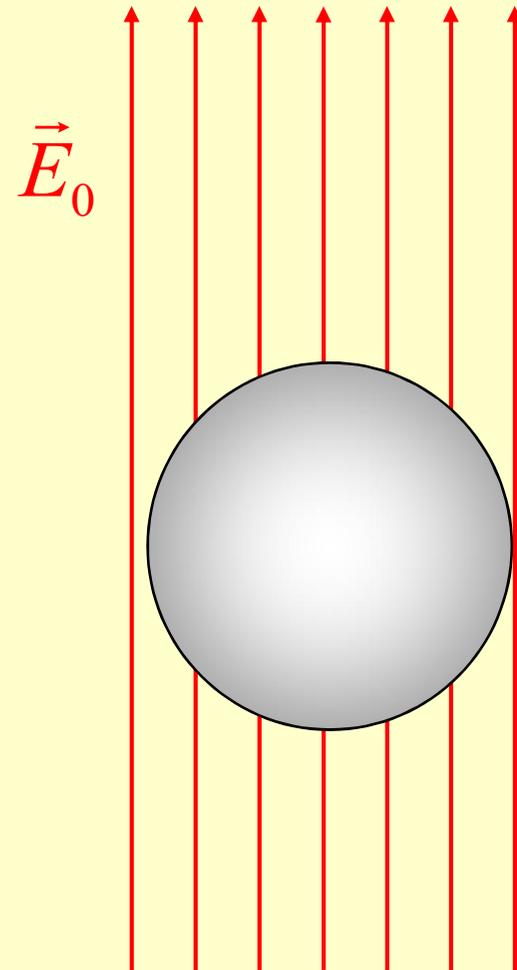
2、求解方法：分离变量法

- ① 求满足特定边界条件的拉普拉斯方程的解。
- ② 区域边界上的电荷将通过边界条件反映出来。

一、球形边值问题

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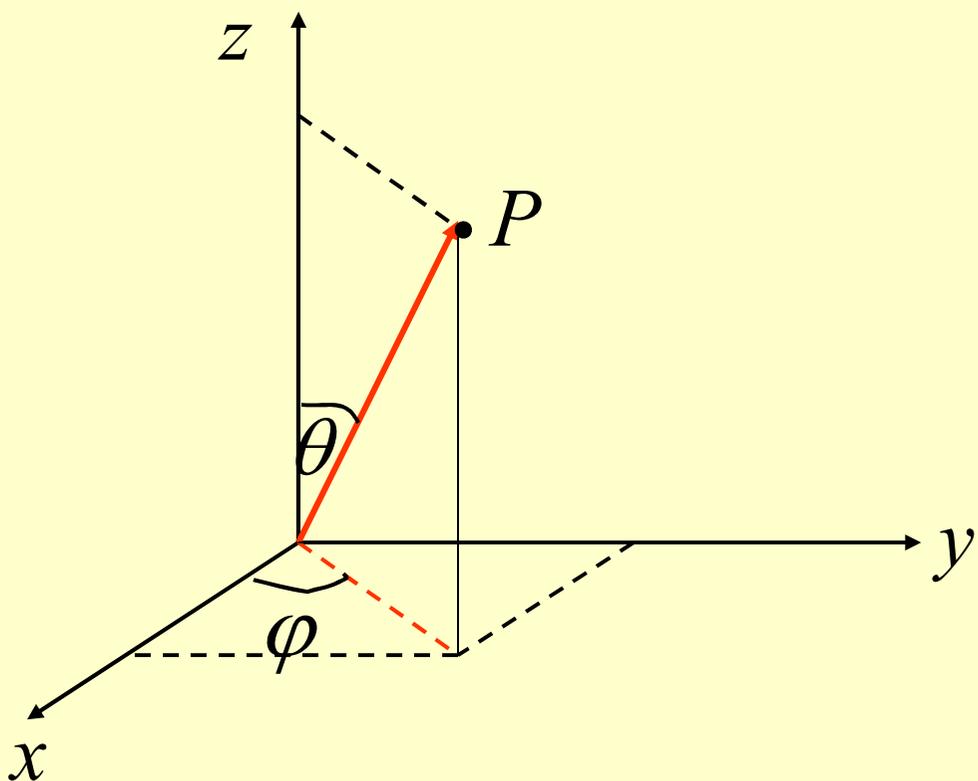


讨论内容：

1. 球对称体系中Laplace方程通解形式；
2. 处于静电场中的介质球的边值问题；
3. 处于静电场中的导体球的边值问题；
4. 在光（电磁波）照射下，球形贵金属纳米颗粒的局域电场增强效应

1、球对称体系中Laplace方程通解形式；

1) 对于球形边值问题，一般采用**球坐标系**最为方便；位置坐标用 (r, θ, φ) 表示



$$r \in [0, \infty)$$

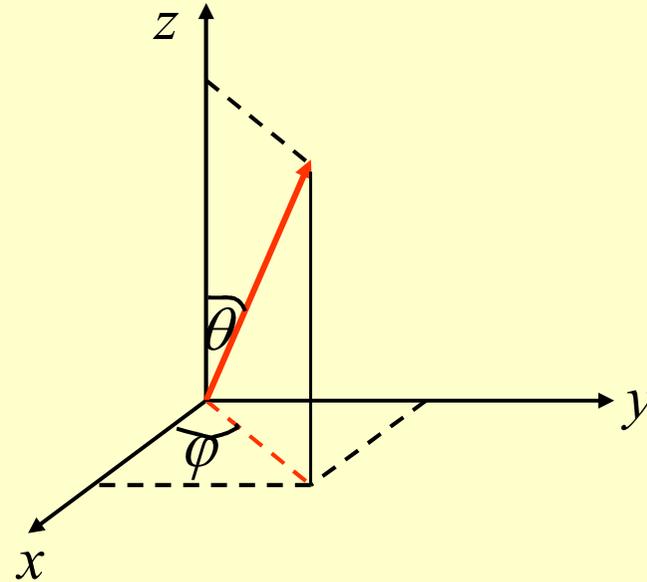
$$\theta \in [0, \pi]$$

$$\varphi \in [0, 2\pi]$$

2) 球坐标系下, Laplace方程的形式:

$$\phi = \phi(r, \theta, \varphi)$$

$$\nabla^2 \phi = 0$$



$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \phi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \phi}{\partial \varphi^2} = 0.$$

3) 球坐标系下, 方程 $\nabla^2 \phi = 0$ 的通解为

$$\phi(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \left(A_{lm} r^l + B_{lm} \frac{1}{r^{l+1}} \right) Y_{lm}(\theta, \varphi)$$

$Y_{lm}(\theta, \varphi)$ 为球谐函数。

$$\varphi = \varphi(r, \theta, \phi)$$

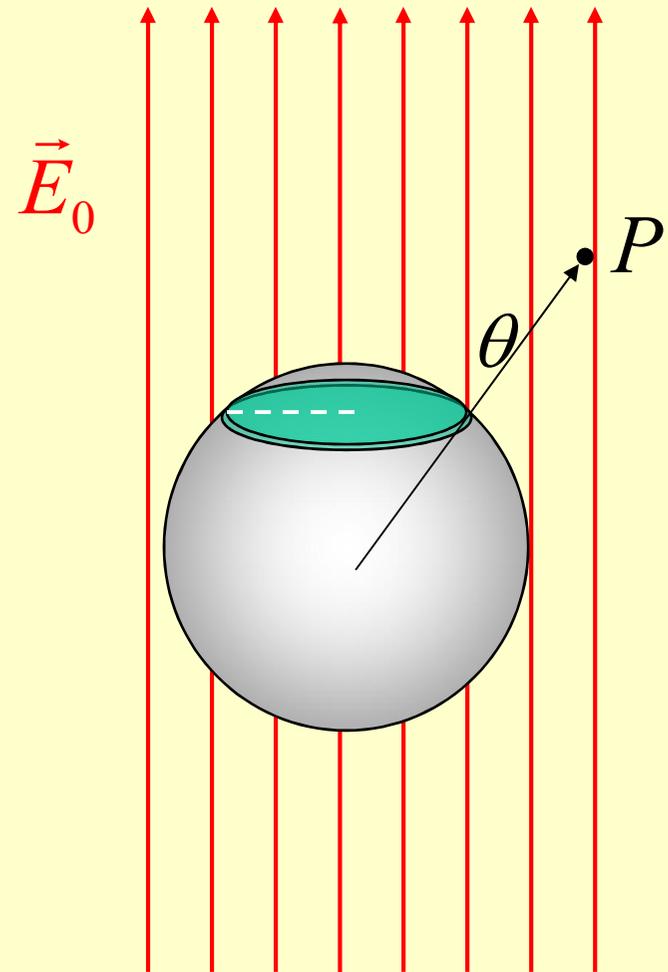
4) 轴对称情况下Laplace方程通解形式

如果体系具有轴对称性，则以对称轴为极轴，电势应方位角 φ 无关。

$\varphi = \varphi(r, \theta, \varphi)$



$\varphi = \varphi(r, \theta)$



$$\phi(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \left(A_{lm} r^l + B_{lm} \frac{1}{r^{l+1}} \right) Y_{lm}(\theta, \varphi),$$

在体系具有轴对称情况下，Laplace方程通解形式简化为

$$\varphi(r, \theta) = \sum_n \left(a_n r^n + \frac{b_n}{r^{n+1}} \right) P_n(\cos \theta) \quad \text{—— (3.3)}$$

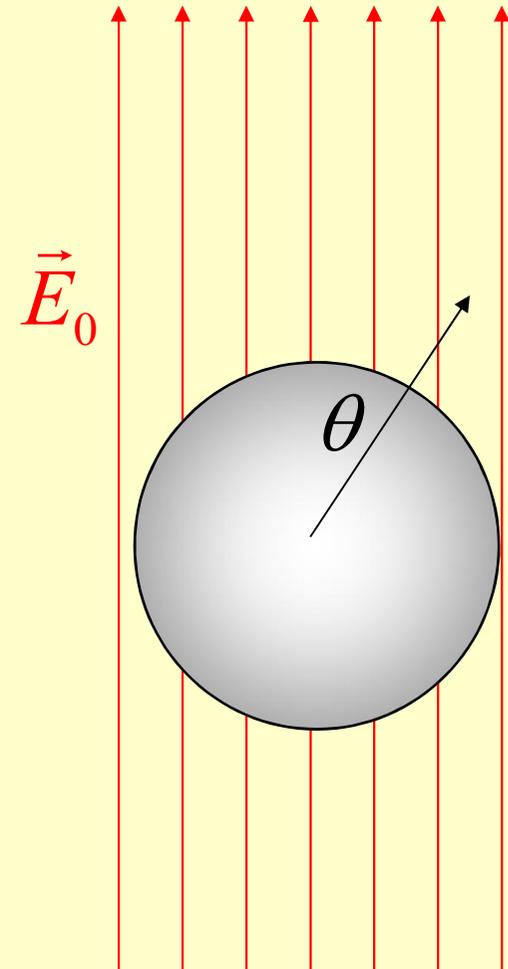
式中 $P_n(\cos \theta)$ 为勒让德 (Legendre) 函数

$$\varphi = \sum_n \left(a_n r^n + \frac{b_n}{r^{n+1}} \right) P_n(\cos \theta)$$

- ❖ a_n 和 b_n 任意常数，其值由边界条件所决定。
- ❖ 如果所讨论的对称性问题为包括南极和北极的整个区域，

$$0 \leq \theta \leq \pi$$

为了保证解的单值性， n 只能取整数或者零。



$$\varphi = \sum_n \left(a_n r^n + \frac{b_n}{r^{n+1}} \right) P_n(\cos \theta)$$

在教材附录 II 中列出了勒让德函数的前几项：

$$P_0(\cos \theta) = 1$$

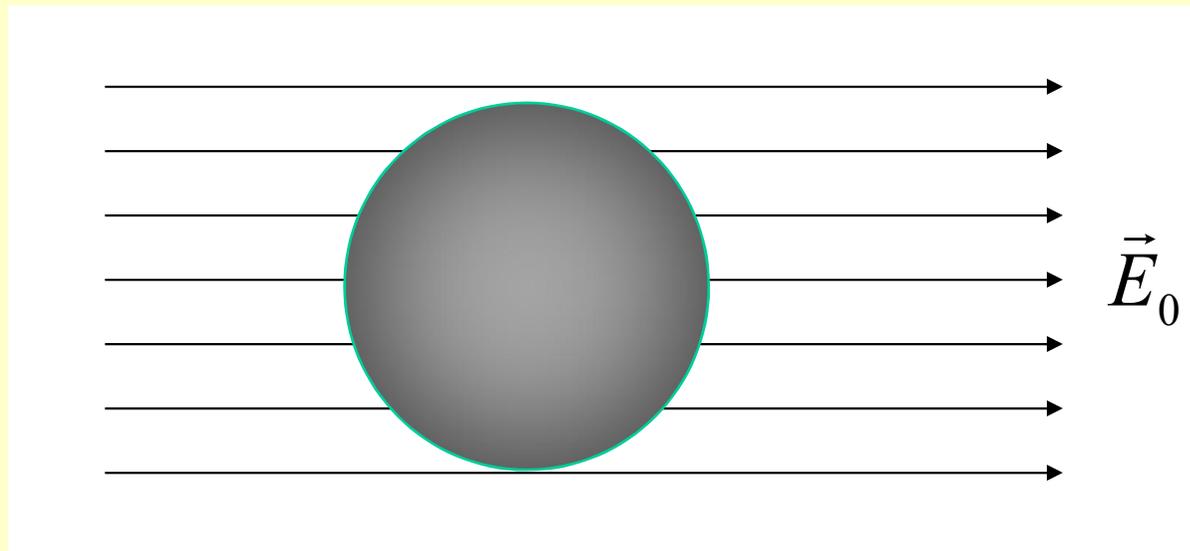
$$P_1(\cos \theta) = \cos \theta$$

$$P_2(\cos \theta) = \frac{1}{2}(3 \cos^2 \theta - 1)$$

$$P_3(\cos \theta) = \frac{1}{2}(5 \cos^2 \theta - 3 \cos \theta)$$

2、处于静电场中的介质球的边值问题

例题1：电容率为 ϵ 的**线性均匀介质球**放置于均匀外场中，求空间的电势分布。



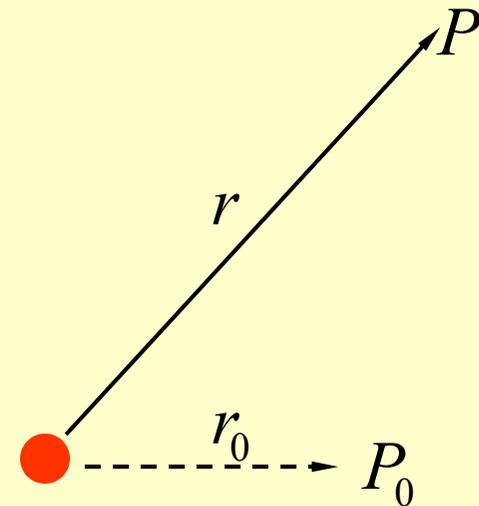
1) 两点之间的电势差的定义： $\phi(P_2) - \phi(P_1) = -\int_{P_1}^{P_2} \vec{E} \cdot d\vec{l}$

2) 对于点电荷，若取无穷远处为零电势点，则空间P点的电势

$$\phi(r) = \frac{Q}{4\pi\epsilon_0 r}$$

3) 若取 P_0 处为零电势点，则空间P点的电势

$$\phi(r) = \frac{Q}{4\pi\epsilon_0} \left(\frac{1}{r} - \frac{1}{r_0} \right)$$



4) 均匀电场的电势表达式

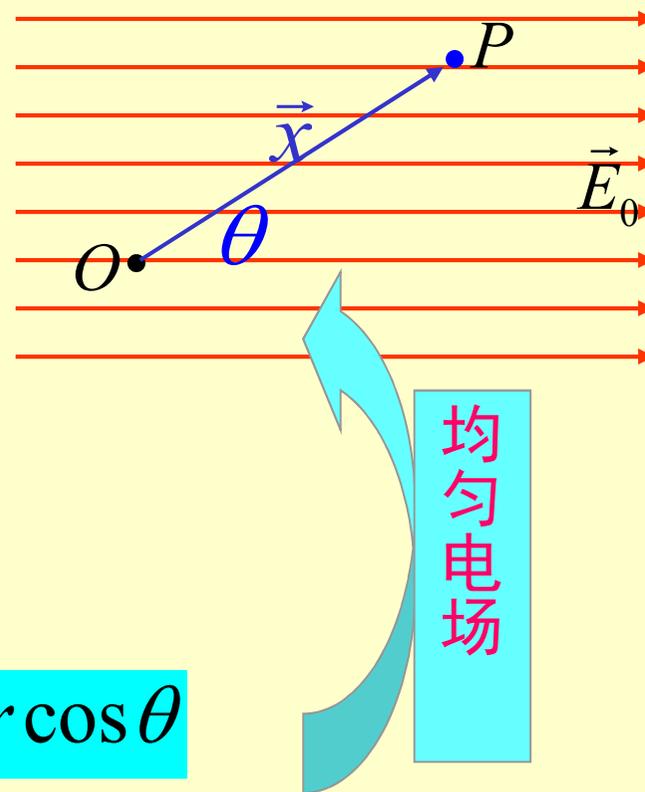
取空间任意一点 O 为坐标原点，设坐标原点的电势为0

任意一点处的电势满足

$$\phi(P) = -\int_O^P \vec{E}_0 \cdot d\vec{l}$$

或者

$$\begin{aligned}\phi(P) &= -\vec{E}_0 \cdot \int_O^P d\vec{l} \\ &= -\vec{E}_0 \cdot \vec{x} = -E_0 r \cos \theta\end{aligned}$$

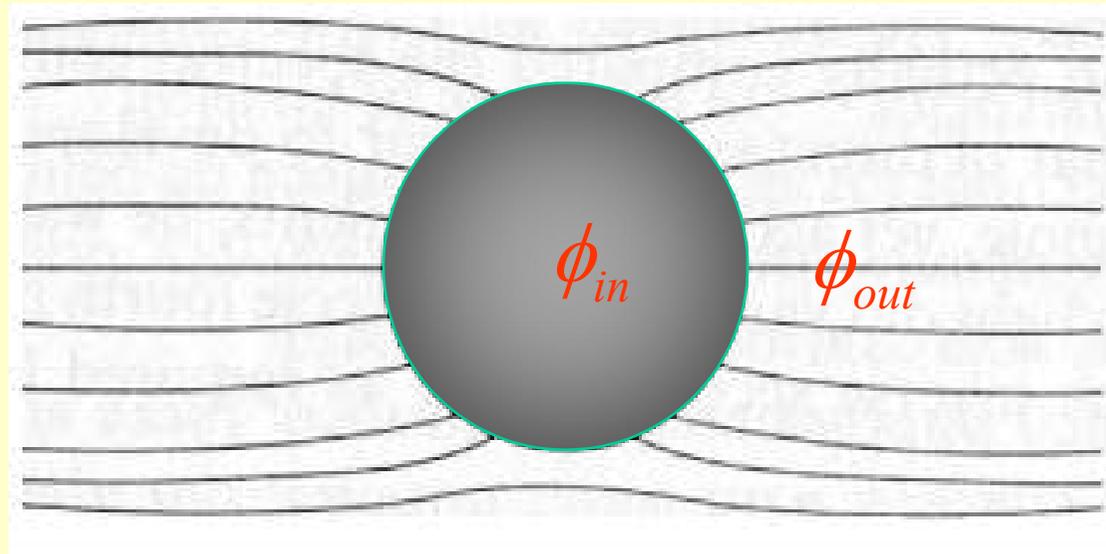


由于在这两个区域都**没有自由电荷的分布**，因此

ϕ_{out} 和 ϕ_{in} 都满足拉普拉斯方程：

$$\nabla^2 \phi_{in} = 0$$

$$\nabla^2 \phi_{out} = 0$$



$$\phi = \sum_n \left(a_n r^n + \frac{b_n}{r^{n+1}} \right) P_n(\cos \theta)$$

在球坐标系中，两个区域电势的通解形式分别为：

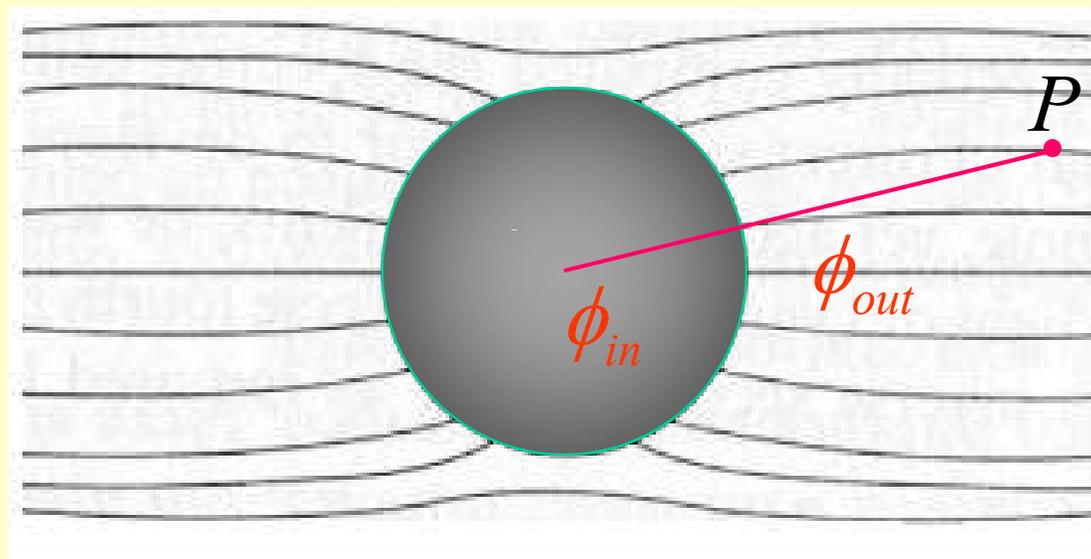
$$\phi_{out} = \sum_{n=0}^{\infty} \left(a_n r^n + \frac{b_n}{r^{n+1}} \right) P_n(\cos \theta) \quad \text{—— (3.11)}$$

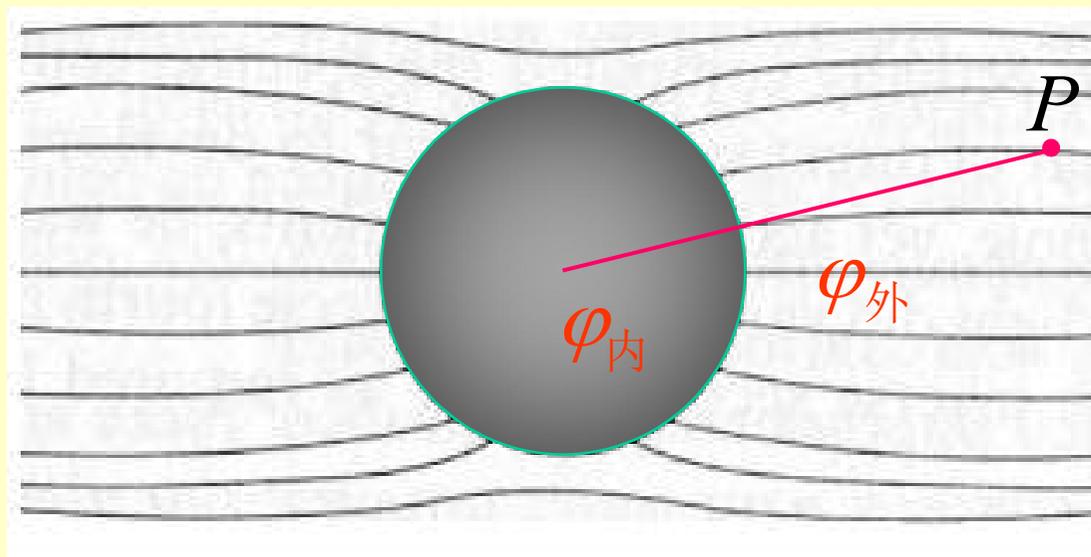
$$\phi_{in} = \sum_{n=0}^{\infty} \left(c_n r^n + \frac{d_n}{r^{n+1}} \right) P_n(\cos \theta) \quad \text{—— (3.12)}$$

其中 a_n 、 b_n 、 c_n 和 d_n 是待定的系数。

边界条件：

- ① 在无穷远处；
- ② 在介质的分界面；
- ③ 在球心处





取球心处的电势为零

① 在无穷远处，电场： $\vec{E} \rightarrow \vec{E}_0$

相应地电势

$$\begin{aligned}\phi_{out} &\rightarrow -E_0 r \cos \theta \\ &= -E_0 r P_1(\cos \theta)\end{aligned}$$

$$\phi_{out} \rightarrow -E_0 r P_1(\cos \theta)$$

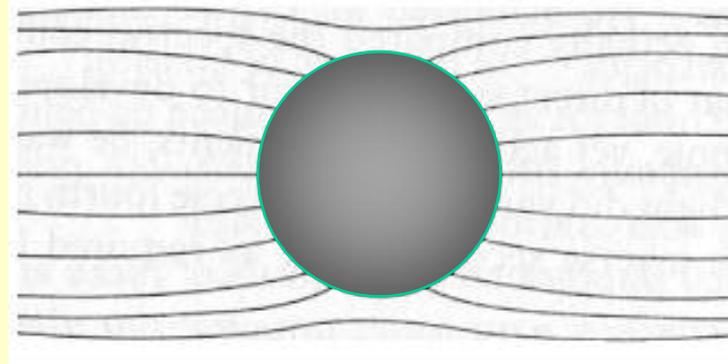
一般形式解：
$$\phi_{out} = \sum_{n=0}^{\infty} \left(a_n r^n + \frac{b_n}{r^{n+1}} \right) P_n(\cos \theta)$$

因此：
$$a_0 = 0$$

$$a_1 = -E_0$$

$$a_n = 0 \quad (n \neq 1)$$

$$\phi_{out} = -E_0 r P_1(\cos \theta) + \sum_{n=0}^{\infty} \frac{b_n}{r^{n+1}} P_n(\cos \theta)$$



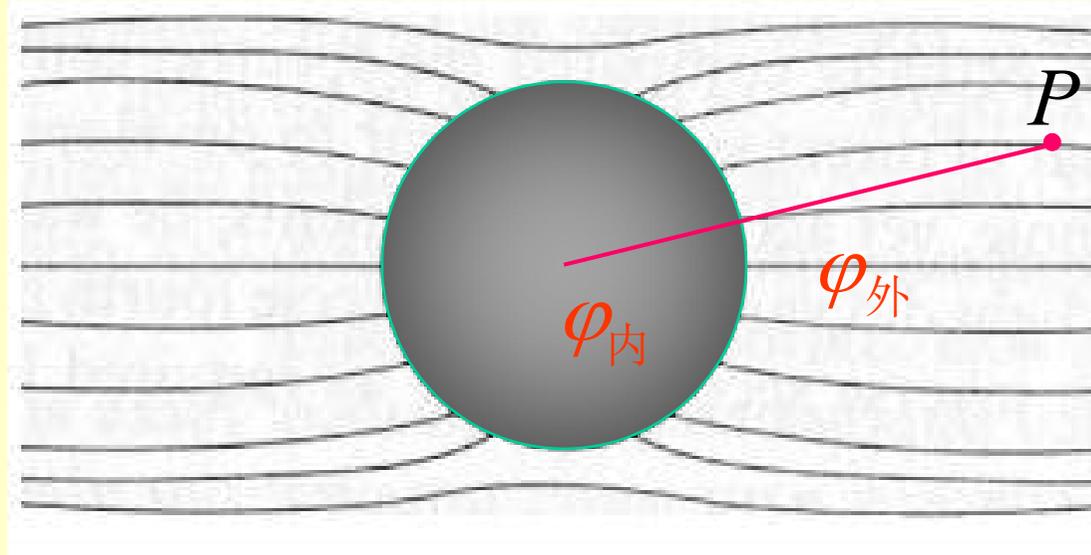
$$\phi_{in} = \sum_{n=0}^{\infty} \left(c_n r^n + \frac{d_n}{r^{n+1}} \right) P_n(\cos \theta)$$



② 在球心 $r = 0$ ，电势应为一有限值（此处为零）

因此有： $d_n = 0$

$$\phi_{in} = \sum_{n=0}^{\infty} c_n r^n P_n(\cos \theta)$$

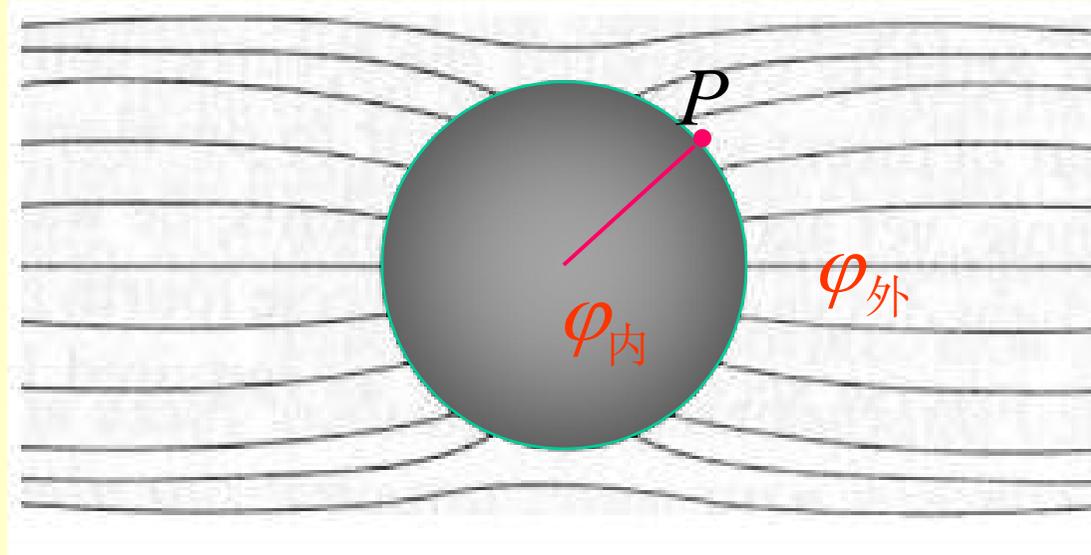


根据上述分析：

$$\phi_{in} = \sum_{n=0}^{\infty} c_n r^n P_n(\cos \theta)$$

$$\phi_{out} = -E_0 r P_1(\cos \theta) + \sum_{n=0}^{\infty} \frac{b_n}{r^{n+1}} P_n(\cos \theta)$$

其中 c_n 、 b_n 是待定的系数。



③ 在介质球面上，电势的边界条件要求

$$\phi_{out} \Big|_{r=R_0} = \phi_{in} \Big|_{r=R_0}$$

$$\epsilon_0 \frac{\partial \phi_{out}}{\partial r} \Big|_{r=R_0} = \epsilon \frac{\partial \phi_{in}}{\partial r} \Big|_{r=R_0}$$

$$\phi_{in} = \sum_{n=0}^{\infty} c_n r^n P_n(\cos \theta)$$

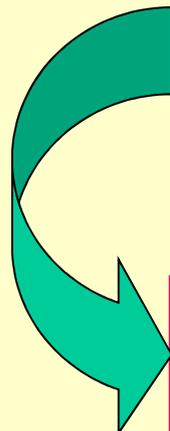
$$\phi_{out} = -E_0 r P_1(\cos \theta) + \sum_{n=0}^{\infty} \frac{b_n}{r^{n+1}} P_n(\cos \theta)$$

$$\phi_{out} \Big|_{r=R_0} = \phi_{in} \Big|_{r=R_0}$$

$$-E_0 R_0 P_1(\cos \theta) + \sum_{n=0}^{\infty} \frac{b_n}{R_0^{n+1}} P_n(\cos \theta) = \sum_{n=0}^{\infty} c_n R_0^n P_n(\cos \theta)$$

$$\phi_{in} = \sum_{n=0}^{\infty} c_n r^n P_n(\cos \theta)$$

$$\phi_{out} = -E_0 r P_1(\cos \theta) + \sum_{n=0}^{\infty} \frac{b_n}{r^{n+1}} P_n(\cos \theta)$$



$$\epsilon_0 \left. \frac{\partial \phi_{out}}{\partial r} \right|_{r=R_0} = \epsilon \left. \frac{\partial \phi_{in}}{\partial r} \right|_{r=R_0}$$

$$\begin{aligned}
 -E_0 P_1(\cos \theta) - \sum_{n=0}^{\infty} \frac{(n+1)b_n}{R_0^{n+2}} P_n(\cos \theta) \\
 = \frac{\epsilon}{\epsilon_0} \sum_{n=0}^{\infty} n c_n R_0^{n-1} P_n(\cos \theta)
 \end{aligned}$$

$$\begin{aligned}
 & -E_0 R_0 P_1(\cos \theta) + \sum_{n=0}^{\infty} \frac{b_n}{R_0^{n+1}} P_n(\cos \theta) \\
 & \qquad \qquad \qquad = \sum_{n=0}^{\infty} c_n R_0^n P_n(\cos \theta) \\
 & -E_0 P_1(\cos \theta) - \sum_{n=0}^{\infty} \frac{(n+1)b_n}{R_0^{n+2}} P_n(\cos \theta) \\
 & \qquad \qquad \qquad = \frac{\varepsilon}{\varepsilon_0} \sum_{n=0}^{\infty} n c_n R_0^{n-1} P_n(\cos \theta)
 \end{aligned}$$

$$-E_0 R_0 P_1(\cos \theta) + \sum_{n=0}^{\infty} \frac{b_n}{R_0^{n+1}} P_n(\cos \theta) = \sum_{n=0}^{\infty} c_n R_0^n P_n(\cos \theta)$$

$$-E_0 P_1(\cos \theta) - \sum_{n=0}^{\infty} \frac{(n+1)b_n}{R_0^{n+2}} P_n(\cos \theta) = \frac{\varepsilon}{\varepsilon_0} \sum_{n=0}^{\infty} n c_n R_0^{n-1} P_n(\cos \theta)$$

比较两式中 $P_1(\cos \theta)$ 前的系数，得到

$$-E_0 R_0 + \frac{b_1}{R_0^2} = c_1 R_0, \quad -E_0 - \frac{2b_1}{R_0^3} = \frac{\varepsilon}{\varepsilon_0} c_1$$

$$\text{解得: } b_1 = \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0 R_0^3, \quad c_1 = \frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0$$

$$-E_0 R_0 P_1(\cos \theta) + \sum_{n=0}^{\infty} \frac{b_n}{R_0^{n+1}} P_n(\cos \theta) = \sum_{n=0}^{\infty} c_n R_0^n P_n(\cos \theta)$$

$$-E_0 P_1(\cos \theta) - \sum_{n=0}^{\infty} \frac{(n+1)b_n}{R_0^{n+2}} P_n(\cos \theta) = \frac{\varepsilon}{\varepsilon_0} \sum_{n=0}^{\infty} n c_n R_0^{n-1} P_n(\cos \theta)$$

比较两式中 $P_n(\cos \theta)$ ($n \neq 1$) 前的系数, 得到

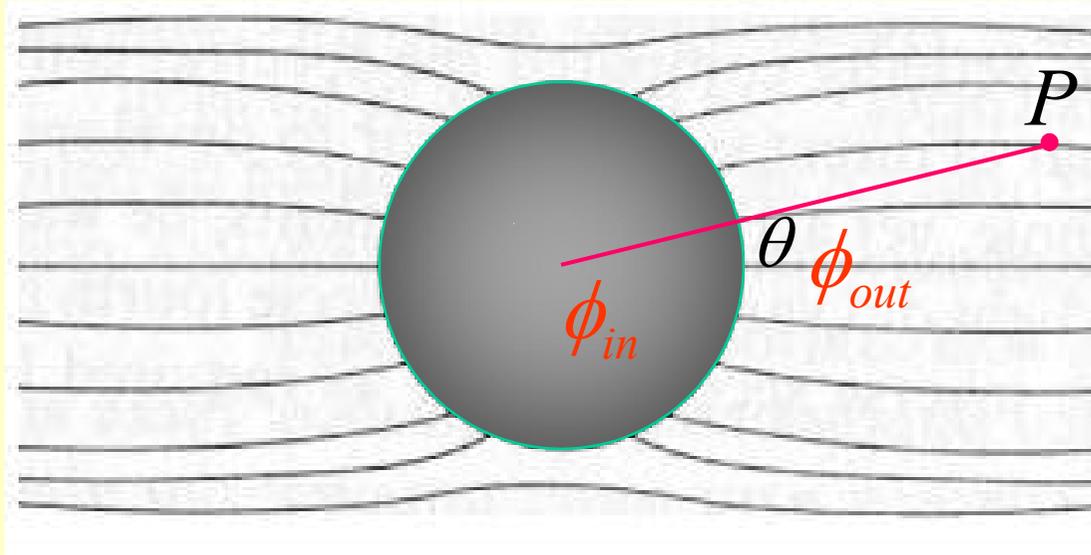
$$\left\{ \begin{array}{l} \frac{b_n}{R_0^{n+1}} = c_n R_0^n \\ \frac{(n+1)b_n}{R_0^{n+2}} = \frac{\varepsilon}{\varepsilon_0} n c_n R_0^{n-1} \end{array} \right. \quad \text{其解为: } \boxed{b_n = c_n = 0 \quad (n \neq 1)}$$

边界条件汇总：

① 在无穷远处： $\phi_{out} \rightarrow -E_0 r \cos \theta$

② 在球心处：电势应为一有限值；

③ 在介质的分界面：
$$\left\{ \begin{array}{l} \phi_{out} \Big|_{r=R_0} = \phi_{in} \Big|_{r=R_0} \\ \epsilon_0 \frac{\partial \phi_{out}}{\partial r} \Big|_{r=R_0} = \epsilon \frac{\partial \phi_{in}}{\partial r} \Big|_{r=R_0} \end{array} \right.$$



这样整个空间的电势分布为

$$\phi_{out} = -E_0 r \cos \theta + E_0 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \frac{R_0^3}{r^2} \cos \theta \quad (r > R_0)$$

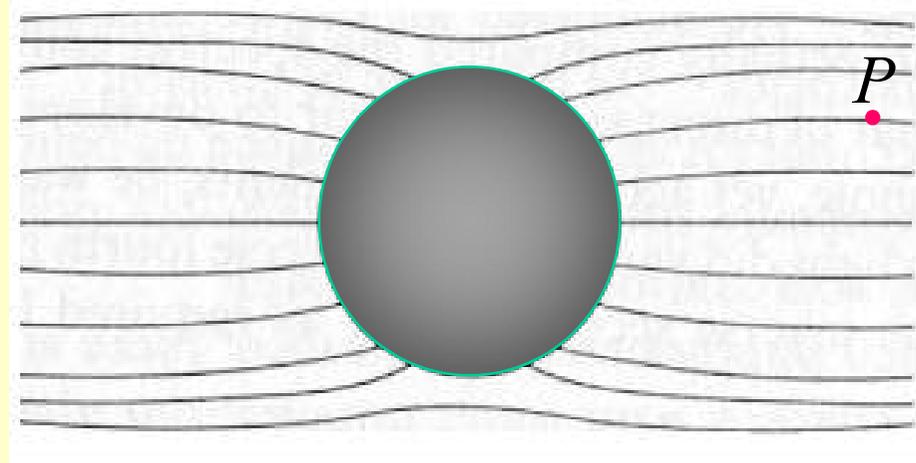
$$\phi_{in} = -\frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0 r \cos \theta \quad (r < R_0)$$

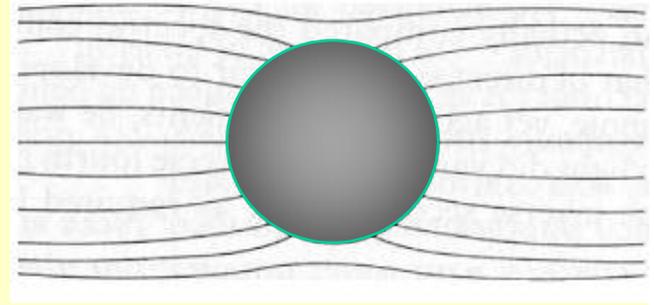
$$\phi_{out} = -E_0 r \cos \theta + E_0 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \frac{R_0^3}{r^2} \cos \theta \quad (r > R_0)$$

$$\phi_{in} = -\frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0 r \cos \theta \quad (r < R_0)$$

讨论:

- 球内区域的电场
- 球外区域的电场





1) 球内区域

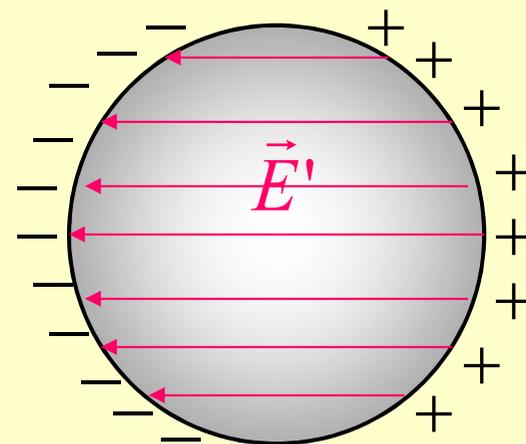
$$\phi_{in} = -\frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0 r \cos\theta \quad (r < R_0)$$

$$\vec{E}_{in} = \frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} \vec{E}_0$$

- 球内的电场为均匀电场；
- 方向与原外电场方向相平行；
- 对于绝缘介质 $\varepsilon > \varepsilon_0$ ，因此有 $E_{in} < E_0$

❖ **原因：** 介质球放置于外场中被极化（均匀），在介质的表面产生了**感应电荷分布**；

❖ 在球内区域，感应电荷所激发的附加场与原外电场的方向相反。



感应电荷在球内区域所激发的退极化场为

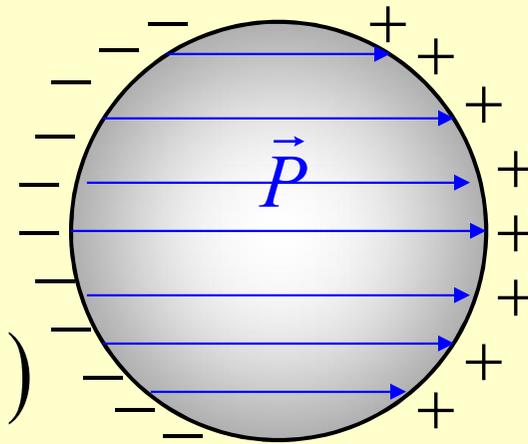
$$\vec{E}_{inside} = \vec{E}_0 + \vec{E}'$$

$$\Rightarrow \vec{E}' = \vec{E}_{inside} - \vec{E}_0 = \frac{\epsilon_0 - \epsilon}{\epsilon + 2\epsilon_0} \vec{E}_0$$

球内介质的极化强度为

$$\begin{aligned}\vec{P} &= \chi_e \varepsilon_0 \vec{E} = (\varepsilon_r - 1) \varepsilon_0 \vec{E} \\ &= \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} 3\varepsilon_0 \vec{E}_0\end{aligned}$$

$(r < R_0)$



介质球的总电偶极矩为

$$\vec{p} = \frac{4\pi R_0^3}{3} \vec{P} = \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} 4\pi \varepsilon_0 R_0^3 \vec{E}_0$$

注意，这里既可以从极化强度来计算电偶极矩，也可以从基本的定义式来计算

$$\vec{p} = \oint \vec{r} dq = \oint \vec{r} \sigma dS$$

$$\phi_{out} = -E_0 r \cos \theta + E_0 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \frac{R_0^3}{r^2} \cos \theta \quad (r > R_0)$$

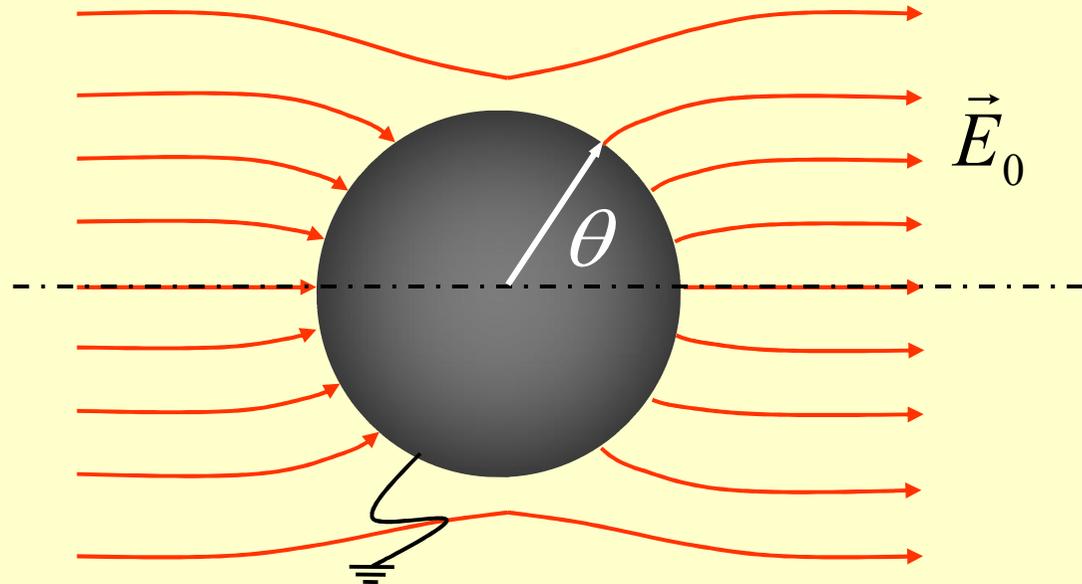
$$\phi_p = \frac{1}{4\pi\varepsilon_0} \frac{\vec{p} \cdot \vec{r}}{r^3}$$

2) 球外区域:

均匀外电场的贡献项: $-E_0 r \cos \theta$

$E_0 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \frac{R_0^3}{r^2} \cos \theta$ 是介质球表面因极化而产生的束缚电荷的贡献, 相当于放置于原点处的电偶极子的贡献。

例题2：半径为 R 的接地导体球放置于均匀外场中，求空间的电势分布。



解：球外空间无自由电荷，电势满足拉普拉斯方程

$$\nabla^2 \phi = 0$$

在球坐标系中，方程通解形式：

$$\phi = \sum_{n=0}^{\infty} \left(a_n r^n + \frac{b_n}{r^{n+1}} \right) P_n(\cos \theta)$$

其中 a_n 、 b_n 是待定的系数。

边界条件：

- 1) 在无穷远处，电场 $\vec{E} \rightarrow \vec{E}_0$
- 2) 球面应为等势面（零电势）

$$\phi = \sum_{n=0}^{\infty} \left(a_n r^n + \frac{b_n}{r^{n+1}} \right) P_n(\cos \theta)$$

1) 在无穷远处, 电场 $\vec{E} \rightarrow \vec{E}_0$

假设球心处的电势为零, 相应地无穷远处电势为

$$\phi \rightarrow -E_0 r P_1(\cos \theta)$$

因此有: $a_0 = 0,$

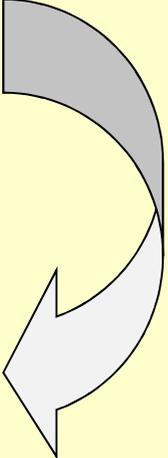
$$a_1 = -E_0,$$

$$a_n = 0 \quad (n \neq 1)$$

$$\phi = -E_0 r P_1(\cos \theta) + \sum_{n=1}^{\infty} \frac{b_n}{r^{n+1}} P_n(\cos \theta)$$

$$\phi = -E_0 r P_1(\cos \theta) + \sum_{n=1}^{\infty} \frac{b_n}{r^{n+1}} P_n(\cos \theta)$$

2) 在球面上, 电势为零电势

$$\phi|_{R=R_0} = -E_0 R_0 P_1(\cos \theta) + \sum_{n=0}^{\infty} \frac{b_n}{R_0^{n+1}} P_n(\cos \theta) \equiv 0$$


则 $b_0 = 0,$

$$-E_0 R_0 + \frac{b_1}{R_0^2} = 0,$$

$$b_1 = E_0 R_0^3$$

$$b_n = 0 \quad (n \geq 2)$$

导体球外空间任一点电势为

$$\begin{aligned}\phi &= -E_0 r \cos \theta + \frac{E_0 R_0^3}{r^2} \cos \theta \\ &= -rE_0 + \frac{1}{4\pi\epsilon_0} \times 4\pi\epsilon_0 E_0 R_0^3 \cdot \frac{\cos \theta}{r^2}\end{aligned}$$

回顾电偶极子的电势：

$$\phi = \frac{1}{4\pi\epsilon_0} \frac{p \cos \theta}{r^2}$$

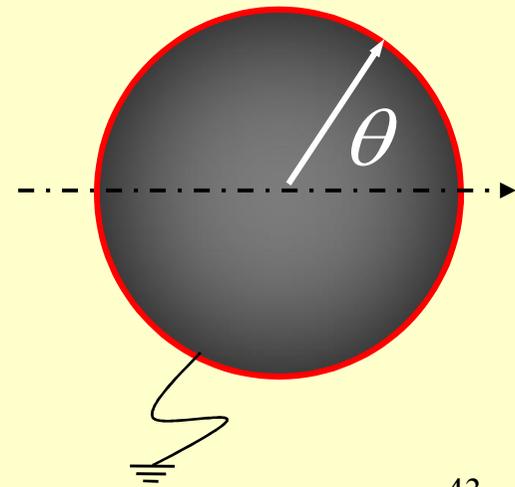
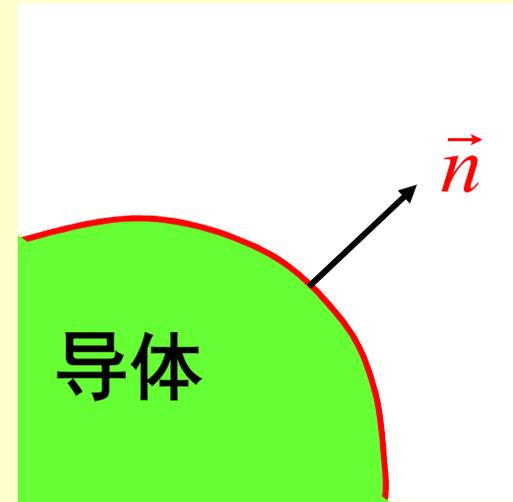
$$\phi = E_0 \left(-r + \frac{R_0^3}{r^2} \right) \cos \theta$$

导体球表面感应电荷的面密度为

$$\sigma_f = -\varepsilon_0 \left. \frac{\partial \phi}{\partial r} \right|_{r=R_0} = 3\varepsilon_0 E_0 \cos \theta$$

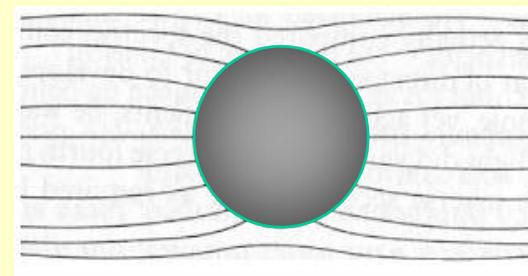
表面感应电荷形成的偶极矩： $\vec{p} = \oint \vec{r} dq = \oint \vec{r} \sigma dS$

$$\begin{aligned} p &= p_x = \oint R_0 \cos \theta \cdot \sigma dS \\ &= \oint 3\varepsilon_0 E_0 R_0 \cos^2 \theta \cdot R_0^2 \sin \theta d\theta d\phi \\ &= 3\varepsilon_0 E_0 R_0^3 \times \frac{4\pi}{3} = 4\pi\varepsilon_0 E_0 R_0^3 \end{aligned}$$



均匀静电场中的介质球：

$$\phi_{in} = -\frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0 r \cos\theta \quad (r < R_0)$$

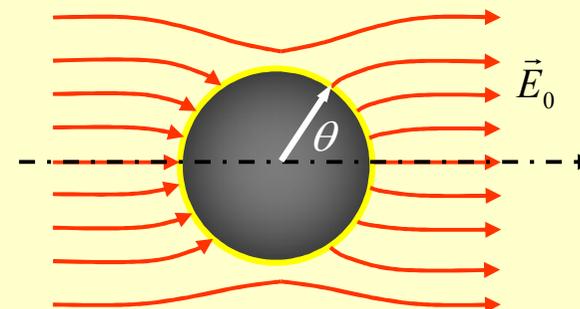


$$\phi_{out} = -E_0 r \cos\theta + E_0 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \frac{R_0^3}{r^2} \cos\theta \quad (r > R_0)$$

对照：均匀静电场中的接地金属导体球：

$$\phi_{in} = 0$$

$$\phi_{out} = -E_0 r \cos\theta + \frac{E_0 R_0^3}{r^2} \cos\theta$$



- 在静电场（包括低频）条件下，金属导体的介电常数：

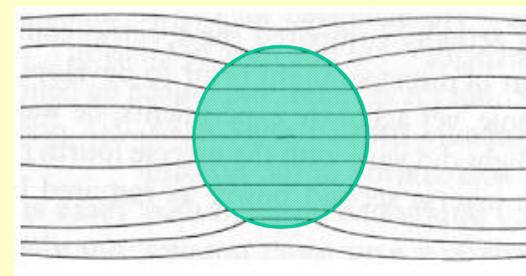
$$\varepsilon \rightarrow -\infty$$

- 从物理上理解，就是电场无法进入金属导体内部，穿透深度趋于零！

电介质球:

$$\phi_{in} = -\frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0 r \cos\theta \quad (r < R_0)$$

$$\phi_{out} = -E_0 r \cos\theta + E_0 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \frac{R_0^3}{r^2} \cos\theta \quad (r > R_0)$$

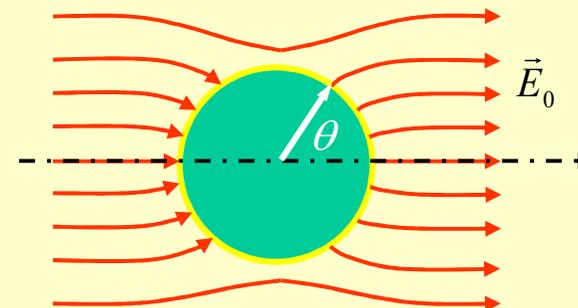


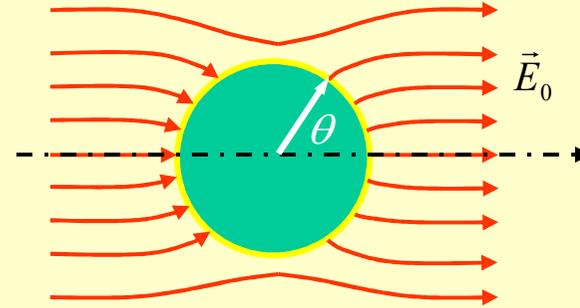
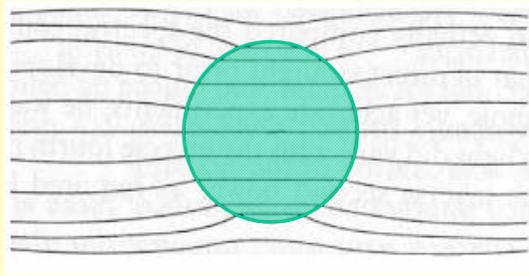
$\varepsilon \rightarrow -\infty$

导体球:

$$\phi_{in} = 0$$

$$\phi_{out} = -E_0 r \cos\theta + \frac{E_0 R_0^3}{r^2} \cos\theta$$





$$\vec{E}_{in} \Big|_{\epsilon \rightarrow -\infty} = \left[\frac{3\epsilon_0}{\epsilon + 2\epsilon_0} \vec{E}_0 \right] \Big|_{\epsilon \rightarrow -\infty} = 0$$

总结：介质球处于均匀外（静）电场的结果：

$$\phi_{in} = -\frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0 r \cos\theta \quad (r < R_0)$$

$$\vec{E}_{in} = \frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} \vec{E}_0$$

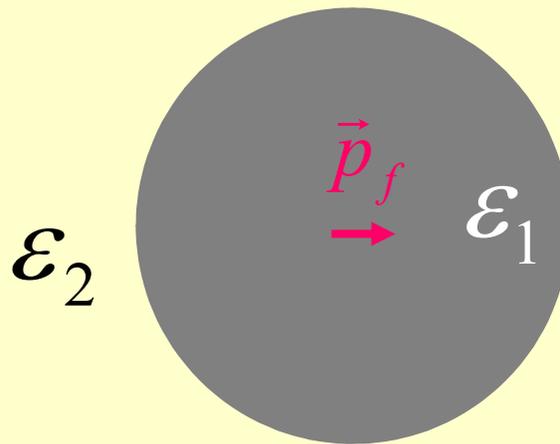
$$\phi|_{out} = -E_0 r \cos\theta + E_0 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} \frac{R_0^3}{r^2} \cos\theta \quad (r > R_0)$$

作业

(2013年10月15日)

第二章 习题 2、3

例题：半径为 R_0 、电容率为 ϵ_1 的均匀介质球的中心有一个由自由电荷组成的电偶极子，其电偶极矩为 ρ_f 。球外充满了电容率为 ϵ_2 的另一种均匀介质。求空间各处的电势和极化电荷分布。



结论1：极化电荷密度与极化强度之间的关系

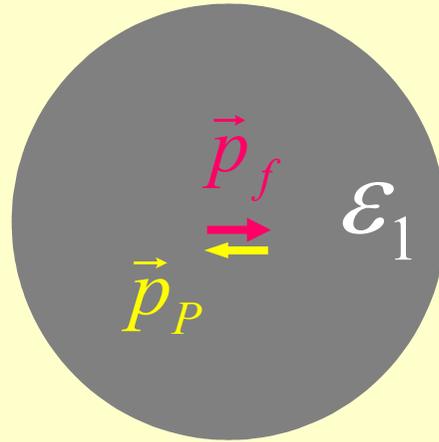
$$\rho_P = -\nabla \cdot \vec{P}$$

结论2：均匀介质内部，自由电荷密度与同处的极化电荷密度之间的关系

$$\rho_P = \left(\frac{\epsilon_0}{\epsilon} - 1 \right) \rho_f$$

$$q_P = \left(\frac{\epsilon_0}{\epsilon} - 1 \right) q_f$$

$$\rho_P = \left(\frac{\epsilon_0}{\epsilon} - 1 \right) \rho_f$$



推论：如果在均匀介质的内部某处出现一个由自由电荷构成的电偶极子 \vec{p}_f ，则在介质内部的同一处，将存在一个由极化电荷构成的电偶极子

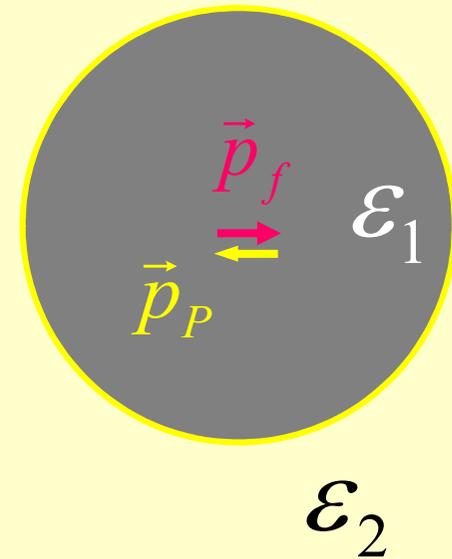
$$\vec{p}_P = \left(\frac{\epsilon_0}{\epsilon_1} - 1 \right) \vec{p}_f$$

系统中三个区域存在电荷：

a) 球心处的自由电偶极子 \vec{p}_f

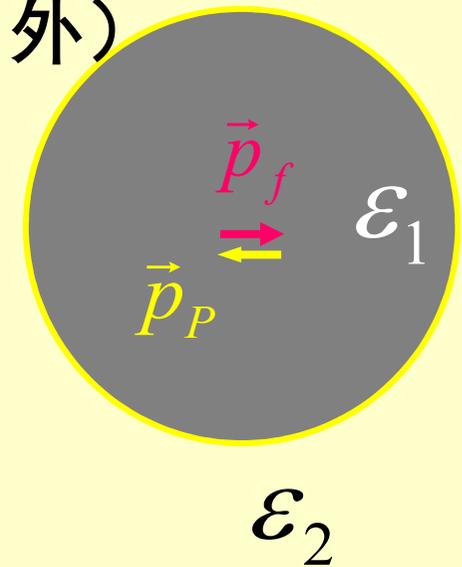
b) 球心处极化电偶极子 \vec{p}_P

c) 在介质的分界面（球面）上的束缚面电荷 σ_p



球心处，自由电偶极子在（介质球内、外）
空间的电势为

$$\phi_f = \frac{1}{4\pi\epsilon_0} \frac{\vec{p}_f \cdot \vec{R}}{R^3}$$

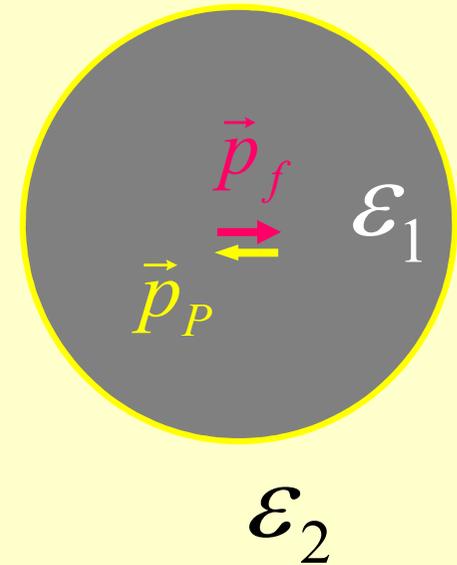


球心处，极化电偶极子在（介质球内、外）
空间的电势为

$$\phi_p = \frac{1}{4\pi\epsilon_0} \frac{\vec{p}_P \cdot \vec{R}}{R^3} = \frac{1}{4\pi\epsilon_0} \frac{-\vec{p}_f \cdot \vec{R}}{R^3} \left(1 - \frac{\epsilon_0}{\epsilon_1}\right)$$

$$\phi_f = \frac{1}{4\pi\epsilon_0} \frac{\vec{p}_f \cdot \vec{R}}{R^3}$$

$$\phi_p = \frac{1}{4\pi\epsilon_0} \frac{\vec{p}_p \cdot \vec{R}}{R^3} = \frac{1}{4\pi\epsilon_0} \frac{-\vec{p}_f \cdot \vec{R}}{R^3} \left(1 - \frac{\epsilon_0}{\epsilon_1}\right)$$



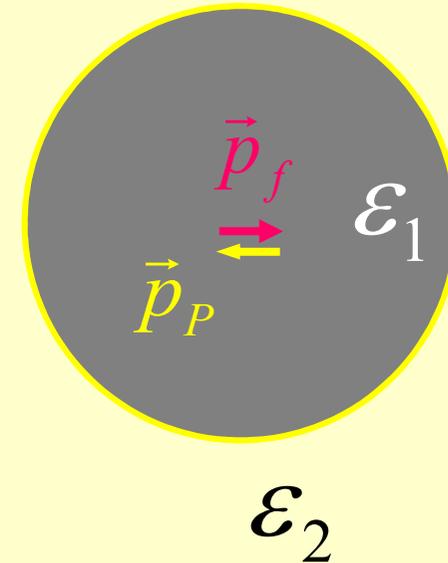
球心处整个电偶极子在空间的电势为

$$\phi_{total \ dipole} = \phi_f + \phi_p = \frac{1}{4\pi\epsilon_1} \frac{\vec{p}_f \cdot \vec{R}}{R^3}$$

球内、外的电势可写成如下形式：

$$\phi_{in} = \frac{1}{4\pi\epsilon_1} \frac{\vec{p}_f \cdot \vec{R}}{R^3} + \phi_{in}'$$

$$\phi_{out} = \frac{1}{4\pi\epsilon_1} \frac{\vec{p}_f \cdot \vec{R}}{R^3} + \phi_{out}'$$



介质分界面上面极化电荷

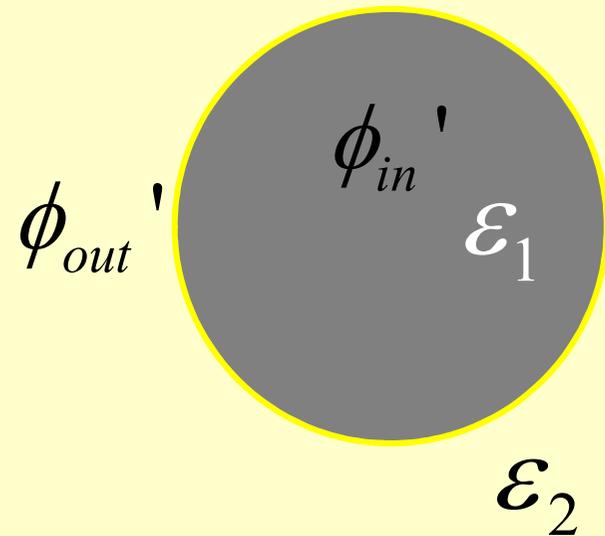
在球内产生的电势—— ϕ_{in}'

在球外产生的电势—— ϕ_{out}'

面极化电荷所激发电场的电势
满足拉普拉斯方程：

$$\nabla^2 \phi_{in}' = 0$$

$$\nabla^2 \phi_{out}' = 0$$



在球坐标系中，其一般形式为：

$$\phi_{in}' = \sum_n \left(a_n R^n + \frac{b_n}{R^{n+1}} \right) P_n(\cos \theta)$$

$$\phi_{out}' = \sum_n \left(c_n R^n + \frac{d_n}{R^{n+1}} \right) P_n(\cos \theta)$$

1) 考虑到球心处面极化电荷的贡献 ϕ_{in}' 应为一有限值, 则


$$\phi_{in}' = \sum_n \left(a_n R^n + \frac{b_n}{R^{n+1}} \right) P_n(\cos \theta)$$
$$\phi_{in}' = \sum_n a_n R^n P_n(\cos \theta)$$

2) 考虑到面极化电荷在无穷远处的贡献 $\phi_{out}' \rightarrow 0$ 则


$$\phi_{out}' = \sum_n \left(c_n R^n + \frac{d_n}{R^{n+1}} \right) P_n(\cos \theta)$$
$$\phi_{out}' = \sum_n \frac{d_n}{R^{n+1}} P_n(\cos \theta)$$

$$\phi_{in} = \frac{1}{4\pi\epsilon_1} \frac{\vec{p}_f \cdot \vec{R}}{R^3} + \phi_{in}'$$

$$\phi_{in}' = \sum_n a_n R^n P_n(\cos\theta)$$

$$\phi_{out} = \frac{1}{4\pi\epsilon_1} \frac{\vec{p}_f \cdot \vec{R}}{R^3} + \phi_{out}'$$

$$\phi_{out}' = \sum_n \frac{d_n}{R^{n+1}} P_n(\cos\theta)$$

3) 在介质的分界面——球面上，边界条件：

$$\left\{ \begin{array}{l} \phi_{in}|_{R=R_0} = \phi_{out}|_{R=R_0} \\ \epsilon_1 \frac{\partial \phi_{in}}{\partial R} \Big|_{R=R_0} = \epsilon_2 \frac{\partial \phi_{out}}{\partial R} \Big|_{R=R_0} \end{array} \right.$$

解得：
$$a_1 = \frac{(\varepsilon_1 - \varepsilon_2)p_f}{2\pi\varepsilon_1(\varepsilon_1 + 2\varepsilon_2)},$$

$$d_1 = R_0^3 a_1,$$

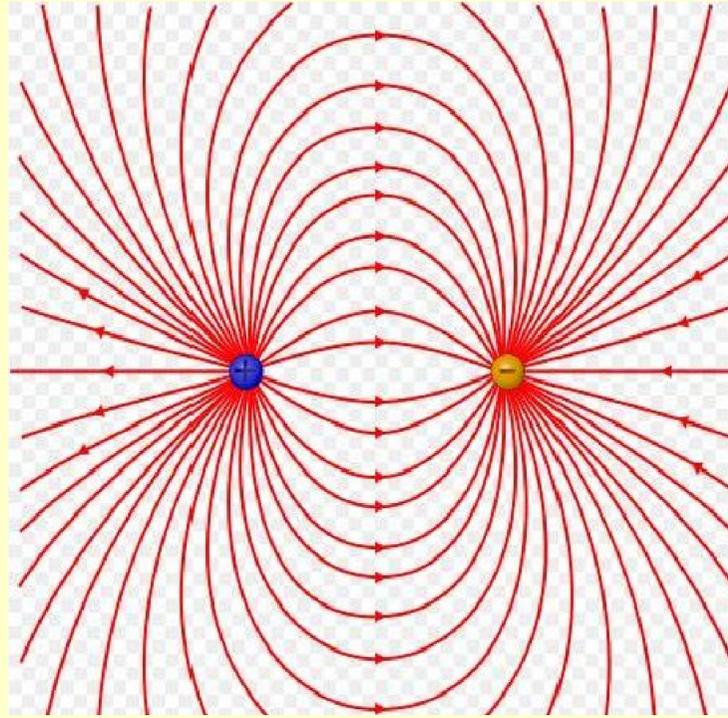
$$a_n = d_n = 0, \quad (n \neq 1)$$

球内外的电势分别为：

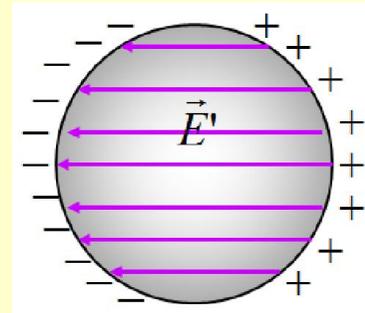
$$\phi_{in} = \frac{1}{4\pi\varepsilon_1} \frac{p_f}{R^2} \cos\theta + \frac{(\varepsilon_1 - \varepsilon_2)}{2\pi(\varepsilon_1 + 2\varepsilon_2)} \frac{p_f}{R_0^3} R \cos\theta,$$

$$\phi_{out} = \frac{3}{4\pi(\varepsilon_1 + 2\varepsilon_2)} \frac{p_f}{R^2} \cos\theta$$

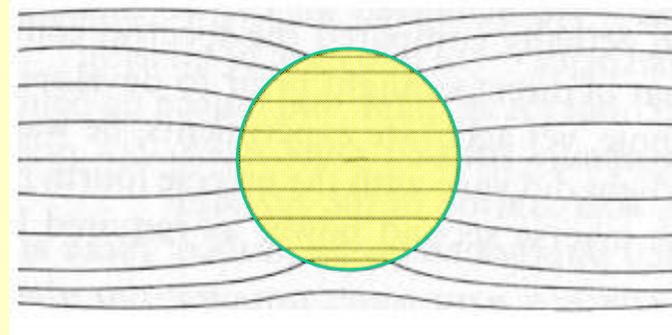
二、静电场球形边值问题的实际应用



对于放置在均匀
外场中的介质球



介质球在外电场中的极化



介质球内电场：

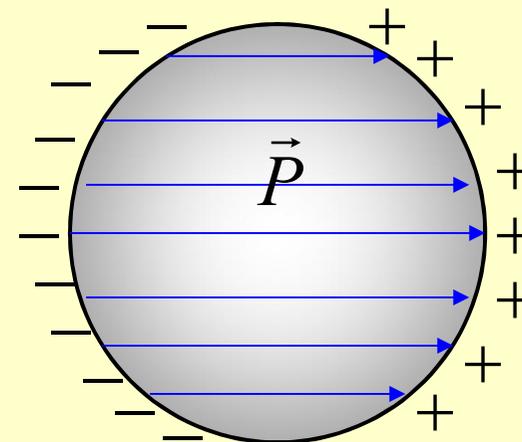
$$\vec{E}_{\text{内}} = \frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} \vec{E}_0$$

球内介质的极化强度为 $\vec{P} = \chi_e \varepsilon_0 \vec{E} = (\varepsilon_r - 1) \varepsilon_0 \vec{E}$

$$= \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} 3\varepsilon_0 \vec{E}_0$$

介质球的总电偶极矩：

$$\vec{p} = \frac{4\pi R_0^3}{3} \vec{P} = \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} 4\pi\varepsilon_0 R_0^3 \vec{E}_0$$



定义：介质球的极化率

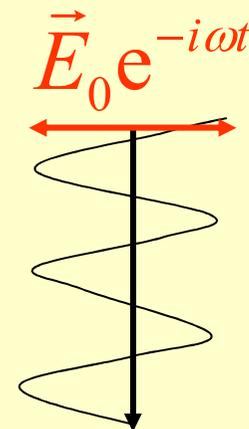
$$\vec{p} = \alpha \vec{E}_0,$$

$$\alpha = \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} 4\pi\varepsilon_0 R_0^3$$

如果外场是随时间变化的电磁场，上述的结果能否适用？

- ① 对于随时间变化的电磁场，表述介质对电磁波响应的物理量——介电常数一般是电磁波的频率或波长的函数：

$$\varepsilon = \varepsilon(\omega)$$



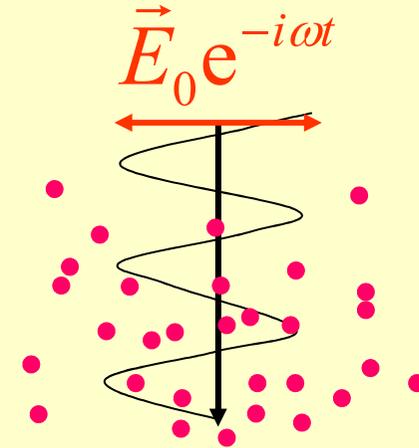
➤ 当球形颗粒尺度远小于电磁波的波长，即当

$$d \ll \lambda$$

$$\vec{E}_{in}(t) = \frac{3\varepsilon_0}{\varepsilon + 2\varepsilon_0} \vec{E}_0 e^{-i\omega t}$$

极化率：

$$\alpha = \frac{\varepsilon(\omega) - \varepsilon_0}{\varepsilon(\omega) + 2\varepsilon_0} 4\pi\varepsilon_0 R_0^3$$



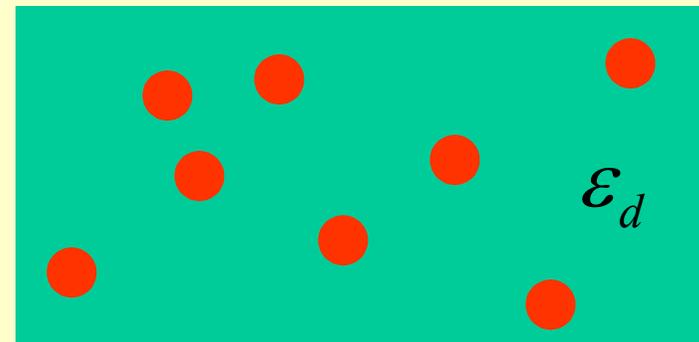
这样的近似处理又叫偶极近似。

③ 如果纳米颗粒所处的背景介质的介电常数为 ϵ_d

$$\alpha = \frac{\epsilon(\omega) - \epsilon_0}{\epsilon(\omega) + 2\epsilon_0} 4\pi\epsilon_0 R_0^3$$

$$\epsilon_0 \rightarrow \epsilon_d$$

$$\alpha = \frac{\epsilon(\omega) - \epsilon_d}{\epsilon(\omega) + 2\epsilon_d} 4\pi\epsilon_0 R_0^3$$



讨论两类球形纳米颗粒体系在可见光作用中的性质

- A. 无机介电材料构成的纳米球形颗粒
- B. 金属纳米球形颗粒——偶极子近似
- C. 金属纳米球形颗粒——严格计算结果
- D. 金属纳米颗粒的局域电场增强现象

可见光区，电磁波的波长在400~800nm，因此当颗粒的尺寸 $<20\text{nm}$ 时，基本上满足上述的偶极近似条件。

$$\frac{E}{E_0} = \frac{3\varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m}$$

A、无机材料构成的球形纳米颗粒

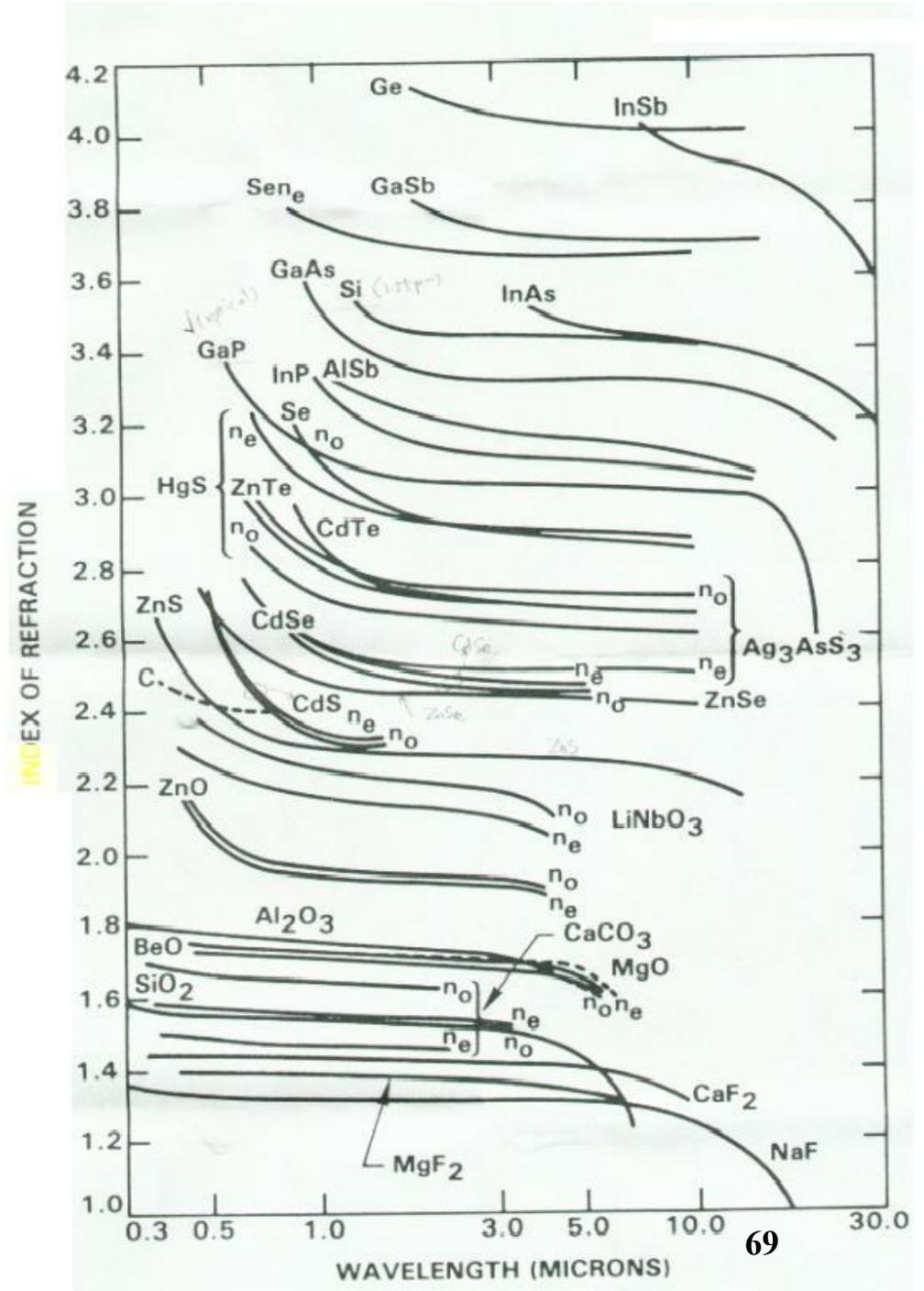
$$n > 1$$

$$\varepsilon_r \mu_r = n^2, \varepsilon_r > 1$$



$$E < E_0$$

颗粒内的电场始终小于入射电磁波的电场！



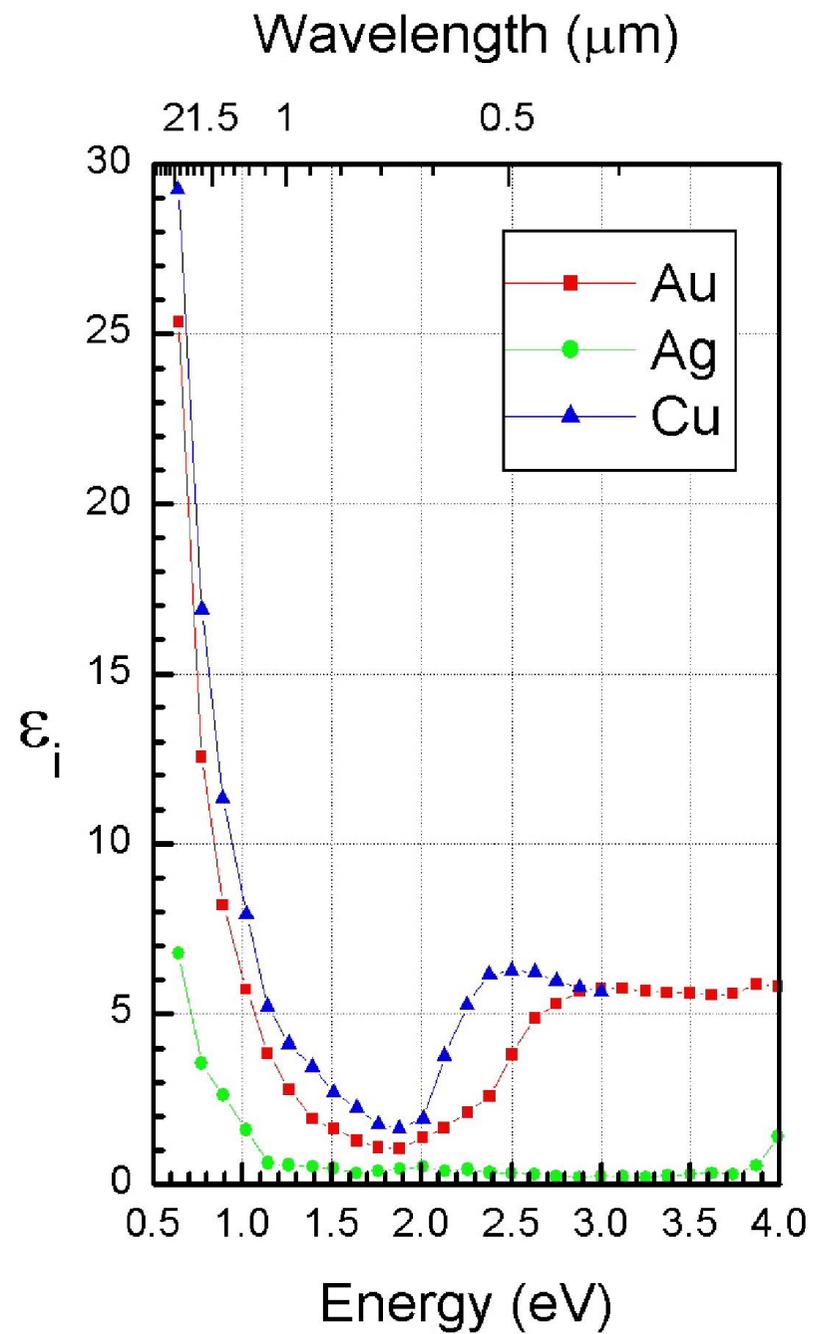
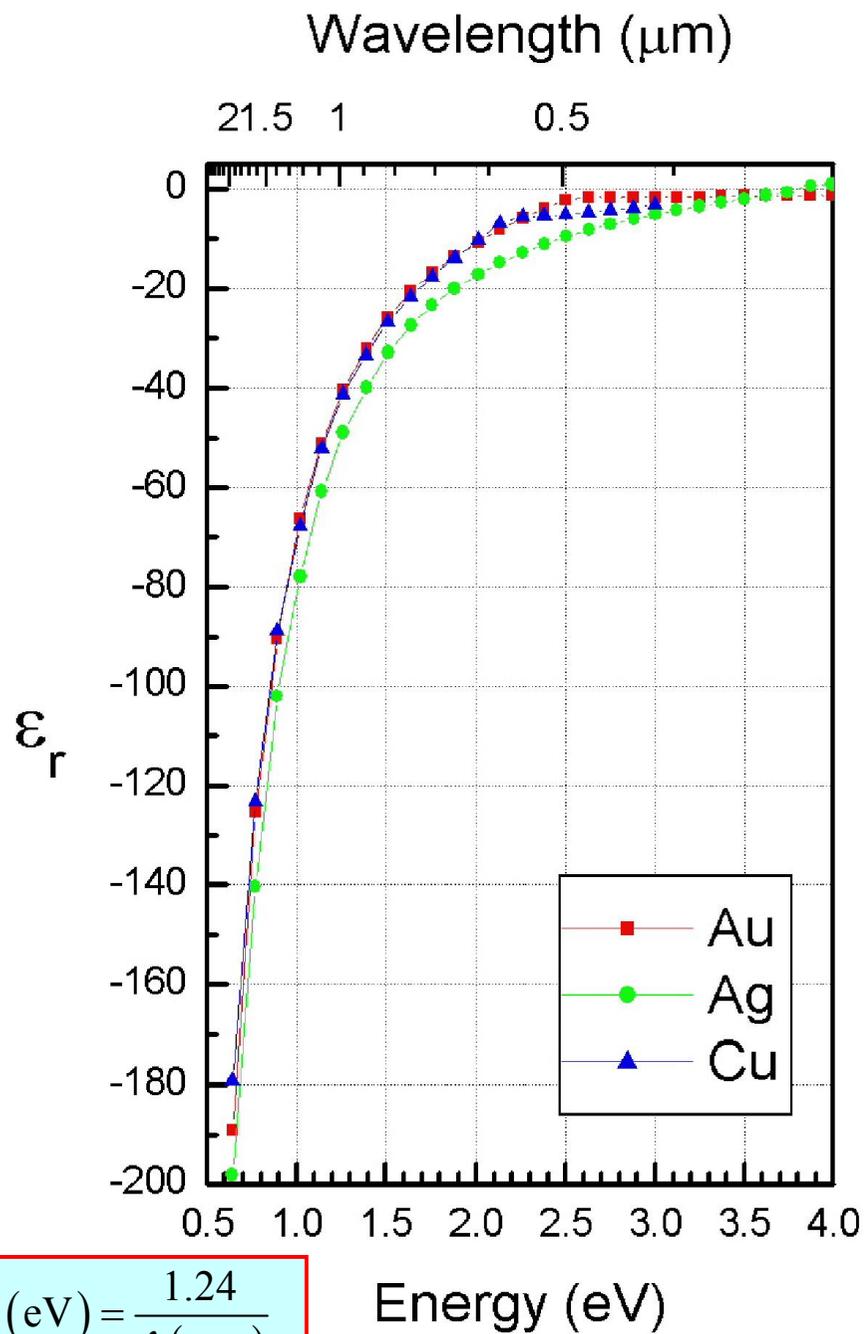
B、贵金属纳米球形颗粒

贵金属在近红外、可见光区的介电性质：

- ① 在低频（包括静电情况）或者微波区，金属导体材料可以看成理想导体；
- ② 在近红外、可见光区，金属导体的介电常数是依赖于波长（或频率）的复数（实部是一个有限的负数，虚部与金属对光波的吸收相联系）。
- ③ 在可见光区，贵金属导体材料的介电常数虚部一般比较小，所以这类材料的光吸收也比较小。

B.几种贵金属导体的介电常数

Johnson et al., *Phys. Rev. B* **6** (1972) 4370.



$$E(\text{eV}) = \frac{1.24}{\lambda(\mu\text{m})}$$

④ 贵金属纳米颗粒，在可见光区，其介电常数的虚部远小于其实部。因此，如果忽略其介电常数的虚部

$$\alpha = \frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d} 4\pi R_0^3$$

共振条件： $\varepsilon(\omega) + 2\varepsilon_d = 0$ 或者 $\varepsilon(\omega_r) = -2\varepsilon_d$

在共振频率 ω_r 处： $\alpha \rightarrow \infty$

理想情况： $\varepsilon_i(\omega) \approx 0$

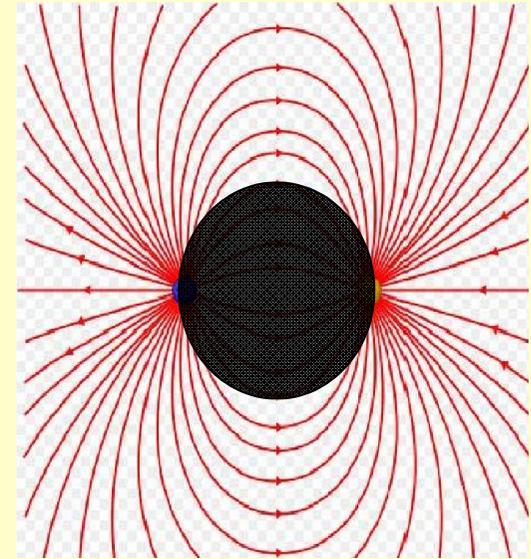
增强因子——无限大

实际情况：贵金属的介电常数存在一个较小的虚部，因此总是能够对入射光的电场产生一定程度的**放大效应**！

$$\alpha = \frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d} 4\pi R_0^3$$

$$|\varepsilon_r(\omega) + 2\varepsilon_d|^2 + |\varepsilon_i(\omega)|^2 = \text{Minimum}$$

表面放大效应：贵金属的介电常数存在一个较小的虚部，因此总是能够产生一定程度的**放大效应**！并且这种放大效应是一种**表面效应**！



共振的物理图像：此时，金属中的电荷高度聚集在金属颗粒的表面，形成所谓的**局域表面等离子激元**（localized surface plasmon）

C: 金属纳米球形颗粒置于外场中的严格数值计算 ——尺寸效应

以理想的金属纳米颗粒为例（忽略其吸收），
假设介电常数的实部可以采用以下的模型
（Drude）模型加以描述：

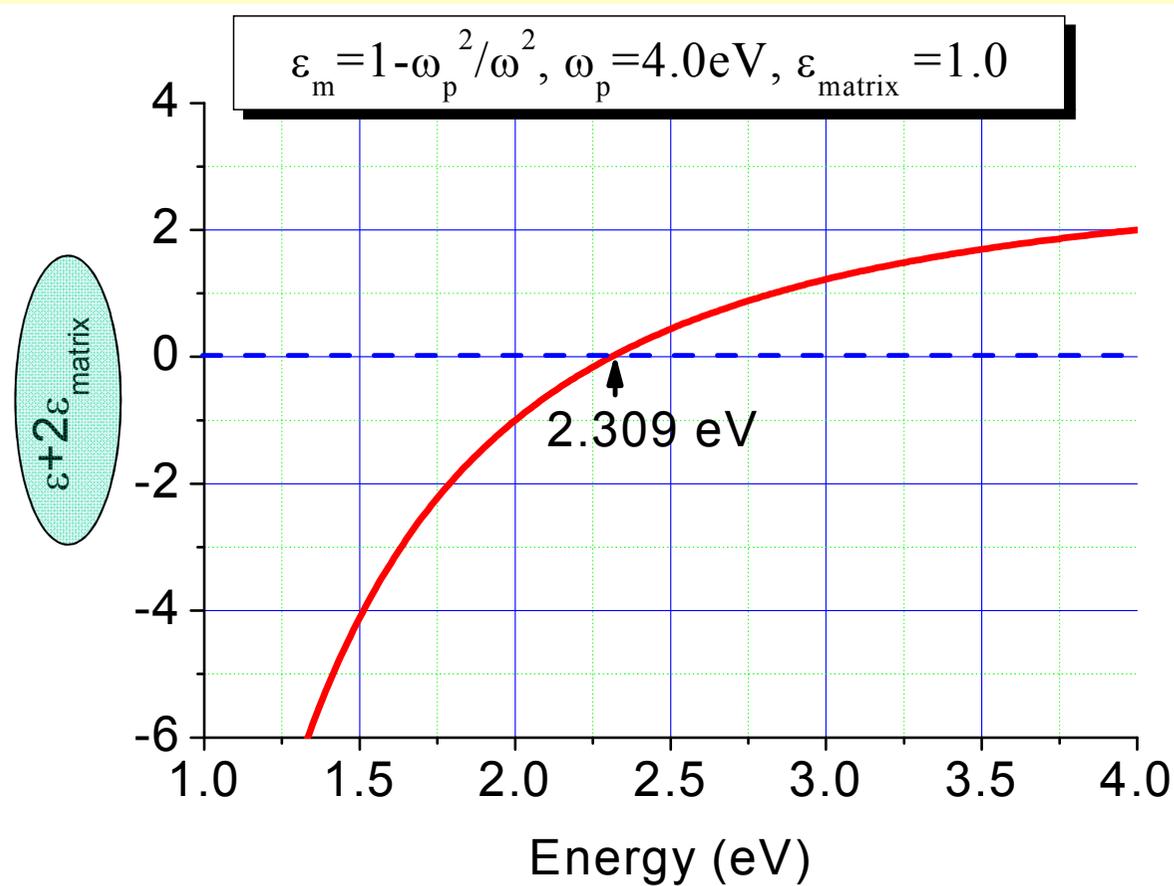
$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

$$\omega_p = 4.0 \text{ eV}$$

$$\varepsilon(\omega) + 2\varepsilon_{matrix} = 0$$

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

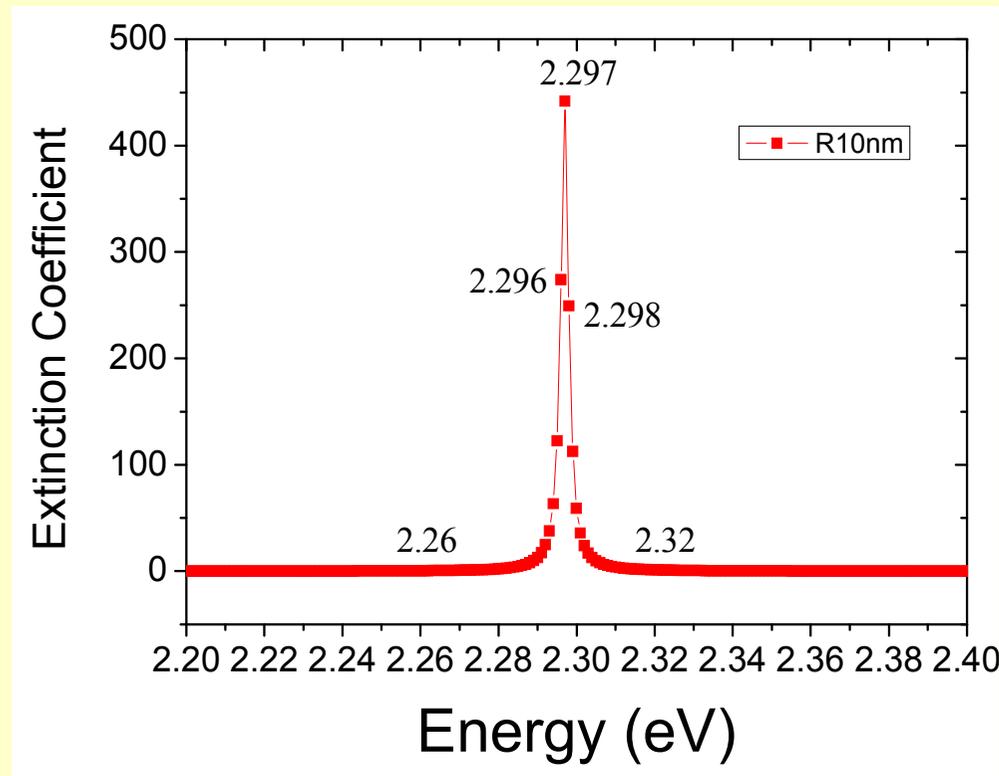
共振频率：
$$\omega_r = \frac{4}{\sqrt{3}} \text{ eV} = 2.309 \text{ eV}$$



$$\hbar\omega_r = 2.305 \text{ eV}$$

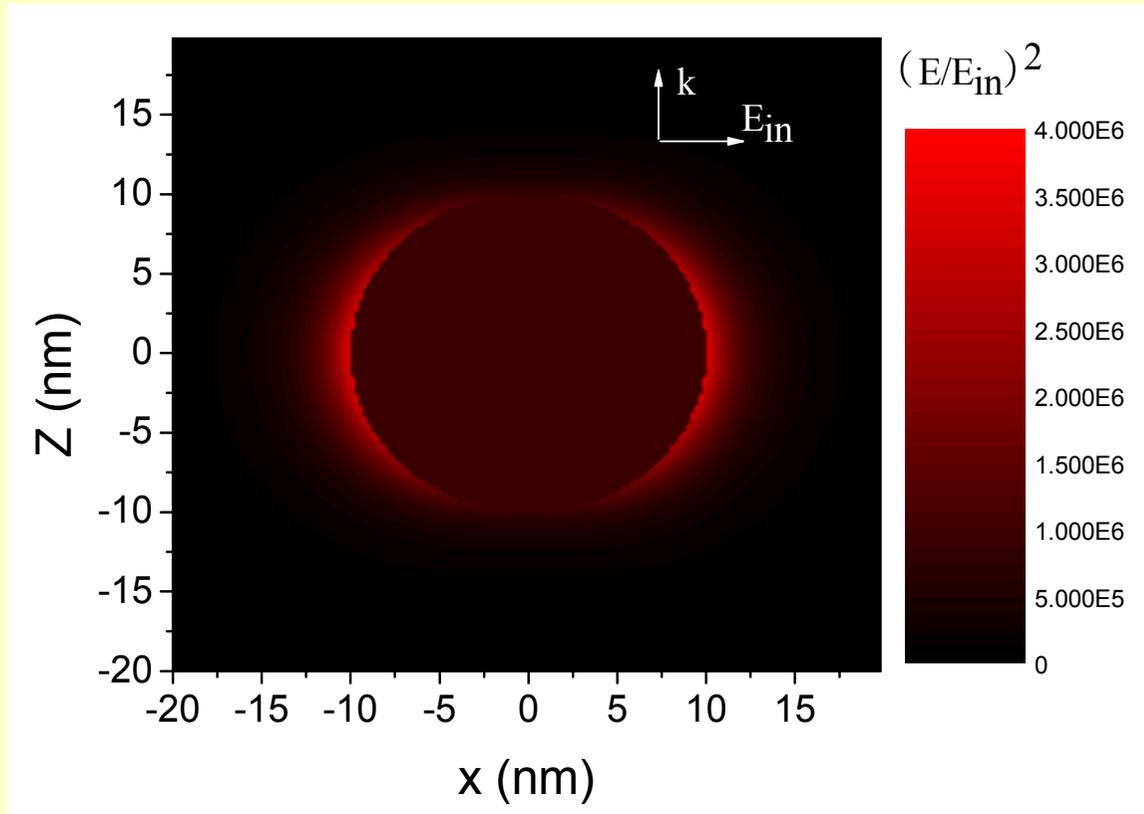
假设颗粒的半径 $R = 10 \text{ nm}$

①采用严格数值计算方法，得到颗粒的消光谱：



数值计算给出的共振位置在 $\hbar\omega_r = 2.297 \text{ eV}$ 处，非常接近偶极近似的理论预测值。

② 采用数值计算的方法，得到对应于消光峰 $\varepsilon = 2.297 \text{ eV}$ 处，颗粒内外的电场分布：



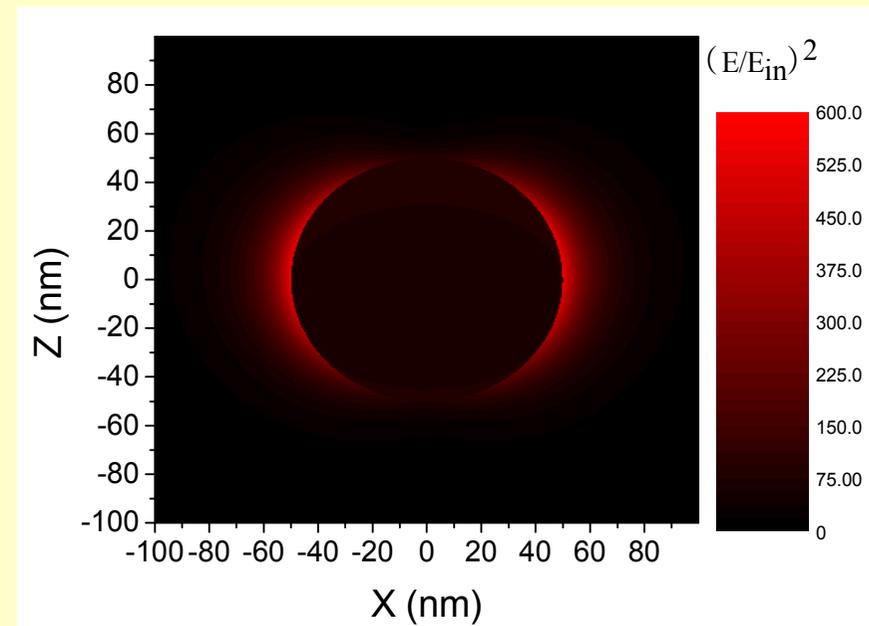
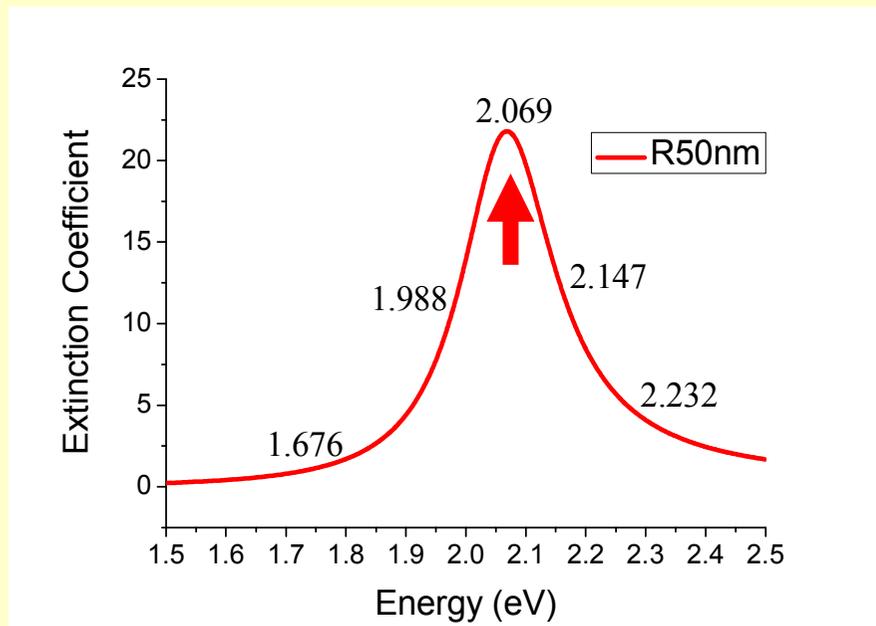
**Near field intensity
enhancement = 10^6 !**

可以看出，纳米球的表面电场有显著的增强，而在其内部，也存在很强的电场增强效应。

假设金纳米球 $R=50\text{ nm}$

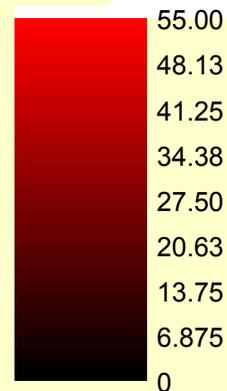
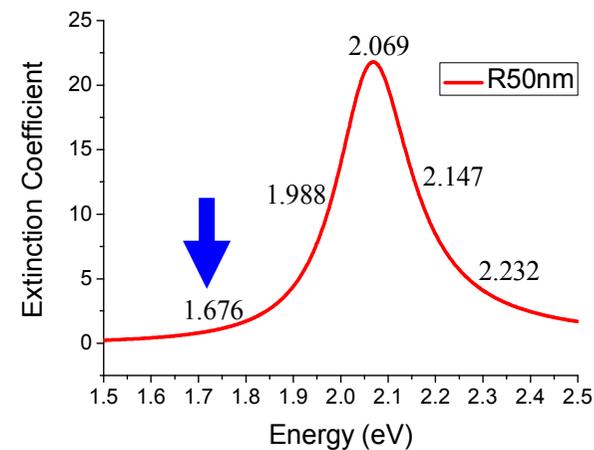
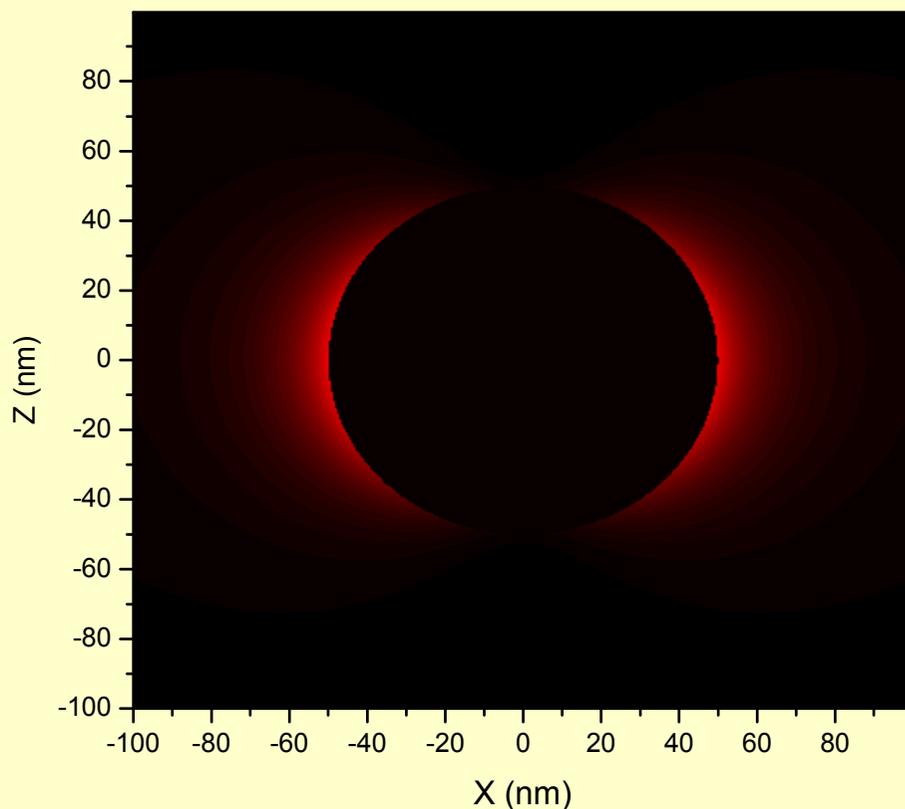
① 数值计算得到的消光谱：

**Near field intensity
enhancement = 600!**



可以看出，此时消光谱仍存在一个共振峰，但峰位与偶极近似值有大的差异。

③ 非共振位置处，金纳米球电场分布



最高值减小到：55

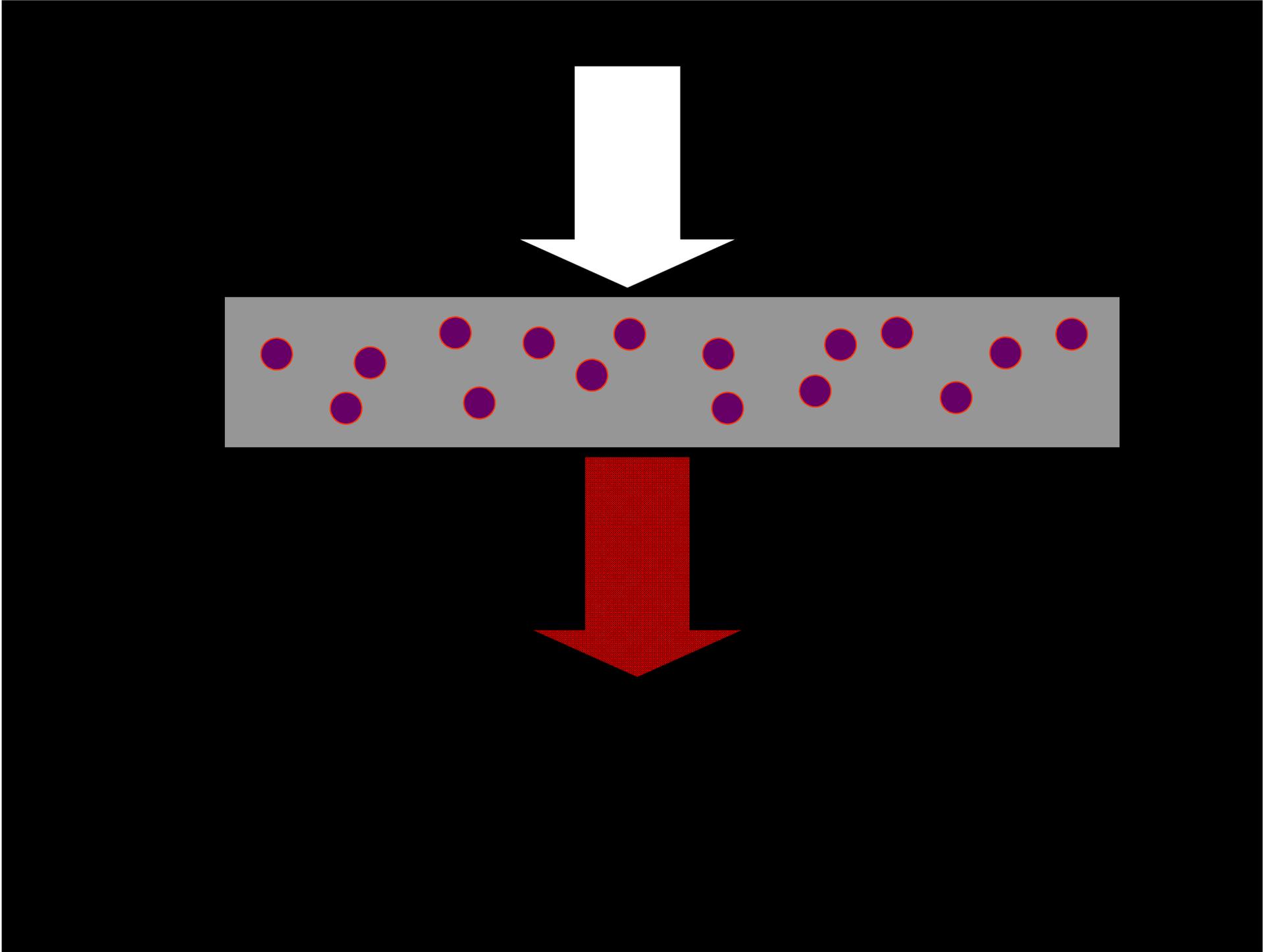
可以看出，球内的电场非常弱，而球外的电场也降低许多。

共振的物理涵义：

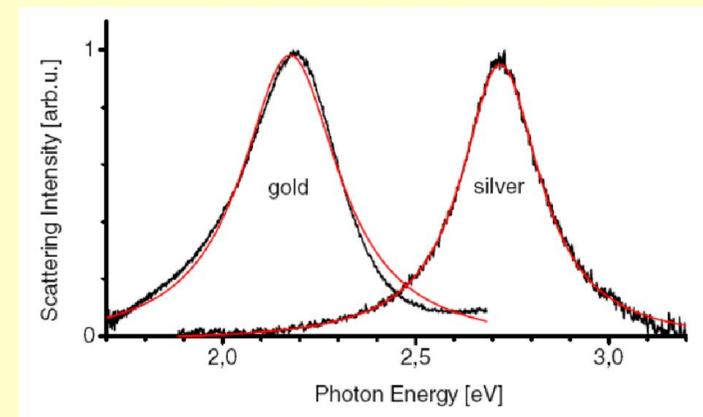
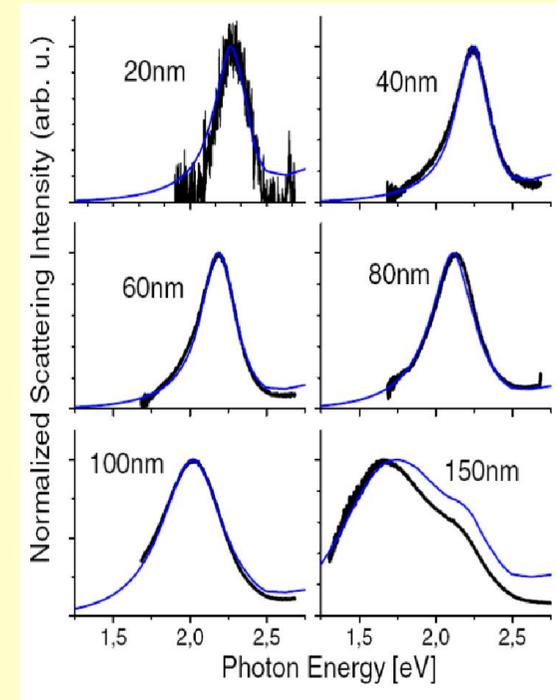
- ① **物理图像**：在共振情形下，电荷密度在金属纳米颗粒表面聚集，形成一种高密度的局域分布；这种共振又称为**局域表面等离子激元共振**（**Localized Surface Plasmon , LSP**）；
- ② **特点**：伴随LSP共振激发，会产生局域的电场增强（或者称为放大）效应；
- ③ **金属纳米颗粒的LSP的频率依赖于颗粒的组分、大小和形状**

$$\alpha = \frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d} 4\pi R_0^3$$

（适用于尺寸小于光波长的球形纳米颗粒）

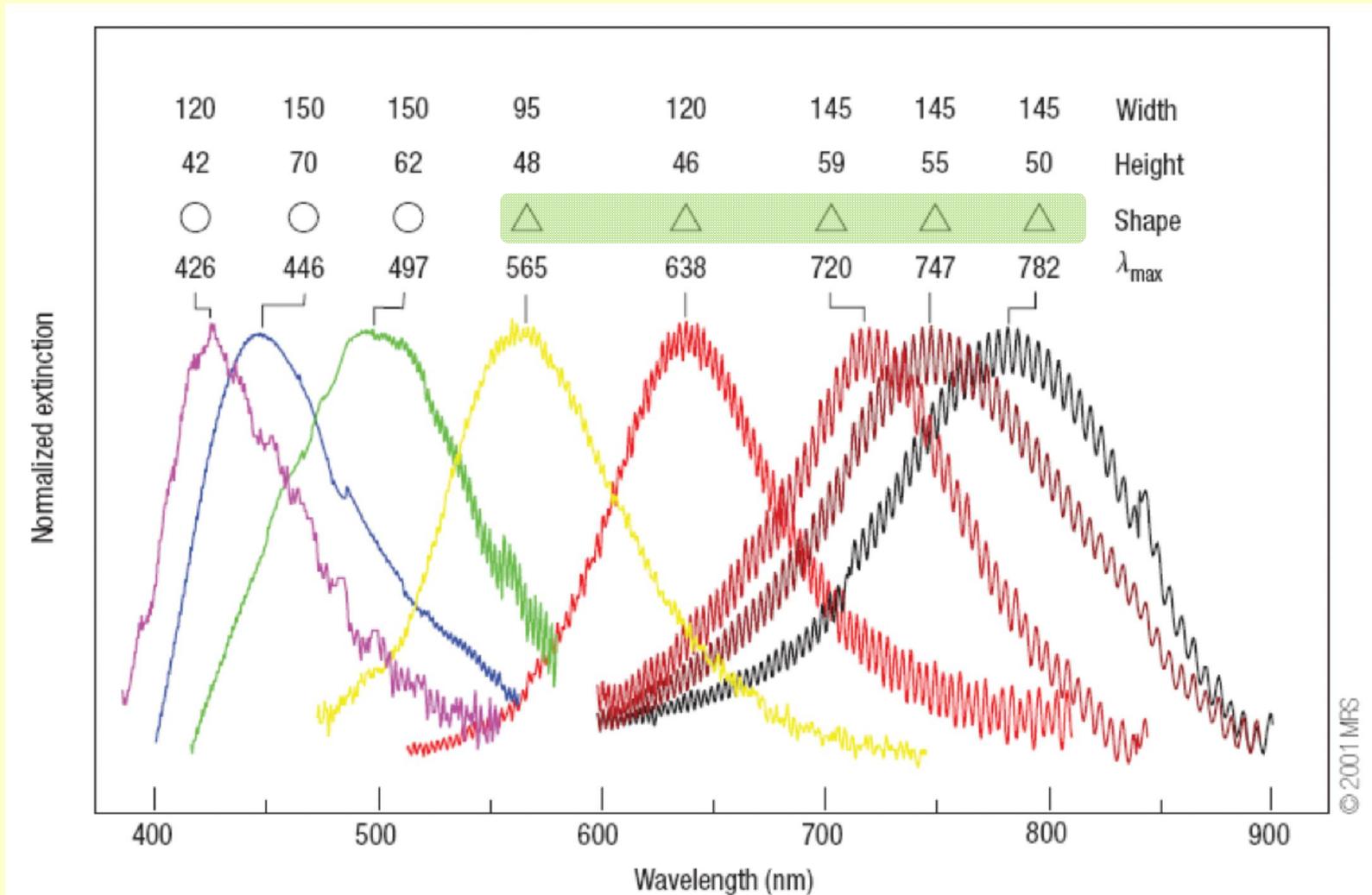


Growth of Monodisperse Metal Colloids



www.tedpella.com

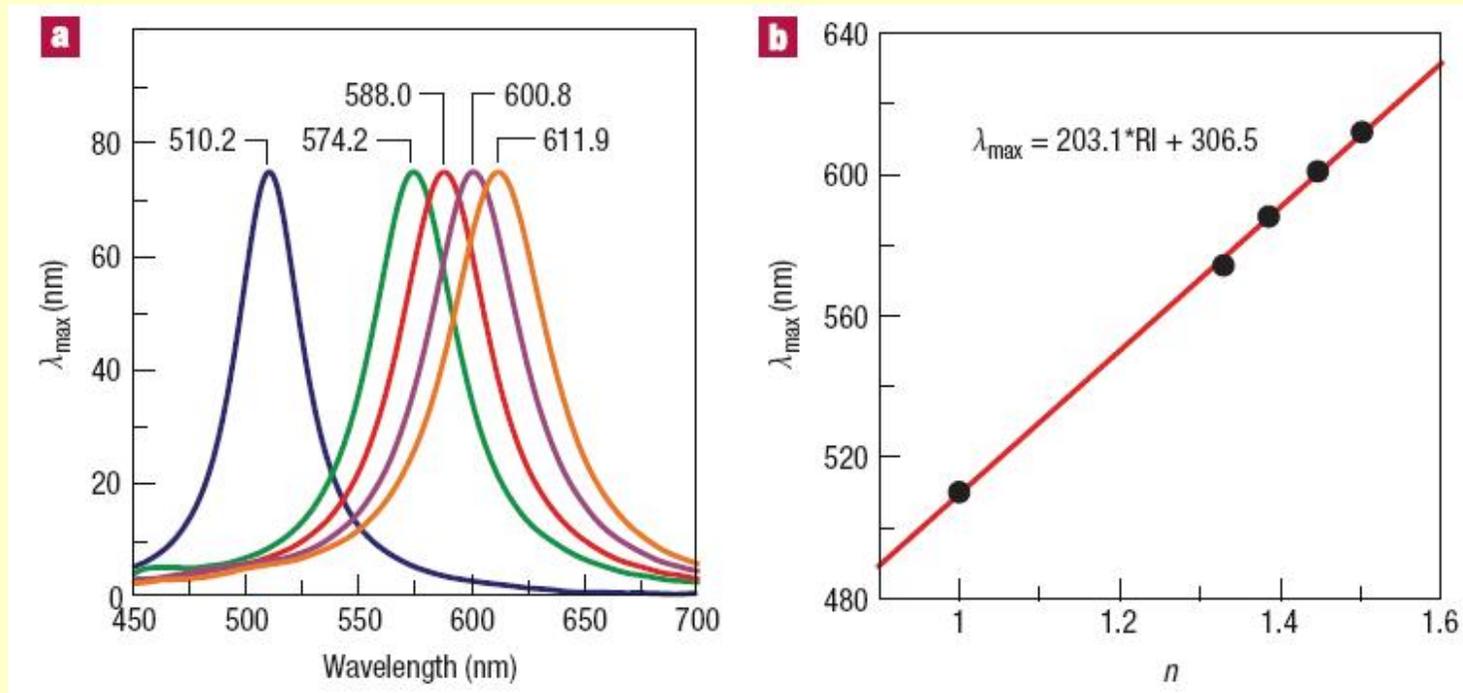
Shape Dependence



Silver

Mater. Res. Soc. Symp. 636, D4.8 (2001).

Surrounding Medium Dependence



Single nanoprism LSP (a), Resonant Rayleigh scattering spectrum from a single silver nanoparticle in various solvent environments (left to right): nitrogen, methanol, propan-1-ol, chloroform and benzene. (b), Plot depicting the linear relationship between the solvent refractive index n and the LSPR λ_{max} ; the regression equation is $\lambda = 203.1n + 306.5$.

Nano Lett. 3, 1057–1062 (2003)

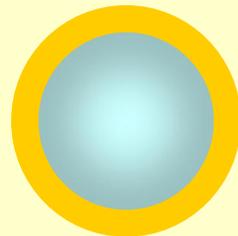
Gold Nanoshells and Gold Colloids



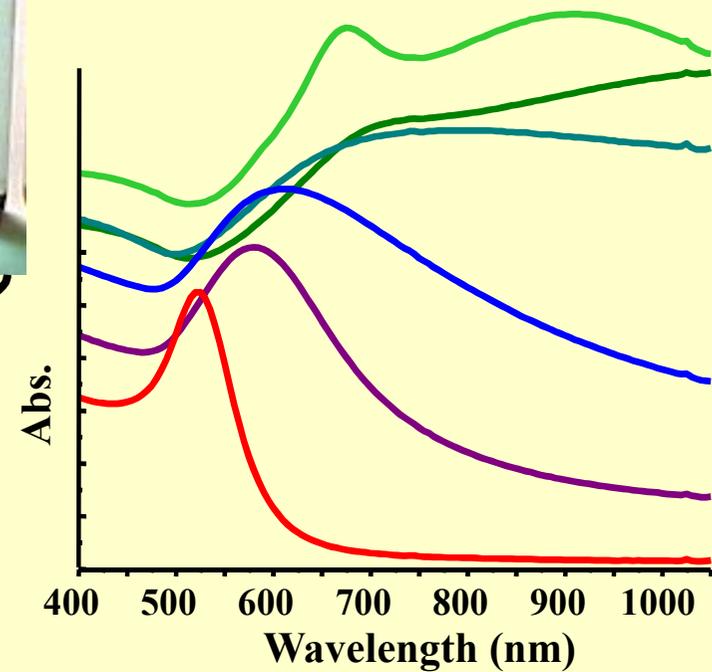
**Au
Colloid**



**Au
Nanoshells**



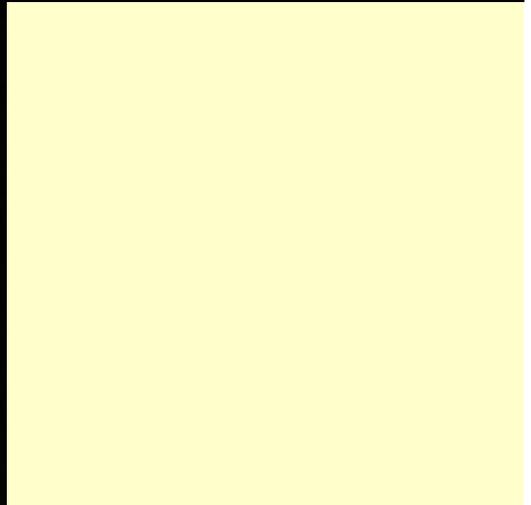
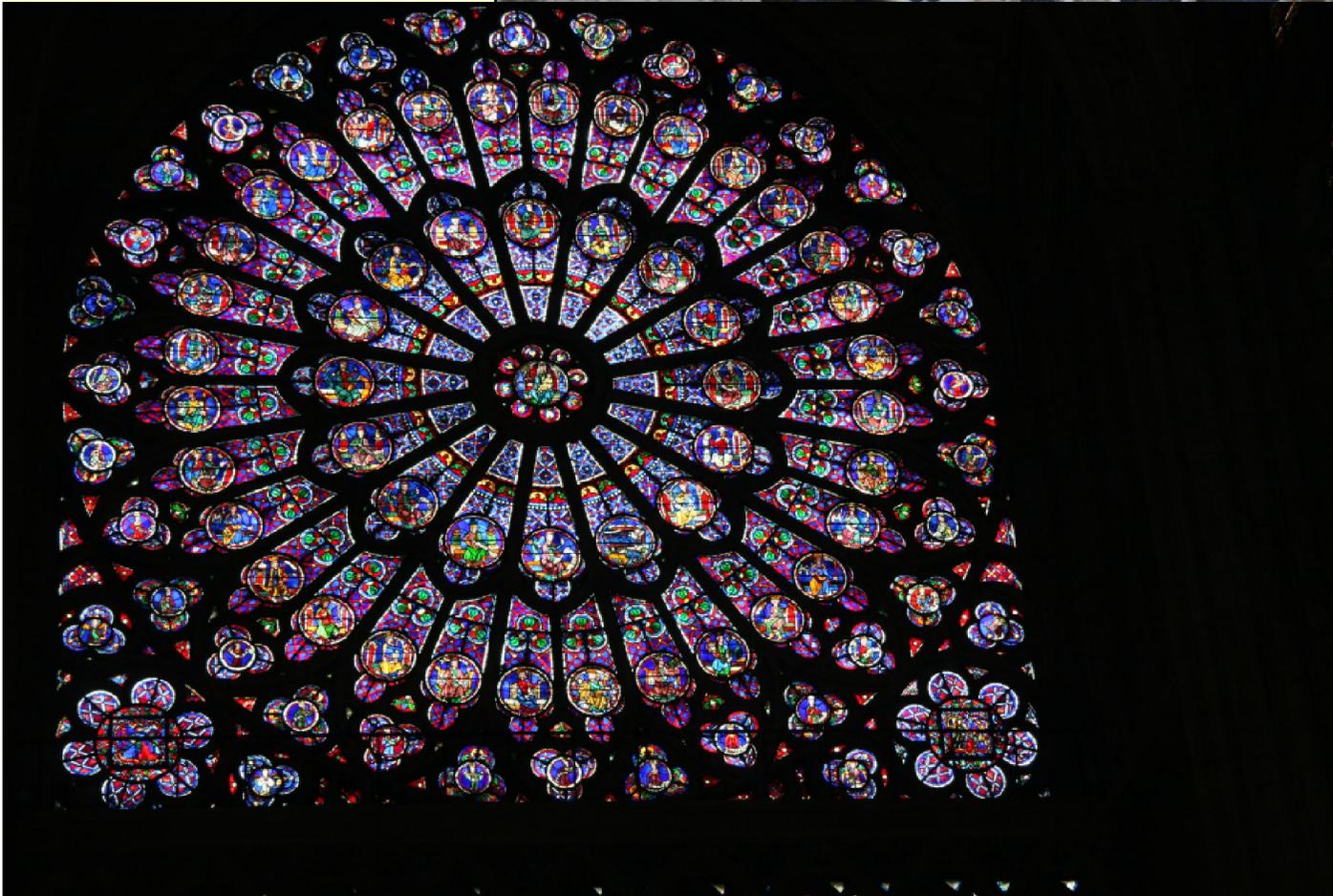
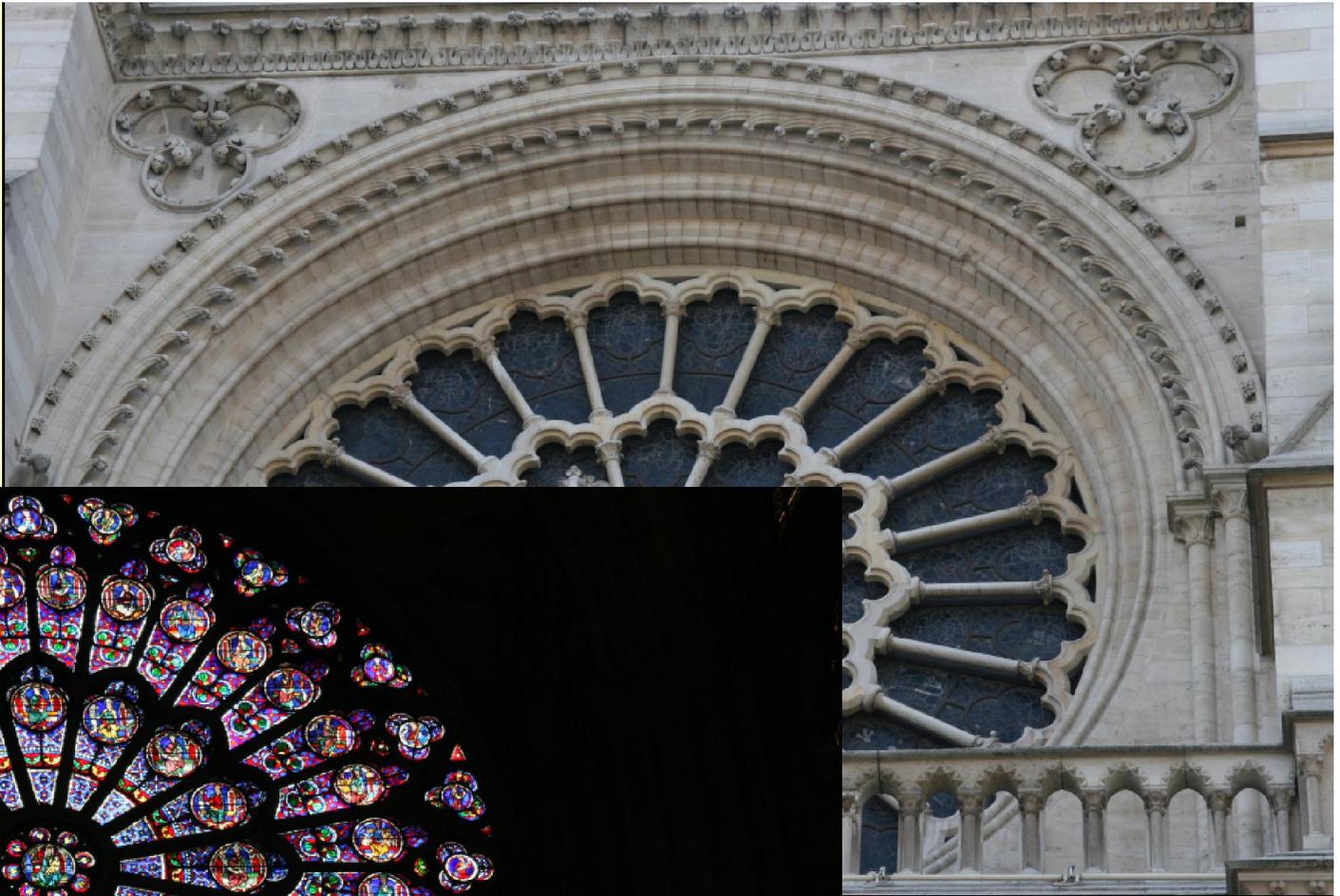
**Absorbance spectra of
gold nanoshells:**



巴黎圣母院外景







D: 金属纳米颗粒的局域电场增强特性的应用

- ① 利用这种强电场效应，可以使得许多原本效率非常低的非线性光学过程的效率得到显著的提高；
- ② 由于这种局域的增强效应发生在距离颗粒表面的纳米尺度范围内，因此可以实现单分子层的检测灵敏度；

Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering

Shuming Nie* and Steven R. Emory

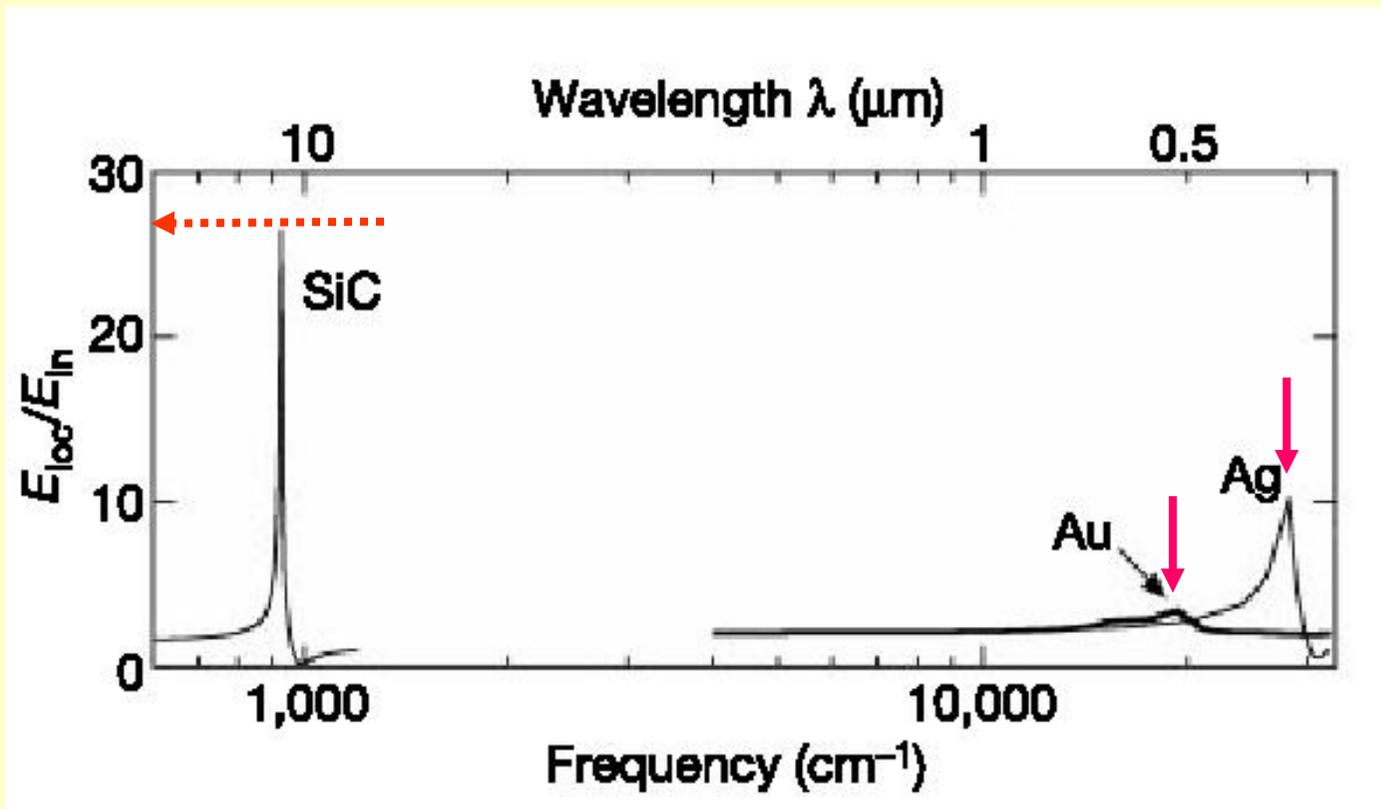
Optical detection and spectroscopy of single molecules and single nanoparticles have been achieved at room temperature with the use of surface-enhanced Raman scattering. Individual silver colloidal nanoparticles were screened from a large heterogeneous population for special size-dependent properties and were then used to amplify the spectroscopic signatures of adsorbed molecules. For single rhodamine 6G molecules adsorbed on the selected nanoparticles, the intrinsic Raman enhancement factors were on the order of 10^{14} to 10^{15} , much larger than the ensemble-averaged values derived from conventional measurements. This enormous enhancement leads to vibrational Raman signals that are more intense and more stable than single-molecule fluorescence.

S. Nie and S. R. Emory, **Science** **275** (1997) 11102.

Phonon-enhanced light-matter interaction

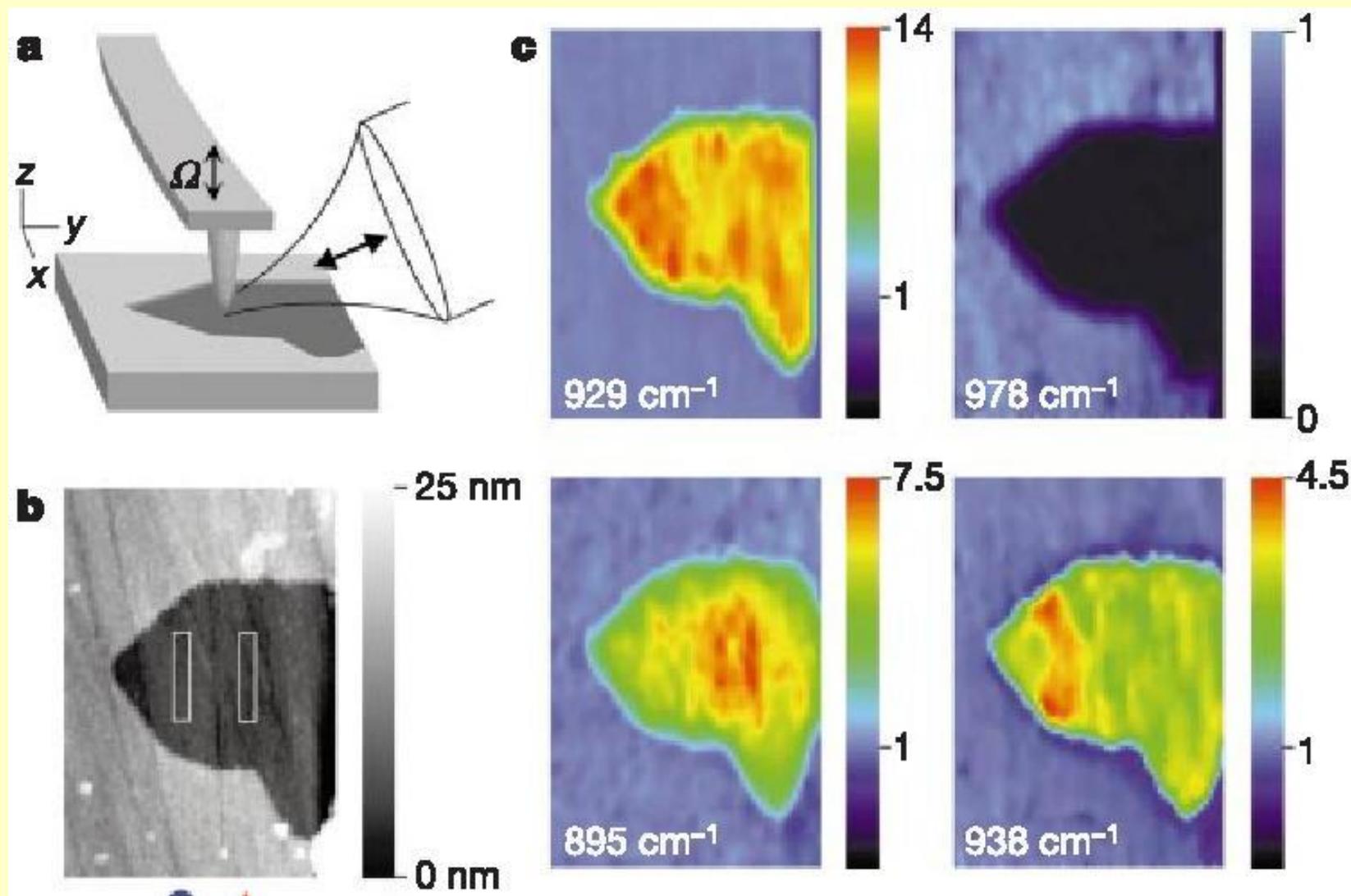
$$\alpha = \frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d} 4\pi R_0^3$$

$$|\varepsilon_r(\omega) + 2\varepsilon_d|^2 + |\varepsilon_i(\omega)|^2 = \text{Minimum}$$



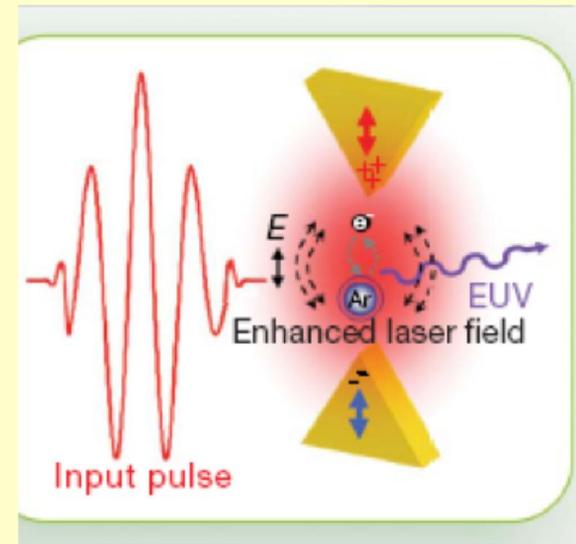
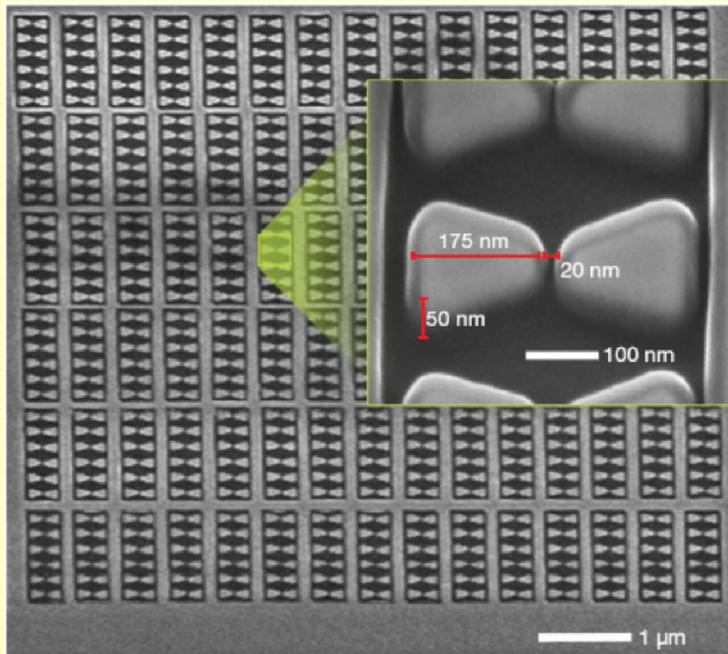
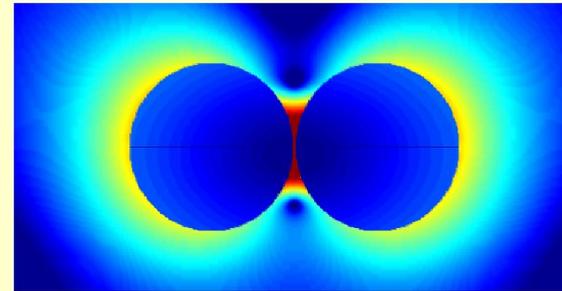
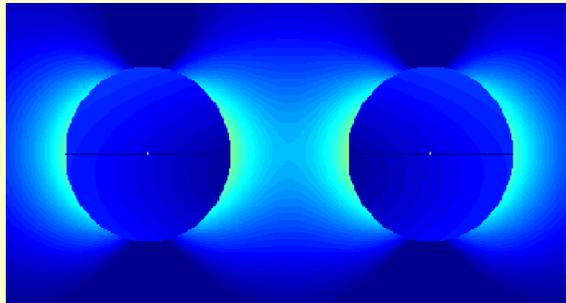
R. Hillenbrand et al., *Nature*, **418** (2002) 159.

实验结果:



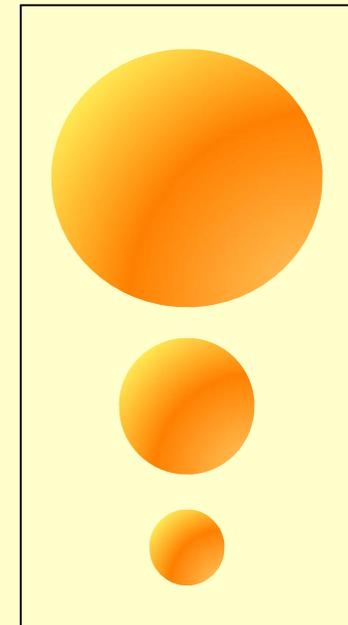
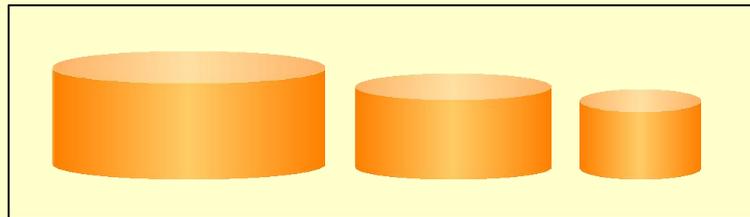
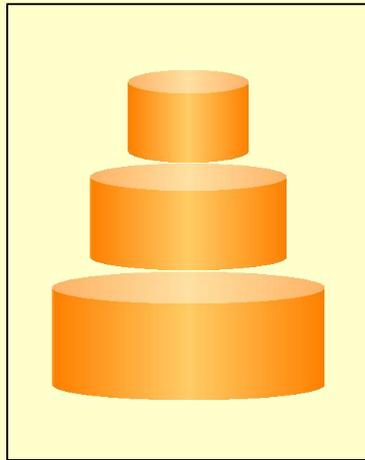
R. Hillenbrand et al., *Nature*, 418 (2002) 159.

Bowtie Au nanostructures for creating hotspots (with enhanced electric field)

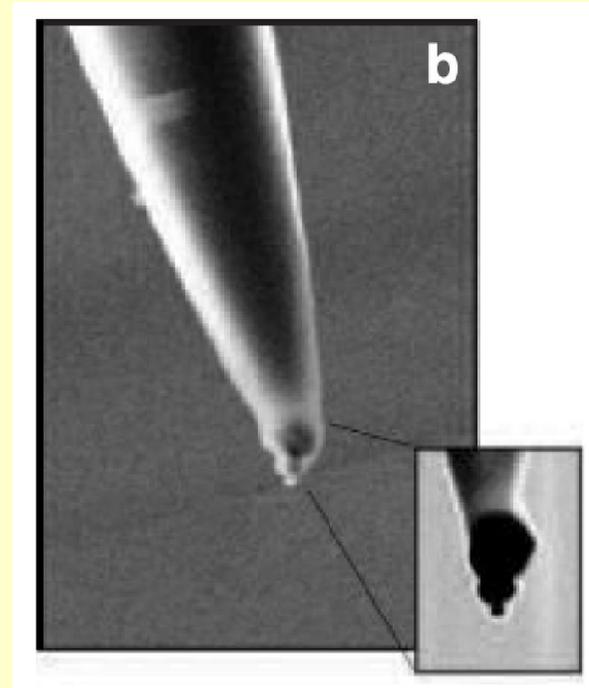
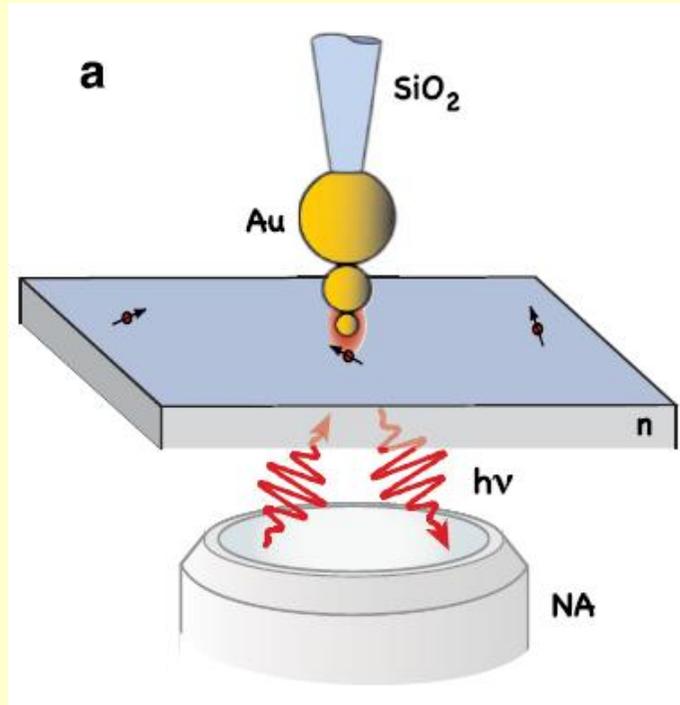


S.C. Kim, et al., Nature, 435, 757 (2008).

Self-Similar Gold-Nanoparticle Antennas for a Cascaded Enhancement of Optical Field



Self-Similar Gold-Nanoparticle Antennas for a Cascaded Enhancement of Optical Field



Theory: M. I. Stockman, PRL 91, 227402 (2003).

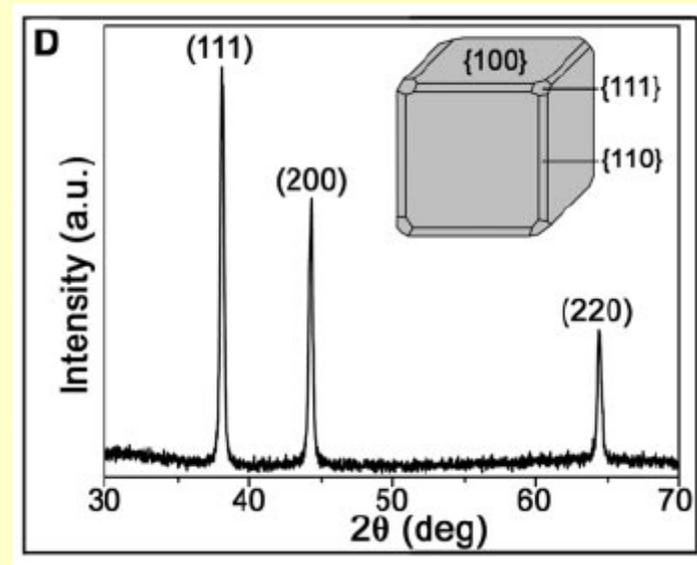
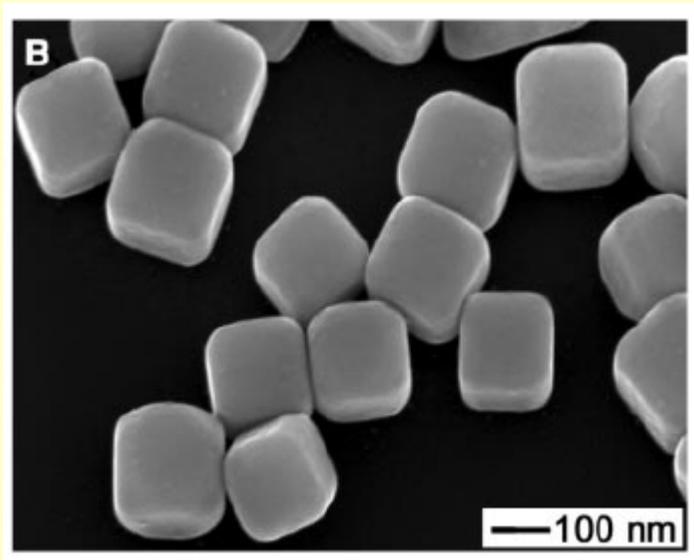
First Expt.: V. G. Kravets et al., PRL 105, 246806 (2010).

Second Expt.: C. Hoppener et al., PRL 109, 017402 (2012)

表面拉曼增强（SERS）生物检测芯片

- 获得反映物质组成结构信息的指纹图谱；
- 表面拉曼增强可将微弱的拉曼信号放大1百万倍；
- SERS芯片应用于医学诊断、药物检测、刑侦和国土安全

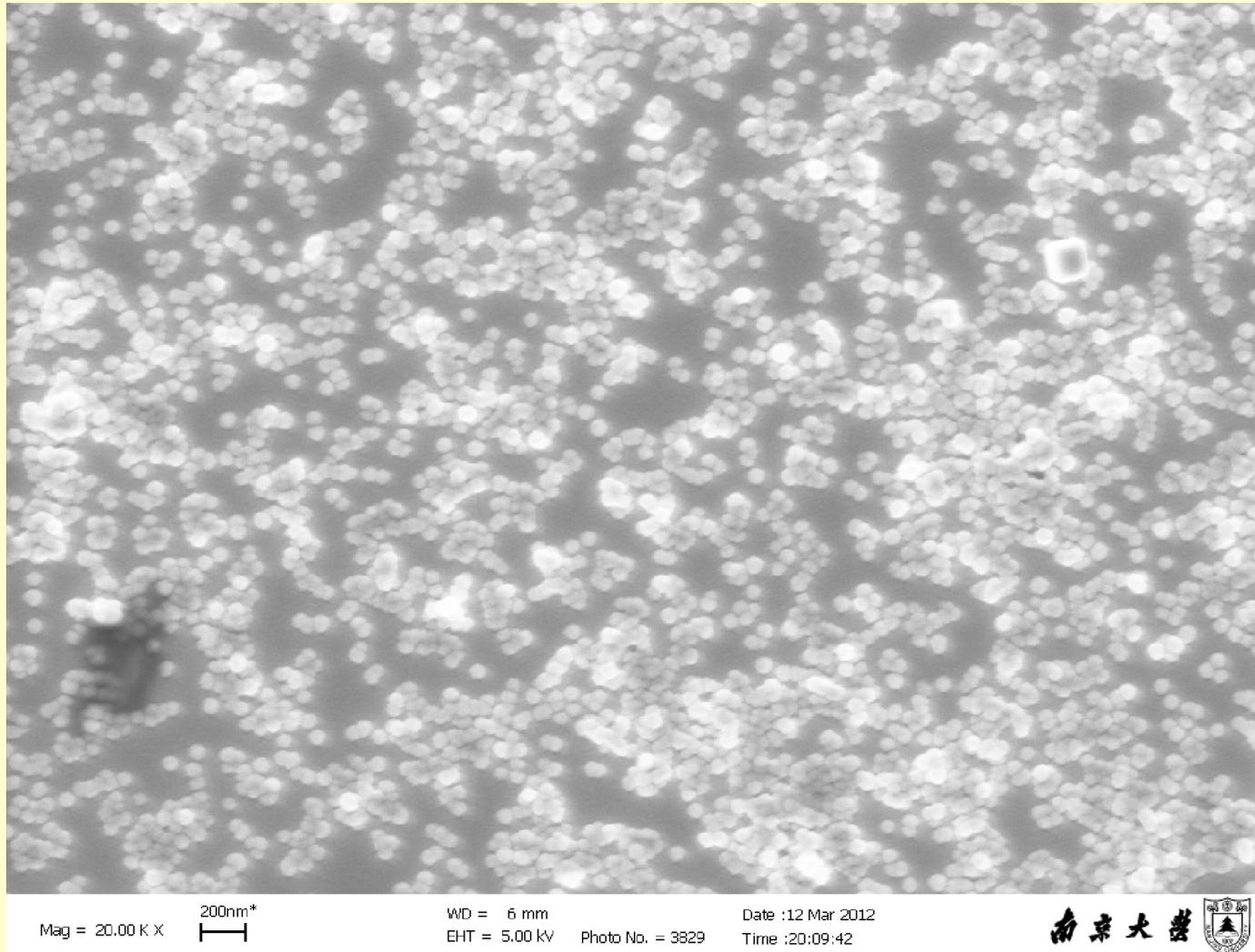
Synthesis of Gold Nanocubes



Y. Sun and Y. Xia, *Science* 298, 2176 (2002)

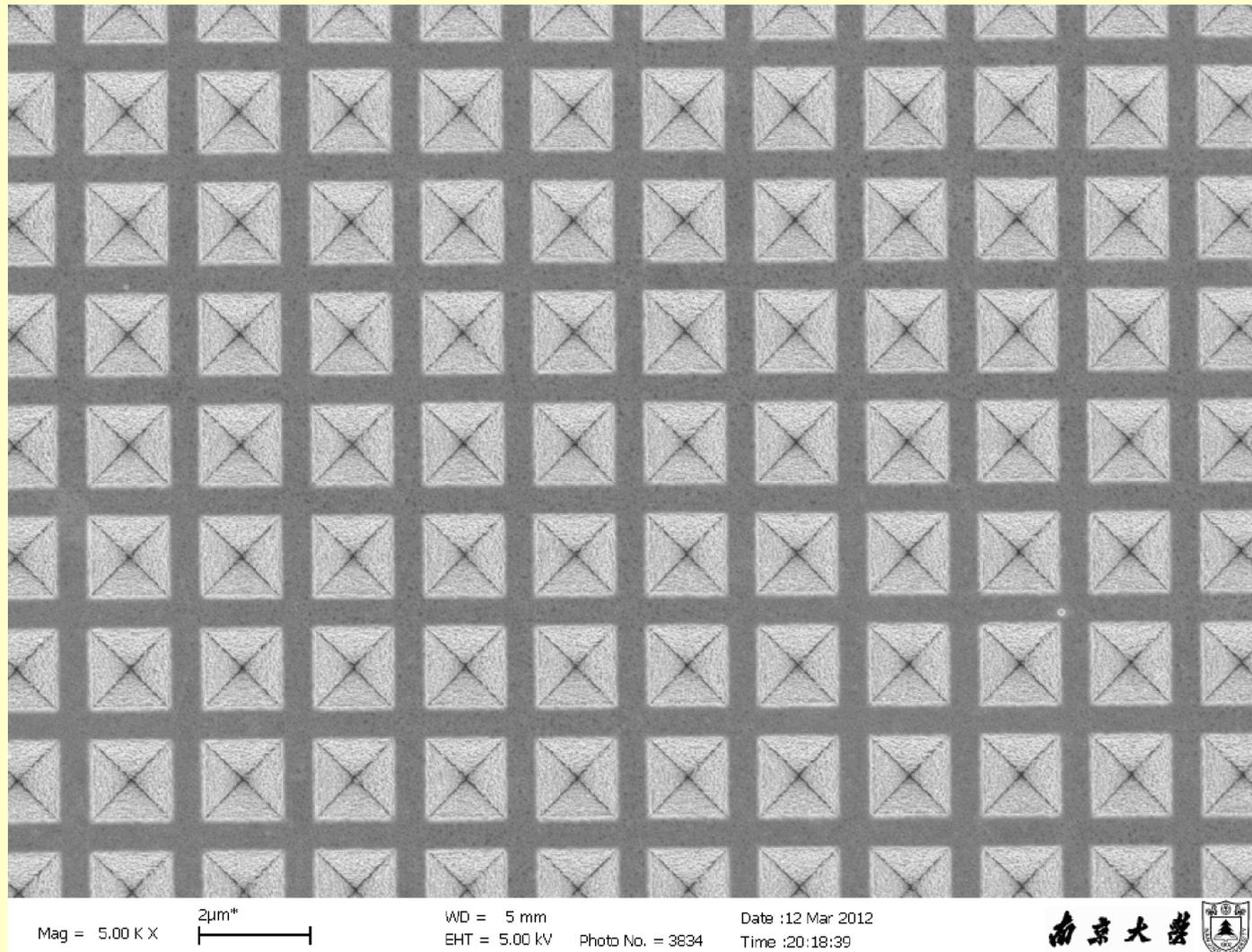
目前市场上的两类拉曼增强生物检测芯片

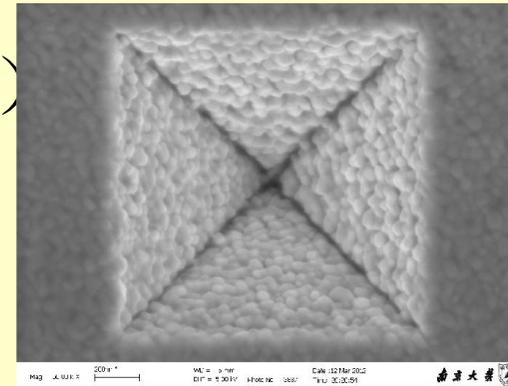
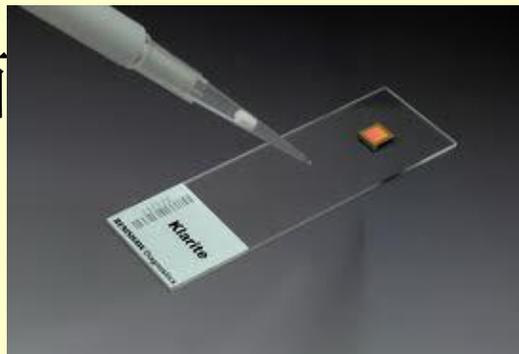
A、金属纳米颗粒组成的无序结构



目前市场上的两类拉曼增强生物检测芯片

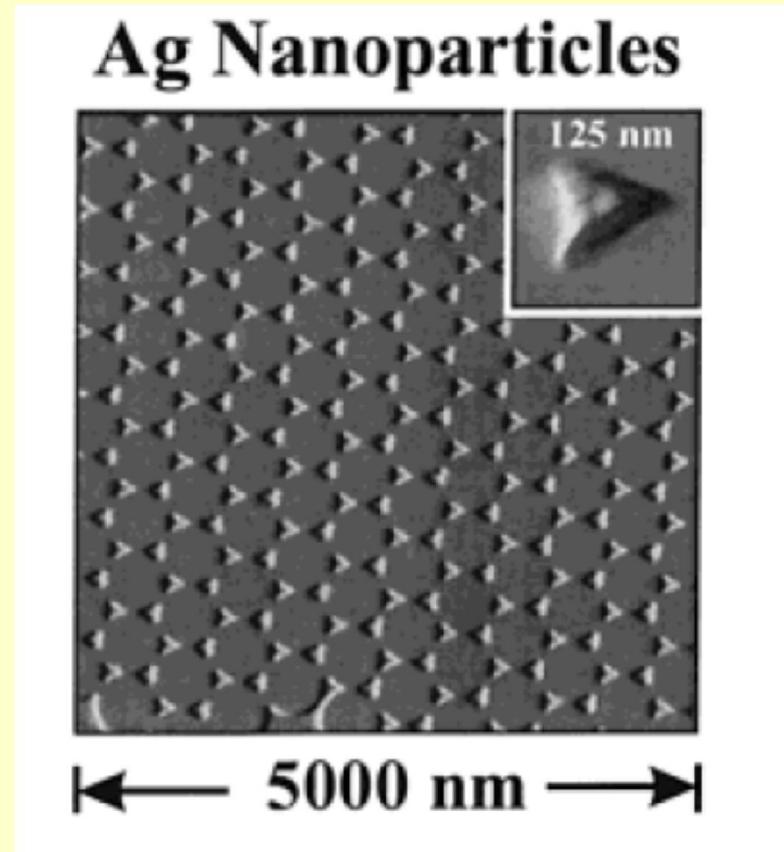
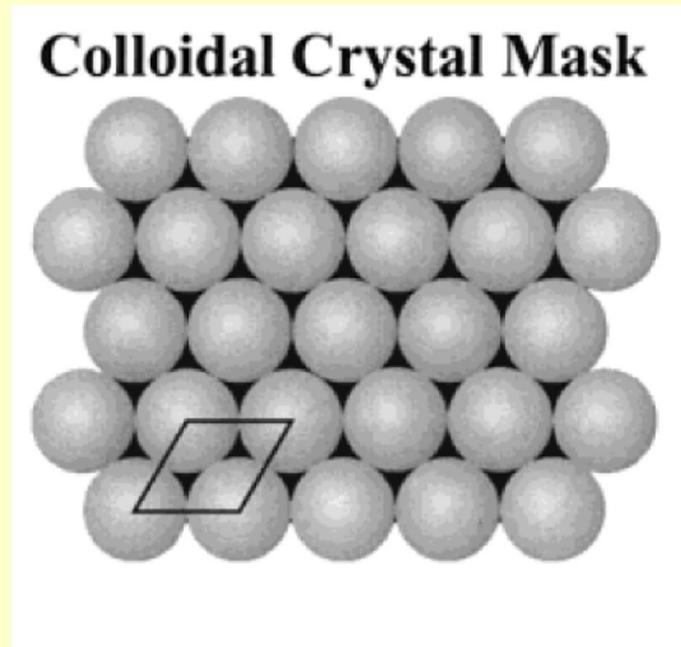
B、周期性的金属纳米结构





Klarite	载玻片式	芯片式
尺寸(mm)	75x25x2	6x10x0.5
有效面积 (mm)	4x4	
有效表面	镀金硅结构	
采样方法	将溶液蒸发，粘结到金材料上进行测量	
拉曼激发参数	633 nm, 785 nm >5 μm 采样点 (>100 μm 建议) 2mW per 10 μm ²	
增强因子, 相对于非增强表面	>10,000 对于大多数材料 >1,000,000 对于粘结材料	

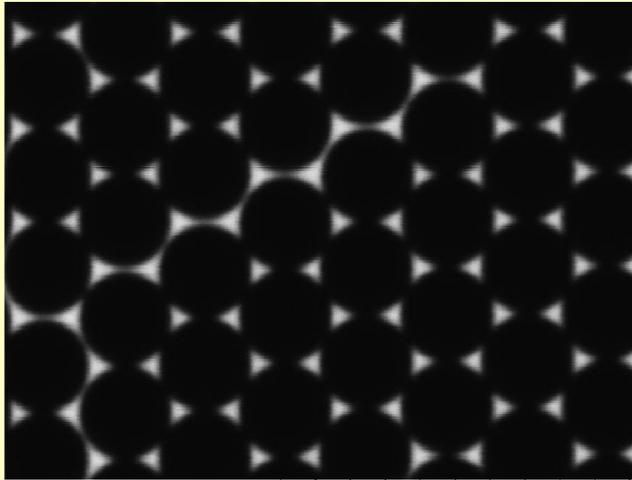
Metallic Nanoparticles via Nanosphere lithography



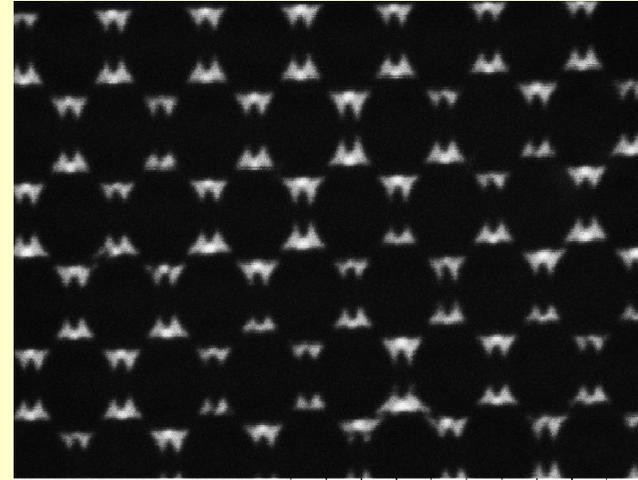
C . L. Haynes and R . P. Van Duyne, *J. Phys. Chem. B* 2001, 105, 5599-5611

Au triangles

(singleton, twins, triplets, quadruplets)



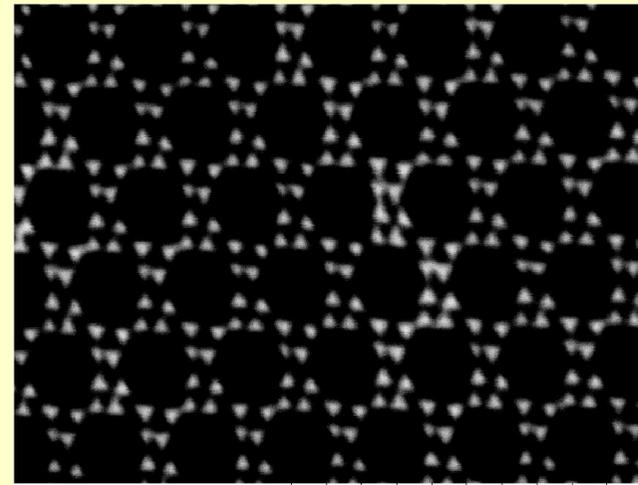
TM3000_5668 2012-09-28 11:24 NL x30k 3.0 um



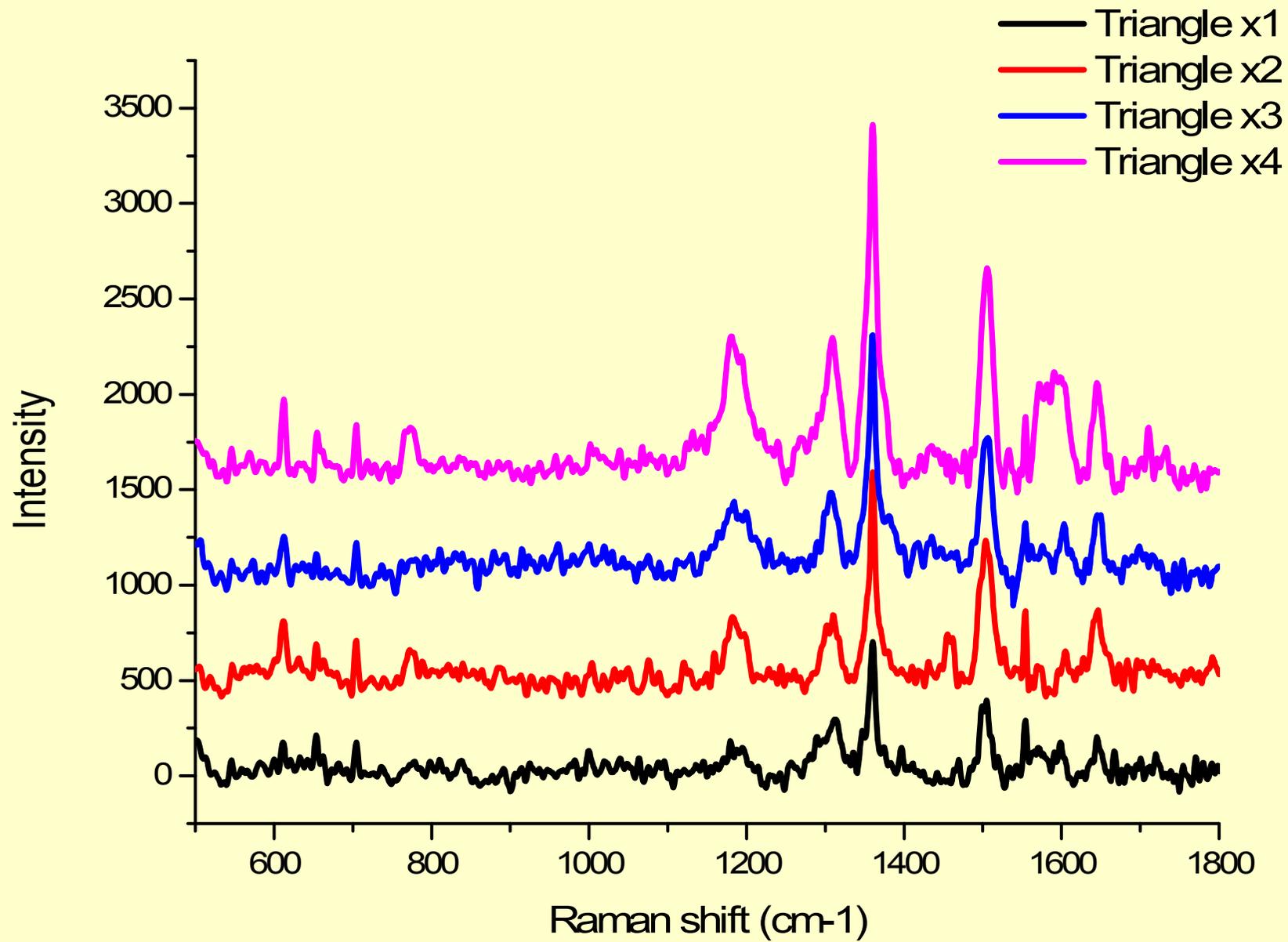
TM3000_1733 2012-03-15 23:02 NL x30k 3.0 um



TM3000_1257 2012-01-10 19:31 NL x30k 3.0 um



TM3000_5684 2012-09-28 21:10 NL x30k 3.0 um



- **注意：**
- **高频波段，理想的金属是介电常数趋于负无穷，而虚部分为零，或者为正无穷大，两者的物理结果是相同；**
- **绝缘介质和金属的介电常数的色散特点，后面我们会做专门的介绍；**
- **在可见光 / 近红外波段，电导率模型已经不适用于金属在这一波段的性质**
- **思考：为何LSP的线宽很宽？**
- **思考：如何实现颗粒内或者表面的磁场的增强？**

相关的参考可以参见《表面等离激元研究新进展》，
王振林，物理学进展，29，287-324（2009）

- ❑ Enhanced optical transmittance
- ❑ Controlling nanoparticle growth
- ❑ Nonlinear optics
- ❑ Subwavelength waveguide
- ❑ Surface-enhanced Raman & PL spectroscopy
- ❑ Biophysics
- ❑ Metamaterials
- ❑ Subwavelength imaging
- ❑ Optical antenna
- ❑ Cloaking
- ❑ Single photon source
- ❑ etc

作业

(2013年10月17日)

第二章 习题 5、8