SPECIAL LECTURE

THERMODYNAMIC INTERPRETATION

ADAPTED FROM LANDAU & LIFSHITZ "ELECTRODYNAMICS OF CONTINUOUS MEDIA," CHAPT II.

WE CONSIDERED DIELECTRIC CONSTANTS ε THAT DOES NOT CHANGE WITH $\vec{E}$ AND CAN ONLY DEPEND ON POSITION IN THE MEDIA. HOWEVER, DIELECTRIC CONSTANTS TYPICALLY DEPEND ON TEMPERATURE, SO THE PROCESS OF CHANGING THE FIELD IN THE MATERIAL IS AN ISOTHERMAL PROCESS. THIS IN TURN REQUIRES THE MATERIAL TO BE IN CONTACT WITH A HEAT BATH SO AS TO EXCHANGE HEAT TO MAINTAIN THE MATERIAL AT CONSTANT TEMPERATURE.

IN CLASS WE FOUND THE INCREASE IN WORK $\delta W = \iiint \vec{E} \cdot \delta \vec{D}\, dV$, THIS IS NOT THE INCREASE IN TOTAL ENERGY SINCE HEAT IS TRANSFERRED TO AND FROM THE BATH. HOWEVER, δW IS THE MAXIMUM POSSIBLE WORK THAT CAN BE TAKEN FROM THE FIELD ENERGY AT A CONSTANT TEMPERATURE. THIS IS THE DEFINITION OF THE FREE ENERGY F OF THE SYSTEM.

F IS NOT THE SAME AS THE TOTAL ENERGY OF THE SYSTEM.

HENCE, $U = \frac{1}{2}\iiint \vec{E}\cdot\vec{D}\, dv$ IS REALLY THE SYSTEM'S FREE ENERGY. IF YOU HAD, HOWEVER, A DIELECTRIC WITHOUT TEMPERATURE DEPENDENCE, THEN THE FREE ENERGY CAN BE CONSIDERED THE TOTAL ENERGY.

WE SHOULD MORE CORRECTLY WRITE $\delta W = \iiint \vec{E}\cdot\delta\vec{D}$ AS A FREE ENERGY INCREMENT δF:

$$\delta F = \iiint \vec{E}\cdot\delta\vec{D}\, dv \Big|_{\substack{\text{CONSTANT}\\ \text{TEMPERATURE}}}.$$

FROM THERMODYNAMICS:

$$F = U - Ts = \frac{1}{2}\iiint \vec{E}\cdot\vec{D}\, dv$$

HERE: U IS THE TOTAL ENERGY

S THE ENTROPY

T THE TEMPERATURE.

THIS LOOKS VERY SIMILAR TO

$$F \sim \iiint P\, dV$$

SO IN A THERMODYNAMIC SENSE, $\vec{E}$ IS LIKE A PRESSURE, AND $\vec{D}$ IS A VOLUME.

WE CAN NOW DERIVE THE TOTAL ENERGY:

$$\delta F = \delta U - T\delta S - S\delta T$$

HOWEVER, THE 1^{ST} LAW READS

$$\delta W = \delta U - T\delta S$$

WITH $\delta W = \iiint \vec{E}\cdot\vec{D}\, dv$

WE THEREFORE HAVE

$$S = -\left.\frac{\partial F}{\partial T}\right|_{\substack{CONSTANT \\ D}}$$

$$= \iiint \frac{1}{2} E^2 \frac{\partial \varepsilon}{\partial T}\, dv$$

$$= \iiint \frac{\vec{E}\cdot\vec{D}}{2}\, \frac{1}{\varepsilon}\frac{\partial \varepsilon}{\partial T}\, dv$$

THE HEAT TRANSFERRED TO THE DIELECTRIC WHEN THE FIELD IS CHANGED AT CONSTANT TEMPERATURE IS

$$\delta Q = T\delta S = \iiint \vec{E}\cdot\delta\vec{D}\, \frac{T}{\varepsilon}\frac{\partial \varepsilon}{\partial T}\, dv$$

EXAMPLE SUPPOSE A DIELECTRIC BEHAVES ACCORDING TO THE CLAUSIUS - MOSSOTTI RELATION:

$$\frac{\varepsilon}{\varepsilon_0} - 1 = N\alpha_0 + \frac{N P_0^2}{3\varepsilon_0 k_B T}$$

WITH N THE DENSITY OF MOLECULES,
P_0 THE INTRINSIC DIPOLE MOMENT
α_0 A CONSTANT ACCOUNTING FOR THE DISTORTION OF THE MOLECULES' SHAPE DUE TO THE APPLIED FIELD.

AND YOU APPLY A FIELD $\delta\vec{D}$, IS HEAT GIVEN OFF OR ABSORBED BY THE DIELECTRIC?

$\varepsilon \sim 1 + \mathbb{C}/T$, WITH $\mathbb{C}$ CONSTANT. HENCE $\partial\varepsilon/\partial T < 0$ AND HENCE $\delta Q < 0$ WITH $\delta\vec{D} > 0$. HENCE HEAT IS REMOVED FROM THE DIELECTRIC WHEN $\delta\vec{D}$ IS APPLIED.

IF THE DIELECTRIC WERE REMOVED FROM THE HEAT BATH, THE TEMPERATURE OF THE DIELECTRIC WOULD RISE WHEN $\delta\vec{D}$ IS APPLIED.