STRESS TENSOR FROM STATISTICAL MECHANICS

J.H.Irving, J.G.Kirkwood (Dynamical point of view, classical)
The Journal of Chemical Physics **18**, 817 (1950)

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S.Morante, G.C.Rossi, M.Testa (Statical point of view, Quantum Mechanical)
The Journal of Chemical Physics **125**, 034101 (2006)

G.C.Rossi, M.Testa (Virtual Works and active deformation)
The Journal of Chemical Physics **132**, 074902 (2010)

This problem has a formal close relationship

with

Ward Identities in Quantum Field Theory

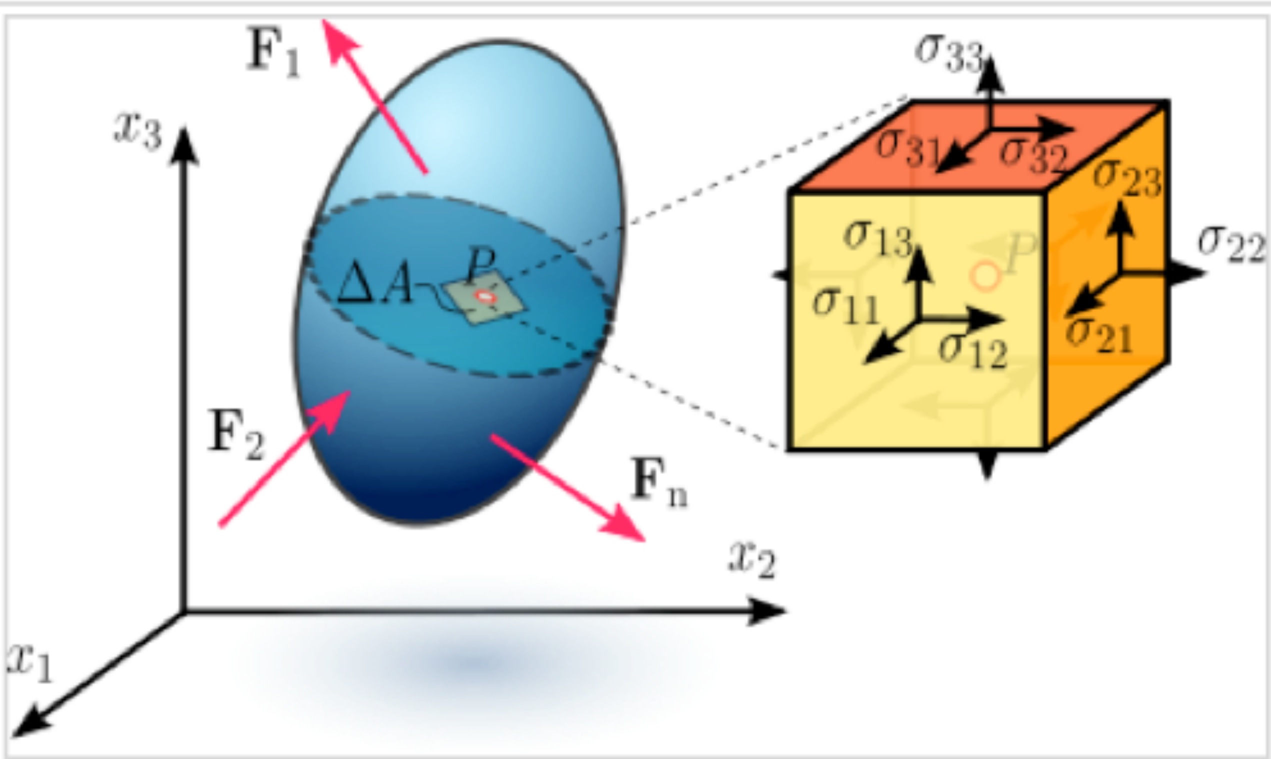
Applications in Material Science, Biology…

Characterization of the Stress Tensor

a) Equilibrium conditions

b) Work done during a deformation

a) Equilibrium conditions



Under the hypothesis of *contact* forces

$$dF^i = \tau^i_{\ k} n^k d\Sigma$$

So that the medium acts on the portion inside the surface Σ

through the force

$$F^i_\Sigma = \int_\Sigma \tau^i{}_k n^k d\Sigma = \int_V \partial_k \tau^{ik} dV$$

In the presence of an external force (e.g. gravity) per unit volume

$$df^{i}_{ext}(\mathbf{r}) = F^{i}_{ext}(\mathbf{r})dV$$

we have the equilibrium condition

$$\int_V \left(F^{i}_{ext}(\mathbf{r}) + F^{i}_{\Sigma}\right)dV = 0$$

Due to arbitrariness of V

$$F^{i}_{ext}(\mathbf{r}) + \partial_k \tau^{ik}(\mathbf{r}) = 0$$

b) Work performed during a deformation

A deformation is defined by

$$\boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{\varepsilon}(\boldsymbol{r})$$

and gives rise to the deformation tensor $\eta^{ab}(\boldsymbol{r})$

$$\eta^{ab}(\boldsymbol{r}) = \frac{1}{2}\left[\partial^a \varepsilon^b(\boldsymbol{r}) + \partial^b \varepsilon^a(\boldsymbol{r})\right]$$

The deformation $\eta^{ab}(\boldsymbol{r})$ changes the metric of the solid (manifold)

$$ds^2 \rightarrow ds'^2 = ds^2 + 2\eta_{ab} dx^a dx^b$$

and produces a work δW

$$\delta W = -\int_V \tau^{ab}(\boldsymbol{r}) \eta_{ab}(\boldsymbol{r}) dV$$

$$(\delta W = p dV)$$

STATISTICAL MECHANICS

Partition Function

$$Z = \int dp\, dq \exp\left(-\beta H\left(q,p\right)\right)$$

$$H(p,q) = \sum_{i=1}^{N} \frac{\left(\mathbf{p}_i\right)^2}{2m} + U(q) + \sum_{i=1}^{N} U_{ext}\left(q_i\right)$$

where (translation and rotation invariant forces)

$$q_{ij} = \sqrt{\left(\mathbf{q}_{ij}\right)^2}$$

$$\mathbf{q}_{ij} = \mathbf{q}_i - \mathbf{q}_j$$

For short range potentials (existence of the stress tensor) $U\left(q\right)$

does not depend on q_{ij} for $q_{ij} > \xi$, where ξ is a microscopic scale.

Weak $U_{ext}\left(q\right)$

Connection with Thermodynamics

$$Z = \exp\left(-\beta A\right)$$

$$A = U - TS$$

We now consider the *canonical* diffeomorphism

$$\mathbf{q}_i \rightarrow \mathbf{q}'_i = \mathbf{q}_i + \boldsymbol{\varepsilon}(\mathbf{q}_i)$$

$$p_i^a = \left[\delta_b^a + \varepsilon_b^a\left(\mathbf{q}_i\right)\right] p_i'^b$$

$$i = 1 \ldots N$$

with

$$\varepsilon_b^a\left(\mathbf{q}_i\right) \equiv \left.\frac{\partial \varepsilon^a\left(\mathbf{r}\right)}{\partial x^b}\right|_{\mathbf{r}=\mathbf{q}_i}$$

The measure *dpdq* is invariant and, since this is a change of variables in the partition function, we must have

$$\left.\frac{\delta \log Z}{\delta \varepsilon^a\left(\mathbf{r}\right)}\right|_{\boldsymbol{\varepsilon}(\mathbf{r})=0} = 0$$

We get (for short range potentials)

$$\frac{\partial}{\partial x^b}\left\langle \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{q}_i)\left(\frac{p_i^a p_i^b}{m}+\frac{1}{2}\sum_{j(\neq i)=1}^{N} q_{ij}^a \mathcal{F}_{ij}^b(\mathbf{q})\right)\right\rangle - \left\langle \delta(\mathbf{r}-\mathbf{q}_i)\mathcal{F}_{i,ext}^a\left[\{\mathbf{q}\}\right]\right\rangle = 0$$

where

$$\mathcal{F}_{ij}^a(\mathbf{q}) = -\frac{\partial U(q)}{\partial q_{ij}}\frac{q_{ij}^a}{q_{ij}}$$

$$\mathcal{F}_{i,ext}^a\left[\{\mathbf{q}\}\right] = -\frac{\partial U_{ext}\left[\{\mathbf{q}\}\right]}{\partial q_i^a}$$

so that, comparing with the macroscopic equilibrium condition,

$$F^i{}_{ext}(\mathbf{r}) + \partial_k \tau^{ik}(\mathbf{r}) = 0$$

we can identify

$$\tau^{ab}(\mathbf{r}) = -\left\langle \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{q}_i)\left(\frac{p_i^a p_i^b}{m}+\frac{1}{2}\sum_{j(\neq i)=1}^{N} q_{ij}^a \mathcal{F}_{ij}^b(q)\right)\right\rangle$$

$$q_{ij}^b \equiv q_i^a - q_j^a \rightarrow q_i'^a - q_j'^a = q_i^a + \varepsilon^a\left(\boldsymbol{q}_i\right) - q_j^a - \varepsilon^a\left(\boldsymbol{q}_j\right) \approx$$

$$\approx q_i^a + \varepsilon^a\left(\boldsymbol{q}_i\right) - q_j^a - \varepsilon^a\left(\boldsymbol{q}_i\right) + \varepsilon_b^a\left(\boldsymbol{q}_i\right) q_{ij}^b = \left[\delta_b^a + \varepsilon_b^a\left(\boldsymbol{q}_i\right)\right] q_{ij}^b$$

$$\varepsilon_b^a\left(\mathbf{q}_i\right) \equiv \left.\frac{\partial \varepsilon^a\left(\mathbf{r}\right)}{\partial x^b}\right|_{\mathbf{r}=\mathbf{q}_i}$$

Quantum Statistical Mechanics

$$Z^{qu} = Tr\left[\exp\left(-\beta H^{qu}\left(q,p\right)\right)\right]$$

A canonical transformation corresponds to an unitary transformation

$$Tr\left[U\left(\boldsymbol{\varepsilon}\right)\exp\left(-\beta H^{qu}\left(q,p\right)\right)U^{+}\left(\boldsymbol{\varepsilon}\right)\right] \equiv Tr\left[\exp\left(-\beta H^{qu}\left[q,p,\varepsilon\right]\right)\right] =$$
$$= Tr\left[\exp\left(-\beta H^{qu}\left(q,p\right)\right)\right]$$

$$H^{qu}\left[q,p,\varepsilon\right] = U\left(\varepsilon\right)H^{qu}\left[q,p\right]U^{+}\left(\varepsilon\right)$$

In our case

$$U(\boldsymbol{\varepsilon}) \approx I + \frac{i}{2\hbar}\sum_{j=1}^{N}\left[\boldsymbol{p}_j \bullet \boldsymbol{\varepsilon}(\boldsymbol{q}_j) + \boldsymbol{\varepsilon}(\boldsymbol{q}_j) \bullet \boldsymbol{p}_j\right]$$

In fact

$$U(\boldsymbol{\varepsilon}) q_i^a U^+(\boldsymbol{\varepsilon}) \approx q_i^a + \boldsymbol{\varepsilon}^a(\boldsymbol{q}_i)$$

$$U(\boldsymbol{\varepsilon}) p_i^a U^+(\boldsymbol{\varepsilon}) \approx p_i^a - \frac{i}{\hbar}\left[p_i^a \boldsymbol{\varepsilon}(\boldsymbol{q}_i) \bullet \boldsymbol{p}_i + \frac{1}{2} p_i^a \boldsymbol{p}_i \bullet \boldsymbol{\varepsilon}(\boldsymbol{q}_i)\right]$$

So that

$$\boldsymbol{\tau}^{ab}(\boldsymbol{r}) = -\left\langle \begin{array}{l} \sum_{i=1}^{N} \delta(\boldsymbol{r}-\boldsymbol{q}_i)\left(\frac{p_i^a p_i^b}{m} + \frac{1}{2}\sum_{j(\neq i)=1}^{N} q_{ij}^a F_{ij}^b(\mathbf{q})\right) + \\ + \frac{1}{2m}\sum_{i=1}^{N}\left[p_i^b \delta(\boldsymbol{r}-\boldsymbol{q}_i) p_i^a + p_i^a \delta(\boldsymbol{r}-\boldsymbol{q}_i) p_i^b + \frac{1}{2} p_i^a p_i^b \delta(\boldsymbol{r}-\boldsymbol{q}_i)\right] \end{array} \right\rangle$$

The Virial Theorem applies

UNIQUENESS???

Active point of view

We interpret the canonical transformation as an active (physical) deformation $\boldsymbol{r}' = \boldsymbol{r} + \boldsymbol{\varepsilon}(\boldsymbol{r})$

This changes the metric of the body as

$$ds^2 \rightarrow ds'^2 = ds^2 + 2\eta_{ab} dx^a dx^b$$

We can interpret

$$H(q,p,\eta,\varepsilon) = H^0(q,p) + \\ -\sum_{i=1}^{N} \eta_{ab}(q_i)\frac{p_i^a p_i^b}{m} - \frac{1}{2}\sum_{j \neq i=1}^{N} \eta_{ab}(q_i) q_{ij}^a F_{ij}^b(\mathbf{q}_{ij}) - \sum_{i=1}^{N} \varepsilon_a(q_i) F_{i,ext}^a(\mathbf{q}_{ij})$$

as the hamiltonian of a system evolving on a manifold with metric η_{ab}. In the physical case, of course η_{ab} **has zero riemannian curvature (constraint)**

Thermodynamically, at constant temperature,

$$dA = -\delta_{rev}W = \int_V \tau^{ab}(\boldsymbol{r})\eta_{ab}(\boldsymbol{r})dV$$

(Geometrically intrinsic)

Allowing an arbitrary infinitesimal η_{ab} we would have

$$\tau^{ab}(\boldsymbol{r}) = \left.\frac{\delta A}{\delta \eta_{ab}(\boldsymbol{r})}\right|_{T,\eta=0}$$

On the other hand the external forces are responsible for a work

$$\delta L_{\text{ext}} = -\int_V F^a_{ext}(\boldsymbol{r})\varepsilon_a(\boldsymbol{r})dV$$

(Geometrically extrinsic)

The total work done (by internal and external forces) is

$$\delta L = \int_V \tau^{ab}(\boldsymbol{r})\eta_{ab}(\boldsymbol{r})dV - \int_V F_{ext}^{a}(\boldsymbol{r})\varepsilon_a(\boldsymbol{r})dV$$

From the Principle of Virtual Works (mechanical equilibrium) this work must vanish, at equilibrium, under the constraint (flatness)

$$\eta^{ab}(\boldsymbol{r}) = \frac{1}{2}\left[\partial^a\varepsilon^b(\boldsymbol{r}) + \partial^b\varepsilon^a(\boldsymbol{r})\right]$$

which can be enforced by Lagrange multipliers $\lambda_{ab}(\boldsymbol{r})$, so that

$$\delta L = \int_V \tau^{ab}(\boldsymbol{r})\eta_{ab}(\boldsymbol{r})dV - \int_V F_{ext}^{a}(\boldsymbol{r})\varepsilon_a(\boldsymbol{r})dV + \\ -\int_V \lambda_{ab}(\boldsymbol{r})\left[\eta^{ab}(\boldsymbol{r}) - \frac{1}{2}\left[\partial^a\varepsilon^b(\boldsymbol{r}) + \partial^b\varepsilon^a(\boldsymbol{r})\right]\right]dV = 0$$

Therefore

$$\tau^{ab}(\boldsymbol{r}) - \lambda^{ab}(\boldsymbol{r}) = 0 \qquad , \qquad F^{a}_{ext}(\boldsymbol{r}) + \partial_b \lambda^{ab}(\boldsymbol{r}) = 0$$

under the condition

$$\eta^{ab}(\boldsymbol{r}) = \frac{1}{2}\left[\partial^a \varepsilon^b(\boldsymbol{r}) + \partial^b \varepsilon^a(\boldsymbol{r})\right]$$

This procedure gives the same expression for $\tau^{ab}(\boldsymbol{r})$ as before

and it is (apparently) unique

What about Surface Stresses?

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