American Physical Society March Meeting
Denver, CO 2020

Local Pressures for Strongly Inhomogeneous States

James Dufty[1], Kai Luo[2], and Jeff Wrighton[1]

[1] **Department of Physics, University of Florida, Gainesville, FL**
[2] **Extreme Materials Initiative, Geophysical Laboratory, Carnegie Institution for Science, Washington, DC**

Work supported under US DOE Grant DE-SC0002139

UF UNIVERSITY of FLORIDA

THANKS TO:

University of Florida Orbital Free DFT Group

Sam Trickey
Jim Dufty
Daniel Mejia Rodriguez
Jeff Wrighton

Kai Luo *
Valentin Karasiev *
Lazaro Calderín *
Keith Runge *

*** no longer at UF but active collaboration**

Software and publications available from
www.qtp.ufl.edu/ofdft

Motivation

- **Identification of a local *thermodynamic* pressure(s) for description of strongly inhomogeneous equilibrium systems (e.g. warm, dense matter).**

- **Possible constraint of equivalence of thermodynamic and *mechanical* concepts of pressure.**

- **Extend definitions to local equilibrium states of hydrodynamics with spatially varying temperature.**

- **Thermodynamic and mechanical definitions of local pressures different.**

- **Practical consequences.**

Non-uniform system at equilibrium

$$\mathcal{H}_N = H_N + \sum_{\alpha=1}^{N} v^{\text{ext}}(\mathbf{q}_\alpha))$$

$$H_N = \sum_{\alpha=1}^{N} \frac{\mathbf{p}_\alpha^2}{2m} + \frac{1}{2} \sum_{\alpha \neq \sigma = 1}^{N} U_N(|\mathbf{q}_\alpha - \mathbf{q}_\sigma|)$$

Equilibrium averages

$$\langle X \rangle^e \equiv \sum_N Tr^{(N)} X_N \rho_N^e, \qquad \rho_N^e = e^{-Q^e(\beta, V|\nu)} e^{-\left(\beta H_N - \int d\mathbf{r} \nu(\mathbf{r}) n(\mathbf{r})\right)}$$

$$\nu(\mathbf{r}) \equiv \nu + v^{\text{ext}}(\mathbf{r}) \qquad n(\mathbf{r}) = \sum_{\alpha=1}^{N} \delta(\mathbf{r} - \mathbf{q}_\alpha)$$

Thermodynamics

$$Q^e(\beta, V \mid \nu) = \ln \sum_N Tr^{(N)} e^{-\left(\beta H_N - \int d\mathbf{r} \nu(\mathbf{r}) n(\mathbf{r})\right)}$$

$$\beta P^e(\beta \mid \nu) V = Q^e(\beta, V \mid \nu)$$

$$\beta P^e(\beta \mid \nu) = \frac{\partial Q^e(\beta, V \mid \nu)}{\partial V}\Big|_{\beta,\nu}$$

$$P^e(\beta \mid \nu) = \frac{1}{3V}\left(2\langle K\rangle^e + \langle \mathcal{V}\rangle^e\right)$$ **same as (intrinsic) virial theorem**

$$K = \sum_{\alpha=1}^{N}\frac{1}{2m}p_{\alpha j}^2, \qquad \mathcal{V} = \frac{1}{2}\sum_{\alpha\neq\gamma=1}^{N}(\mathbf{q}_\gamma - \mathbf{q}_\alpha)\cdot\mathbf{F}_{\alpha\gamma}(|\mathbf{q}_\alpha - \mathbf{q}_\gamma|)$$

local pressure

$$P^e(\beta \mid \nu) \equiv \frac{1}{V}\int d\mathbf{r}\, p^e(\mathbf{r}, \beta \mid \nu)$$

Aside – relationship to DFT

$$\frac{\delta Q^e(\beta, V \mid \nu)}{\delta \nu(\mathbf{r})} = n^e(\mathbf{r})$$

$$\beta F^e(\beta, V \mid n^e) = -\beta P^e(\beta \mid \nu)V + \int d\mathbf{r}\,\nu(\mathbf{r})\,n^e(\mathbf{r})$$

$$F^e(\beta, V \mid n^e) = \int d\mathbf{r}\; f^e(\mathbf{r}, \beta \mid n^e)$$

Not unique – one choice:

$$p_0(\mathbf{r},\beta \mid \nu) = \frac{1}{3}\langle 2K_0(\mathbf{r}) + \mathcal{V}_0(\mathbf{r})\rangle^e$$

$$K_0(\mathbf{r}) = \frac{1}{4m}\sum_{\alpha=1}^{N}\left[p_\alpha^2, \delta(\mathbf{r}-\mathbf{q}_\alpha)\right]_+$$

$$\mathcal{V}_0(\mathbf{r}) = \frac{1}{2}\sum_{\alpha\neq\sigma=1}^{N} F_{\alpha\sigma i}(|\mathbf{q}_\alpha-\mathbf{q}_\sigma|)(\mathbf{q}_\sigma-\mathbf{q}_\alpha)\delta(\mathbf{r}-\mathbf{q}_\alpha)$$

More generally:

$$p^e(\mathbf{r},\beta \mid \nu) = p_0^e(\mathbf{r},\beta \mid \nu) + \Delta p_0^e(\mathbf{r},\beta \mid \nu)$$

$$\int d\mathbf{r}\Delta p^e(\mathbf{r},\beta \mid \nu) = 0$$

How to choose $\Delta p^e(\mathbf{r},\beta \mid \nu)$? Compare mechanical concept of pressure.

local conservation law for average momentum density (Heisenberg dynamics)

$$\partial_t \langle p_i(\mathbf{r},t)\rangle + \partial_j \langle t_{ij}(\mathbf{r},t)\rangle = -\langle n(\mathbf{r},t)\rangle \partial_i v^{\text{ext}}(\mathbf{r},t)$$

with

$$\mathbf{p}(\mathbf{r},t) = \frac{1}{2}\sum_{\alpha=1}^{N} \left[\mathbf{p}_\alpha(t), \delta(\mathbf{r}-\mathbf{q}_\alpha(t))\right]_+$$

Equilibrium average

$$\partial_j \langle t_{ij}(\mathbf{r})\rangle^e = -\langle n(\mathbf{r})\rangle^e \partial_i v^{\text{ext}}(\mathbf{r})$$

"pressure tensor" $$p^e_{ij}(\mathbf{r}) = \langle t_{ij}(\mathbf{r})\rangle^e$$

mechanical pressure $$p^e(\mathbf{r}) = \frac{1}{3}\langle t_{ii}(\mathbf{r})\rangle^e$$

Direct calculation gives

$$\frac{1}{V}\int d\mathbf{r}\frac{1}{3}\langle t_{ii}(\mathbf{r})\rangle^e = \frac{1}{3V}\left(2\langle K\rangle^e + \langle \mathcal{V}\rangle^e\right) = P^e(\beta \mid \nu)$$

So good candidate for local pressure

Consistency of thermodynamic and mechanical concepts suggests the local pressure should be chosen as

$$p^e(\mathbf{r}, \beta \mid \nu) = p_0^e(\mathbf{r}, \beta \mid \nu) + \Delta p_0^e(\mathbf{r}, \beta \mid \nu) = \frac{1}{3}\langle t_{ii}(\mathbf{r})\rangle^e$$

$$\Delta p_0^e(\mathbf{r}, \beta \mid \nu) = \frac{1}{3}\langle t_{ii}(\mathbf{r})\rangle^e - p_0^e(\mathbf{r}, \beta \mid \nu)$$

It follows directly that

$$\int d\mathbf{r} \Delta p^e(\mathbf{r}, \beta \mid \nu) = 0$$

Coupling of thermodynamic and mechanical properties

(Pozhar, Gubbins, and Percus, Phys. Rev E48, 1819 (1993))

$$\partial_j p_{ij}^e(\mathbf{r}, \beta \mid \nu) = -n^e(\mathbf{r})\partial_i v^{\mathrm{ext}}(\mathbf{r})$$

$$p_{ij}^e(\mathbf{r}, \beta \mid \nu) = \frac{1}{3} p^e(\mathbf{r}, \beta \mid \nu)\,\delta_{ij} + \widetilde{p}_{ij}^e(\mathbf{r}, \beta \mid \nu)$$

$$p_{ij}^e(\mathbf{r}, \beta \mid \nu) \equiv \langle t_{ij}(\mathbf{r})\rangle^e$$

Summary

Two local pressures identified, but not the same.

$$p^e(\mathbf{r},\beta \mid \nu) \neq p_0^e(\mathbf{r},\beta \mid \nu)$$

Both can be written as local virial averages

$$p_0^e(\mathbf{r},\beta \mid \nu) = \frac{1}{3}\langle 2K_0(\mathbf{r}) + \mathcal{V}_0(\mathbf{r})\rangle^e$$

$$p^e(\mathbf{r},\beta \mid \nu) = \frac{1}{3}\left(2\langle K(\mathbf{r})\rangle^e + \langle \mathcal{V}(\mathbf{r})\rangle^e\right)$$

$$K(\mathbf{r}) = K_0(\mathbf{r}) + \frac{1}{8m}\nabla_{\mathbf{r}}^2 n(\mathbf{r})$$

$$\mathcal{V}(\mathbf{r}) = \mathcal{V}_0(\mathbf{r}) + \frac{1}{2}\sum_{\alpha\neq\sigma=1}^{N} F_{\alpha\sigma i}\left(|\mathbf{q}_\alpha - \mathbf{q}_\sigma|\right)\left[\mathcal{D}_i(\mathbf{r},\mathbf{q}_\alpha,\mathbf{q}_\sigma) - (\mathbf{q}_\sigma - \mathbf{q}_\alpha)_i\delta(\mathbf{r}-\mathbf{q}_\alpha)\right]$$

However, thermodynamic pressure *can be chosen* to be the same as mechanical

$$p^e(\mathbf{r},\beta \mid \nu) = p_0^e(\mathbf{r},\beta \mid \nu) + \Delta p_0^e(\mathbf{r},\beta \mid \nu) = \frac{1}{3}\langle t_{ii}(\mathbf{r})\rangle^e$$

Macroscopic conservation laws – origins of hydrodynamics

$$\partial_t \langle p_i(\mathbf{r},t)\rangle + \partial_j \langle t_{ij}(\mathbf{r},t)\rangle = -\langle n(\mathbf{r},t)\rangle \partial_i v^{\text{ext}}(\mathbf{r},t)$$

$$\langle X(t)\rangle \equiv \sum_N Tr^{(N)} X_N \rho_N(t)$$

$$\langle \mathbf{p}(\mathbf{r},t)\rangle \equiv m \langle n(\mathbf{r},t)\rangle \mathbf{u}(\mathbf{r},t)$$

$$D_t u_i(\mathbf{r},t) + \partial_j \langle t_{0ij}(\mathbf{r},t)\rangle = -\langle n(\mathbf{r},t)\rangle \partial_i v^{\text{ext}}(\mathbf{r},t)$$

local rest frame, both pressure tensor and dissipation

$$\rho_N(t) = \rho_N^{\ell}[\beta(t),\nu(t)] + \Delta_N(t)$$

$$\langle t_{0ij}(\mathbf{r})\rangle = \langle t_{0ij}(\mathbf{r})\rangle^{\ell} + \delta\langle t_{0ij}(\mathbf{r})\rangle$$

$$\langle t_{0ij}(\mathbf{r})\rangle^{\ell} = \sum_N Tr^{(N)} t_{0ij}(\mathbf{r}) \rho_N^{\ell}[\beta,\nu]$$

Local equilibrium hydrodynamic pressure tensor, pressure

$$p_{ij}^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)\equiv\left\langle t_{ij}\left(\mathbf{r}\right)\right\rangle^{\ell}$$

$$p^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)\equiv\frac{1}{3}\left\langle t_{ii}\left(\mathbf{r}\right)\right\rangle^{\ell}=\frac{1}{3}\left[2\left\langle K(\mathbf{r})\right\rangle^{\ell}+\left\langle\mathcal{V}(\mathbf{r})\right\rangle^{\ell}\right]$$

Local equilibrium "thermodynamic" pressure

generalization of grand canonical ensemble

$$\rho_{N}^{\ell}\left[\beta,\nu\right]=e^{-Q^{\ell}[\beta,\nu]-\int d\mathbf{r}(\beta(\mathbf{r})e(\mathbf{r})-\nu(\mathbf{r})n(\mathbf{r}))}$$

$$Q^{\ell}[\beta,\nu]=\ln\sum_{N}Tr^{(N)}e^{-\int d\mathbf{r}(\beta(\mathbf{r})e(\mathbf{r})-\nu(\mathbf{r})n(\mathbf{r}))}$$

"thermodynamics"

$$\int d\mathbf{r}\beta\left(\mathbf{r}\right)p_{0}^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)\equiv Q^{\ell}[\beta,\nu]$$

$$\Downarrow$$

$$p_{0}^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)=\frac{1}{3}\left[2\left\langle K_{0}\left(\mathbf{r}\right)\right\rangle^{\ell}+\left\langle\mathcal{V}_{0}\left(\mathbf{r}\right)\right\rangle^{\ell}\right]$$

Hydrodynamic and thermodynamic pressures different

$$p^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)=p_{0}^{\ell}\left(\mathbf{r}\mid\beta.\nu\right)+\Delta p_{0}^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)$$

Global pressures are the same

$$\int d\mathbf{r}\Delta p_{0}^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)=0$$

but cannot add $\Delta p_{0}^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)$ ***to*** $p_{0}^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)$ ***for alternative thermodynamic choice :***

$$\int d\mathbf{r}\beta\left(\mathbf{r}\right)\Delta p_{0}^{\ell}\left(\mathbf{r}\mid\beta,\nu\right)\neq 0$$

***Comment*: difference persists in the uniform temperature limit**

Can hydrodynamic pressure/ pressure tensor be chosen differently?

Yes

$$\partial_j t'_{ij}(\mathbf{r},t) = \partial_j t_{ij}(\mathbf{r},t)$$

$$t'_{ij}(\mathbf{r},t) = t_{ij}(\mathbf{r},t) + \epsilon_{jkn}\partial_k A_{ni}(\mathbf{r},t)$$

But still cannot correct the pressure differences

$$\partial_j \epsilon_{jkn}\partial_k A_{ni}(\mathbf{r},t) = 0 \neq \partial_j \left(p^{\ell}_{ij}\left(\mathbf{r} \mid \beta,\nu\right) - p^{\ell}_{0ij}\left(\mathbf{r} \mid \beta,\nu\right)\right)$$

Summary

- Local pressures can be defined from equilibrium grand potential (thermodynamics), but not unique.
- Local pressure can be defined from equilibrium average stress tensor (mechanics)
- Local pressures can be equated by appropriate thermodynamic choice
- Similar results for local equilibrium states, but freedom to require equivalence excluded by spatially varying temperature.
- Different pressure for hydrodynamics requires care in using DFT results (thermodynamics) for practical calculations