

Supporting Information for

Local pressure for inhomogeneous fluids

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S.1. CONSERVATION OF NUMBER AND MOMENTUM DENSITIES

The dynamics of operators is defined by

$$\partial_t X(t) = i [\mathcal{H}_N(t), X(t)], \quad (\text{S.1})$$

with the Hamiltonian given by

$$\mathcal{H}_N(t) = H_N(t) + \sum_{\alpha=1}^N v^{\text{ext}}(\mathbf{q}_\alpha(t), t), \quad (\text{S.2})$$

$$H_N(t) = \sum_{\alpha=1}^N \frac{p_\alpha^2(t)}{2m} + \frac{1}{2} \sum_{\alpha \neq \sigma=1}^N U_N(|\mathbf{q}_\alpha(t) - \mathbf{q}_\sigma(t)|). \quad (\text{S.3})$$

The operators corresponding to the number and momentum densities are

$$n(\mathbf{r}, t) = \sum_{\alpha=1}^N \delta(\mathbf{r} - \mathbf{q}_\alpha(t)), \quad \mathbf{p}(\mathbf{r}, t) = \sum_{\alpha=1}^N \frac{1}{2} [\mathbf{p}_\alpha(t), \delta(\mathbf{r} - \mathbf{q}_\alpha(t))]_+. \quad (\text{S.4})$$

The brackets $[A, B]_+$ with a subscript $+$ denote an anti-commutator.

Local conservation laws follow exactly from this Hamiltonian dynamics¹. The simplest is the conservation of number density

$$\begin{aligned} \partial_t n(\mathbf{r}, t) &= i [\mathcal{H}_N(t), n(\mathbf{r}, t)] = \sum_{\alpha=1}^N i \left[\frac{p_\alpha^2(t)}{2m}, \delta(\mathbf{r} - \mathbf{q}_\alpha(t)) \right] \\ &= \sum_{\alpha=1}^N i \left\{ \frac{p_{\alpha j}(t)}{2m} [p_{\alpha j}(t), \delta(\mathbf{r} - \mathbf{q}_\alpha(t))] + [p_{\alpha j}(t), \delta(\mathbf{r} - \mathbf{q}_\alpha(t))] \frac{p_{\alpha j}(t)}{2m} \right\} \\ &= \frac{1}{2m} \sum_{\alpha=1}^N \{ p_{\alpha j}(t) \partial_{q_{\alpha j}(t)} \delta(\mathbf{r} - \mathbf{q}_\alpha(t)) + \partial_{q_{\alpha j}(t)} \delta(\mathbf{r} - \mathbf{q}_\alpha(t)) p_{\alpha j}(t) \} \end{aligned} \quad (\text{S.5})$$

or, with the definition of $\mathbf{p}(\mathbf{r})$ in (S.4), the microscopic continuity equation is obtained

$$\partial_t n(\mathbf{r}, t) + \frac{1}{m} \nabla \cdot \mathbf{p}(\mathbf{r}, t) = 0. \quad (\text{S.6})$$

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Use has been made of the property

$$i [p_{\alpha j}(t), A(\mathbf{q}_\alpha(t))] = \partial_{q_{\alpha j}(t)} A(\mathbf{q}_\alpha(t)). \quad (\text{S.7})$$

The time derivative of $\mathbf{p}(\mathbf{r}, t)$ follows in a similar way

$$\begin{aligned} \partial_t p_j(\mathbf{r}, t) &= \frac{1}{2} \sum_{\alpha=1}^N \left\{ [p_{\alpha j}(t), i [\mathcal{H}_N(t), \delta(\mathbf{r} - \mathbf{q}_\alpha(t))]]_+ + [i [\mathcal{H}_N(t), p_{\alpha j}(t)], \delta(\mathbf{r} - \mathbf{q}_\alpha(t))]_+ \right\} \\ &= \frac{1}{2} \sum_{\alpha=1}^N \left\{ \left[p_{\alpha j}(t), i \left[\frac{p_\alpha^2(t)}{2m}, \delta(\mathbf{r} - \mathbf{q}_\alpha(t)) \right] \right]_+ + [i [\mathcal{H}_N(t), p_{\alpha j}(t)], \delta(\mathbf{r} - \mathbf{q}_\alpha(t))]_+ \right\} \\ &= \frac{1}{4m} \sum_{\alpha=1}^N \left[p_{\alpha j}(t), [p_{\alpha k}(t), \partial_{q_{\alpha k}(t)} \Delta(\mathbf{r} - \mathbf{q}_\alpha(t))]_+ \right]_+ - \frac{1}{2} \sum_{\alpha=1}^N \delta(\mathbf{r} - \mathbf{q}_\alpha(t)) \partial_{q_{\alpha j}(t)} v^{\text{ext}}(\mathbf{q}_\alpha(t), t) \\ &\quad - \frac{1}{4} \sum_{\alpha=1}^N \sum_{\beta=1}^N [\delta(\mathbf{r} - \mathbf{q}_\alpha(t)), \partial_{q_{\alpha j}(t)} V(|\mathbf{q}_\beta(t) - \mathbf{q}_\sigma(t)|)]_+ \\ &= -\partial_{r_k} \frac{1}{4m} \sum_{\alpha=1}^N [p_{\alpha j}(t), [p_{\alpha k}(t), \delta(\mathbf{r} - \mathbf{q}_\alpha(t))]_+]_+ + \frac{1}{2} \sum_{\alpha=1}^N \delta(\mathbf{r} - \mathbf{q}_\alpha(t)) F_{\alpha j}^{\text{ext}}(\mathbf{q}_\alpha(t)) \\ &\quad + \frac{1}{2} \sum_{\alpha=1}^N \sum_{\beta=1}^N F_{\alpha \beta j}(|\mathbf{q}_\alpha(t) - \mathbf{q}_\beta(t)|) \delta(\mathbf{r} - \mathbf{q}_\alpha(t)) \end{aligned} \quad (\text{S.8})$$

where $F_{\alpha \beta j}(|\mathbf{q}_\alpha(t) - \mathbf{q}_\beta(t)|)$ is the j^{th} component of the force on particle α due to particle β

$$F_{\alpha \beta j}(|\mathbf{q}_\alpha - \mathbf{q}_\beta|) = -\partial_{q_{\alpha j}(t)} V(|\mathbf{q}_\alpha(t) - \mathbf{q}_\beta(t)|), \quad (\text{S.9})$$

and $F_{\alpha j}^{\text{ext}}(\mathbf{q}_\alpha(t))$ is the j^{th} component of the force on particle α due to the external potential

$$F_{\alpha j}^{\text{ext}}(\mathbf{q}_j) = -\partial_{q_{\alpha j}(t)} u(\mathbf{q}_\alpha(t), t). \quad (\text{S.10})$$

The last term on the right side of (S.8) can be rewritten as

$$\begin{aligned} \sum_{\alpha \neq \beta=1}^N F_{\alpha \beta j}(|\mathbf{q}_\alpha(t) - \mathbf{q}_\beta(t)|) \delta(\mathbf{r} - \mathbf{q}_\alpha(t)) &= \sum_{\alpha \neq \beta=1}^N F_{\beta \alpha j}(|\mathbf{q}_\beta(t) - \mathbf{q}_\alpha(t)|) \delta(\mathbf{r} - \mathbf{q}_\beta(t)) \\ &= - \sum_{\alpha \neq \beta=1}^N F_{\alpha \beta j}(|\mathbf{q}_\alpha(t) - \mathbf{q}_\beta(t)|) \delta(\mathbf{r} - \mathbf{q}_\beta(t)) \end{aligned} \quad (\text{S.11})$$

as follows from Newton's third law. Therefore

$$\begin{aligned} \sum_{\alpha \neq \beta=1}^N F_{\alpha \beta j}(|\mathbf{q}_\alpha(t) - \mathbf{q}_\beta(t)|) \delta(\mathbf{r} - \mathbf{q}_\alpha(t)) &= \frac{1}{2} \sum_{\alpha \neq \beta=1}^N F_{\alpha \beta j}(|\mathbf{q}_\alpha(t) - \mathbf{q}_\beta(t)|) \\ &\quad \times (\delta(\mathbf{r} - \mathbf{q}_\alpha(t)) - \delta(\mathbf{r} - \mathbf{q}_\beta(t))). \end{aligned} \quad (\text{S.12})$$

Next note the identity

$$\delta(\mathbf{r} - \mathbf{q}_1) - \delta(\mathbf{r} - \mathbf{q}_2) = \int_{\lambda_2}^{\lambda_1} d\lambda \frac{d}{d\lambda} \delta(\mathbf{r} - \mathbf{x}(\lambda)), \quad \mathbf{x}(\lambda_1) = \mathbf{q}_1, \quad \mathbf{x}(\lambda_2) = \mathbf{q}_2. \quad (\text{S.13})$$

Here $\mathbf{x}(\lambda)$ is an arbitrary path for the vector \mathbf{x} moving from $\mathbf{x}(\lambda_2) = \mathbf{q}_2$ to $\mathbf{x}(\lambda_1) = \mathbf{q}_1$. Carrying out the derivative gives

$$\delta(\mathbf{r} - \mathbf{q}_1) - \delta(\mathbf{r} - \mathbf{q}_2) = -\partial_{r_k} \mathcal{D}_k(\mathbf{r}, \mathbf{q}_1, \mathbf{q}_2), \quad (\text{S.14})$$

where

$$\mathcal{D}_k(\mathbf{r}, \mathbf{q}_1, \mathbf{q}_2) = \int_{\lambda_2}^{\lambda_1} d\lambda \frac{dx_k(\lambda)}{d\lambda} \delta(\mathbf{r} - \mathbf{x}(\lambda)). \quad (\text{S.15})$$

Use of (S.14) in (S.12) and (S.8) gives the momentum conservation law

$$\partial_t p_j(\mathbf{r}, t) + \partial_{r_k} t_{jk}(\mathbf{r}, t) = f_j(\mathbf{r}, t) \quad (\text{S.16})$$

where the total momentum flux $t_{\alpha\beta}(\mathbf{r}, t)$ is the sum of a kinetic and potential part

$$t_{\alpha\beta}(\mathbf{r}, t) = t_{\alpha\beta}^K(\mathbf{r}, t) + t_{\alpha\beta}^P(\mathbf{r}, t), \quad (\text{S.17})$$

$$t_{jk}^K(\mathbf{r}, t) = \frac{1}{4m} \sum_{\alpha=1}^N [p_{\alpha j}(t), [p_{\alpha k}(t), \delta(\mathbf{r} - \mathbf{q}_\alpha(t))]]_+, \quad (\text{S.18})$$

$$t_{jk}^P(\mathbf{r}, t) = \frac{1}{4} \sum_{\alpha \neq \beta=1}^N F_{\alpha\beta j}(|\mathbf{q}_\alpha(t) - \mathbf{q}_\beta(t)|) \mathcal{D}_k(\mathbf{r}, \mathbf{q}_\alpha(t), \mathbf{q}_\beta(t)). \quad (\text{S.19})$$

The right side of (S.16) is the force density of the external potential

$$f_j(\mathbf{r}, t) = \sum_{\alpha=1}^N \delta(\mathbf{r} - \mathbf{q}_j(t)) F_{\alpha j}^{\text{ext}}(\mathbf{q}_\alpha(t)). \quad (\text{S.20})$$

S.2. DETERMINATION OF MOMENTUM FLUX

The straightforward derivation of the momentum conservation law in Appendix S.1 leads to a momentum flux (as in the text the dependence on t will be left implicit as it plays no role in the following)

$$\begin{aligned} t_{ij}(\mathbf{r}) &= \frac{1}{4m} \sum_{\alpha=1}^N [p_{i\alpha}, [p_{j\alpha}, \delta(\mathbf{r} - \mathbf{q}_\alpha)]]_+ \\ &+ \frac{1}{2} \sum_{\alpha \neq \sigma=1}^N F_{\alpha\sigma i}(|\mathbf{q}_\alpha - \mathbf{q}_\sigma|) \mathcal{D}_j(\mathbf{r}, \mathbf{q}_\alpha, \mathbf{q}_\sigma), \end{aligned} \quad (\text{S.21})$$

where the operator $\mathcal{D}_j(\mathbf{r}, \mathbf{q}_\alpha, \mathbf{q}_\sigma)$ is given by

$$\mathcal{D}_j(\mathbf{r}, \mathbf{q}_1, \mathbf{q}_2) \equiv \int_{\mathcal{C}} d\lambda \frac{dx_j(\lambda)}{d\lambda} \delta(\mathbf{r} - \mathbf{x}(\lambda)), \quad \mathbf{x}(\lambda_1) = \mathbf{q}_1, \quad \mathbf{x}(\lambda_2) = \mathbf{q}_2. \quad (\text{S.22})$$

Here \mathcal{C} is an arbitrary continuous path connecting $\mathbf{x}(\lambda)$ between λ_1 and λ_2 . Consider the simplest choice a linear path

$$\mathbf{x}(\lambda) = \mathbf{q}_1 + (\mathbf{q}_2 - \mathbf{q}_1)\lambda. \quad (\text{S.23})$$

Then

$$\mathcal{D}_j(\mathbf{r}, \mathbf{q}_1, \mathbf{q}_2) \rightarrow (q_{2j} - q_{1j}) \int_0^1 d\lambda \delta(\mathbf{r} - \mathbf{q}_1 - (\mathbf{q}_2 - \mathbf{q}_1)\lambda), \quad \mathbf{x}(\lambda_1) = \mathbf{q}_1, \quad \mathbf{x}(\lambda_2) = \mathbf{q}_2. \quad (\text{S.24})$$

Since $F_{\alpha\sigma i}(|\mathbf{q}_\alpha - \mathbf{q}_\sigma|) \propto (q_{2i} - q_{1i})$ use of (S.24) in (S.21) leads to a form for the momentum flux that is symmetric, $t_{ij}(\mathbf{r}) = t_{ji}(\mathbf{r})$, and consequently its divergence with respect to first and second indices are the same

$$\partial_j t_{ij}(\mathbf{r}) = \partial_j t_{ji}(\mathbf{r}). \quad (\text{S.25})$$

Next define another symmetric momentum flux whose divergences are the same as those of (S.25)

$$t'_{ij}(\mathbf{r}) = t_{ij}(\mathbf{r}) + \epsilon_{ikl}\epsilon_{jmn}\partial_k\partial_m A_{ln}(\mathbf{r}), \quad (\text{S.26})$$

for some unspecified tensor field $A_{ln}(\mathbf{r})$ and ϵ_{ikl} is the Levi-Cevita tensor. This added term is seen to be the curl of a vector associated with each component of $t_{ij}(\mathbf{r})$ (i.e., noting that $t_{ij}(\mathbf{r})$ transforms as vector for components i at fixed j , and vice versa). With the additional condition $A_{ln}(\mathbf{r}) = A_{nl}(\mathbf{r})$, it is verified that

$$t'_{ij}(\mathbf{r}) = t'_{ji}(\mathbf{r}), \quad (\text{S.27})$$

$$\partial_j t'_{ij}(\mathbf{r}) = \partial_j t'_{ji}(\mathbf{r}). \quad (\text{S.28})$$

The two indefinite features of the momentum flux have now been made explicit with the contour fixed by symmetry and the choice of a term with vanishing divergence. It is interesting to note that the contribution from different contours, denoted by $\Delta\mathcal{D}_j(\mathbf{r}, \mathbf{q}_1, \mathbf{q}_2)$ has a vanishing divergence, since the endpoints of the integration in (S.24) are the same for all contours. Consequently, the divergence of $\Delta\mathcal{D}_j$ vanishes, $\partial_j \Delta\mathcal{D}_j = 0$. It follows that $\Delta\mathcal{D}_j$ is the curl of some vector. Hence, the difference between contours is included in the form (S.26).

S.3. PERCUS PRESSURE TENSOR

The free energy is obtained from the grand potential by a Legendre transform

$$\beta F(\beta, V | \bar{n}) = -Q^e(\beta, V | \nu) + \int d\mathbf{r} \bar{n}(\mathbf{r}) \nu(\mathbf{r}) \quad (\text{S.29})$$

where $\bar{n}(\mathbf{r}) = \langle n(\mathbf{r}) \rangle$ is the average number density. The free energy and grand potential are expressed as integrals of their respective densities

$$F(\beta, V | \bar{n}) = \int d\mathbf{r} f(\mathbf{r}, \beta | \bar{n}), \quad Q^e(\beta, V | \nu) = \int d\mathbf{r} \beta p_T(\mathbf{r}, \beta | \nu) \quad (\text{S.30})$$

so that

$$\beta p_T(\mathbf{r}, \beta | \nu) = \bar{n}(\mathbf{r}) \nu(\mathbf{r}) - f(\mathbf{r}, \beta | \bar{n}). \quad (\text{S.31})$$

The Percus pressure tensor² is defined by

$$p_{ij}(\mathbf{r}, \beta | \bar{n}) \equiv \delta_{ij} p_T(\mathbf{r}, \beta | \nu) + \int d\mathbf{r}' r'_i \int_0^1 d\gamma \frac{\delta f(\mathbf{r} + \gamma \mathbf{r}' - \mathbf{r}', \beta | \bar{n})}{\delta \bar{n}(\mathbf{r} + \gamma \mathbf{r}')} \partial_j \bar{n}(\mathbf{r} + \gamma \mathbf{r}'). \quad (\text{S.32})$$

The corresponding mechanical pressure is

$$p_m(\mathbf{r}, \beta | \bar{n}) = p_T(\mathbf{r}, \beta | \nu) + \frac{1}{3} \int d\mathbf{r}' \int_0^1 d\gamma \frac{\delta f(\mathbf{r} + \gamma \mathbf{r}' - \mathbf{r}', \beta | \bar{n})}{\delta \bar{n}(\mathbf{r} + \gamma \mathbf{r}')} r'_i \partial_i \bar{n}(\mathbf{r} + \gamma \mathbf{r}'). \quad (\text{S.33})$$

No motivation nor interpretation for this result is provided.

First, prove the force balance equation. Separate the pressure tensor into two parts

$$p_{ij}(\mathbf{r}, \beta | \bar{n}) = \delta_{ij} p_T(\mathbf{r}, \beta | \bar{n}) + \Delta P_{ij}(\mathbf{r}, \beta | \bar{n}), \quad (\text{S.34})$$

$$\Delta P_{ij}(\mathbf{r}, \beta | \bar{n}) = \int d\mathbf{r}' r'_i \int_0^1 d\gamma \frac{\delta f(\mathbf{r} + \gamma \mathbf{r}' - \mathbf{r}', \beta | \bar{n})}{\delta \bar{n}(\mathbf{r} + \gamma \mathbf{r}')} \partial_j \bar{n}(\mathbf{r} + \gamma \mathbf{r}').$$

Then

$$\begin{aligned} \delta_{ij} \partial_i \beta p_T(\mathbf{r}, \beta | \bar{n}) &= \delta_{ij} \partial_i (\bar{n}(\mathbf{r}) \nu(\mathbf{r}) - \beta f(\mathbf{r}, \beta | \bar{n})) \\ &= \bar{n}(\mathbf{r}) \partial_j \nu(\mathbf{r}) + \nu(\mathbf{r}) \partial_j \bar{n}(\mathbf{r}) - \partial_j \beta f(\mathbf{r}, \beta | \bar{n}) \end{aligned} \quad (\text{S.35})$$

and

$$\begin{aligned}
\partial_i \beta \Delta p_{ij}(\mathbf{r}, \beta | \bar{n}) &= \int d\mathbf{r}' r'_i \partial_i \int_0^1 d\gamma \frac{\delta \beta f(\mathbf{r} + \gamma \mathbf{r}' - \mathbf{r}', \beta | \bar{n})}{\delta \bar{n}(\mathbf{r} + \gamma \mathbf{r}')} \partial_j \bar{n}(\mathbf{r} + \gamma \mathbf{r}') \\
&= \int d\mathbf{r}' \int_0^1 d\gamma \partial_\gamma \left(\frac{\delta \beta f(\mathbf{r} + \gamma \mathbf{r}' - \mathbf{r}', \beta | \bar{n})}{\delta \bar{n}(\mathbf{r} + \gamma \mathbf{r}')} \partial_j \bar{n}(\mathbf{r} + \gamma \mathbf{r}') \right) \\
&= \int d\mathbf{r}' \left(\frac{\delta \beta f(\mathbf{r}, \beta | \bar{n})}{\delta \bar{n}(\mathbf{r} + \mathbf{r}')} \partial_j \bar{n}(\mathbf{r} + \mathbf{r}') - \frac{\delta \beta f(\mathbf{r} - \mathbf{r}', \beta | \bar{n})}{\delta \bar{n}(\mathbf{r})} \partial_j \bar{n}(\mathbf{r}) \right) \\
&= \int d\mathbf{r}_1 \frac{\delta \beta f(\mathbf{r}, \beta | \bar{n})}{\delta \bar{n}(\mathbf{r}_1)} \partial_{1j} \bar{n}(\mathbf{r}_1) - \frac{\delta \beta F(\beta | \bar{n})}{\delta \bar{n}(\mathbf{r})} \partial_j \bar{n}(\mathbf{r}) \\
&= -(\nu(\mathbf{r}) \partial_j \bar{n}(\mathbf{r}) - \partial_j \beta f(\mathbf{r}, \beta | \bar{n}))
\end{aligned} \tag{S.36}$$

so the force balance equation is verified

$$\partial_i \beta p_{ij}(\mathbf{r}, \beta | \bar{n}) = \bar{n}(\mathbf{r}) \partial_j \nu(\mathbf{r}). \tag{S.37}$$

For the pressure to qualify as a thermodynamic pressure it should satisfy

$$\int d\mathbf{r} \beta p_m(\mathbf{r}, \beta | \nu) = Q^e(\beta, V | \nu). \tag{S.38}$$

Use of the Percus form (S.33) gives this condition to be

$$\int d\mathbf{r} \frac{1}{3} \int d\mathbf{r}' \int_0^1 d\gamma \frac{\delta f(\mathbf{r} + \gamma \mathbf{r}' - \mathbf{r}', \beta | \bar{n})}{\delta \bar{n}(\mathbf{r} + \gamma \mathbf{r}')} r'_i \partial_i \bar{n}(\mathbf{r} + \gamma \mathbf{r}') = 0. \tag{S.39}$$

The Appendix of Ref. 3 claims that this is true, but no proof is given.

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- [1] Dufty JW, Luo K, Wrighton JM. Generalized hydrodynamics revisited. Phys Rev Research. 2020;2:023036.
 - [2] Percus JK. The pressure tensor in a non-uniform fluid. Chem Phys Lett. 1986;123:311–314.
 - [3] Pozhar LA. Transport theory of inhomogeneous fluids. World Scientific, 1994.