ICFP – Soft Matter

Stress tensor – Solution

Anke Lindner, Vincent Démery

We consider N particles in a box of volume V; we denote $\boldsymbol{x}_i$ and $\boldsymbol{p}_i$ the position and momentum of the particle i. The particles interact through the isotropic pair potential $v(x)$, which can result from any elementary interaction (contact, electrostatic, Van der Waals, etc.).

1 Stress tensor as the current of momentum

1. We define the density $\rho(\boldsymbol{x})$ and density of momentum $\boldsymbol{\pi}(\boldsymbol{x})$ in this system by

$$\rho(\boldsymbol{x}) = \sum_i \delta(\boldsymbol{x}-\boldsymbol{x}_i), \tag{1}$$

$$\boldsymbol{\pi}(\boldsymbol{x}) = \sum_i \boldsymbol{p}_i \delta(\boldsymbol{x}-\boldsymbol{x}_i). \tag{2}$$

We can write conservation equations. The one for ρ reads

$$\partial_t \rho(\boldsymbol{x},t) = -\sum_i \dot{\boldsymbol{x}}_i(t)\cdot\nabla\delta(\boldsymbol{x}-\boldsymbol{x}_i(t)) = -\frac{1}{m}\nabla\cdot\boldsymbol{\pi}(\boldsymbol{x},t), \tag{3}$$

where we have use that $\dot{\boldsymbol{x}}_i = \boldsymbol{p}_i/m$.

2. The time derivative of $\boldsymbol{\pi}$ involves the stress tensor:

$$\partial_t \boldsymbol{\pi}(\boldsymbol{x},t) = \nabla\cdot\boldsymbol{\sigma}(\boldsymbol{x},t). \tag{4}$$

We will make this more explicit to determine the stress tensor.

The particles follow Newton's law:

$$\dot{\boldsymbol{p}}_i(t) = \sum_{j\neq i} \boldsymbol{f}_{ji}(t), \tag{5}$$

where $\boldsymbol{f}_{ji}$ is the force exerted by the particle i on the particle j. The force is given by

$$\boldsymbol{f}_{ji} = -\hat{\boldsymbol{x}}_{ji} v'(\boldsymbol{x}_{ji}), \tag{6}$$

where $\boldsymbol{x}_{ji} = \boldsymbol{x}_i - \boldsymbol{x}_j$ and $\hat{\boldsymbol{x}}_{ji} = \boldsymbol{x}_{ji}/|\boldsymbol{x}_{ji}|$.

We now write the evolution of the density of momentum, using greek indices for the coordinates:

$$\partial_t \pi_\mu(\boldsymbol{x},t) = \sum_i \left[-\frac{p_{i\mu}p_{i\nu}}{m}\partial_\nu\delta(\boldsymbol{x}-\boldsymbol{x}_i) - \sum_{j\neq i}\frac{x_{ji\mu}}{|\boldsymbol{x}_{ji}|}\delta(\boldsymbol{x}-\boldsymbol{x}_i)v'(\boldsymbol{x}_{ji}) \right]. \tag{7}$$

The first part can be written as

$$\sum_i \left[-\frac{p_{i\mu}p_{i\nu}}{m}\partial_\nu\delta(\boldsymbol{x}-\boldsymbol{x}_i)\right] = \partial_\nu \sum_i \left[-\frac{p_{i\mu}p_{i\nu}}{m}\delta(\boldsymbol{x}-\boldsymbol{x}_i)\right] = \partial_\nu \sigma^{\mathrm{id}}_{\mu\nu}(\boldsymbol{x}), \tag{8}$$

where we have introduced the ideal gas stress

$$\sigma^{\mathrm{id}}_{\mu\nu}(\boldsymbol{x}) = \sum_i \left[-\frac{p_{i\mu}p_{i\nu}}{m}\delta(\boldsymbol{x}-\boldsymbol{x}_i)\right]. \tag{9}$$

3. The second part can be written as a sum over pairs:

$$\sum_i \left[-\sum_{j\neq i} \frac{x_{ji\mu}}{|\boldsymbol{x}_{ji}|} \delta(\boldsymbol{x}-\boldsymbol{x}_i) v'(\boldsymbol{x}_{ji}) \right] = \sum_{\langle i,j\rangle} \frac{x_{ij\mu}}{|\boldsymbol{x}_{ij}|} v'(\boldsymbol{x}_{ij}) \left[\delta(\boldsymbol{x}-\boldsymbol{x}_i) - \delta(\boldsymbol{x}-\boldsymbol{x}_j)\right]. \tag{10}$$

We want to write this as a divergence; we note that (App. A)

$$\delta(\boldsymbol{x}-\boldsymbol{x}_i) - \delta(\boldsymbol{x}-\boldsymbol{x}_j) = \partial_\nu \left[x_{ij\nu} \int_0^1 \delta(\boldsymbol{x}-\boldsymbol{x}_i - \lambda[\boldsymbol{x}_j - \boldsymbol{x}_i]) \mathrm{d}\lambda \right]. \tag{11}$$

To keep simpler expressions in the following we denote

$$\delta_{[\boldsymbol{x}_i,\boldsymbol{x}_j]}(\boldsymbol{x}) = \int_0^1 \delta(\boldsymbol{x}-\boldsymbol{x}_i - \lambda[\boldsymbol{x}_j - \boldsymbol{x}_i]) \mathrm{d}\lambda \tag{12}$$

Now the pair contribution to the stress tensor becomes

$$\sum_i \left[-\sum_{j\neq i} \frac{x_{ji\mu}}{|\boldsymbol{x}_{ji}|} \delta(\boldsymbol{x}-\boldsymbol{x}_i) v'(\boldsymbol{x}_{ji}) \right] = \partial_\nu \left[\sum_{\langle i,j\rangle} \frac{x_{ij\mu} x_{ij\nu}}{|\boldsymbol{x}_{ij}|} v'(\boldsymbol{x}_{ij}) \delta_{[\boldsymbol{x}_i,\boldsymbol{x}_j]}(\boldsymbol{x}) \right] = \partial_\nu \sigma^{\mathrm{pair}}_{\mu\nu}(\boldsymbol{x}), \tag{13}$$

where we identify the pair contribution to the stress tensor:

$$\sigma^{\mathrm{pair}}_{\mu\nu}(\boldsymbol{x}) = \sum_{\langle i,j\rangle} \frac{x_{ij\mu} x_{ij\nu}}{|\boldsymbol{x}_{ij}|} v'(\boldsymbol{x}_{ij}) \delta_{[\boldsymbol{x}_i,\boldsymbol{x}_j]}(\boldsymbol{x}). \tag{14}$$

This is the Irving-Kirkwood formula [1].

2 Ideal gas contribution

4. To get better insight in the ideal gas contribution, we can average it over the momentum, using the Maxwell distribution (see App. B),

$$\langle p_{i\mu} p_{i\nu} \rangle = mkT \delta_{\mu\nu}, \tag{15}$$

then

$$\left\langle \sigma^{\mathrm{id}}_{\mu\nu}(\boldsymbol{x}) \right\rangle_{\boldsymbol{p}} = -kT\delta_{\mu\nu}\rho(\boldsymbol{x}), \tag{16}$$

which is the perfect gas law.

3 Pair contribution and response to deformation

5. The energy due to the pair interaction is

$$U_{\mathrm{pair}} = \sum_{\langle i,j\rangle} v(\boldsymbol{x}_{ij}). \tag{17}$$

Now assume that we deform the system by applying a small displacement field $\boldsymbol{u}(\boldsymbol{x})$. The strain field is

$$\epsilon_{\mu\nu} = \frac{1}{2}(\partial_\mu u_\nu + \partial_\nu u_\mu). \tag{18}$$

The new positions are $\boldsymbol{x}'_i = \boldsymbol{x}_i + u(\boldsymbol{x}_i)$. The distance between the particles i and j are now

$${\boldsymbol{x}'_{ij}}^2 \simeq \boldsymbol{x}_{ij}^2 + 2x_{ij\mu}[u_\mu(\boldsymbol{x}_j) - u_\mu(\boldsymbol{x}_i)]. \tag{19}$$

We can write the difference of the displacements as

$$u_\mu(\boldsymbol{x}_j) - u_\mu(\boldsymbol{x}_i) = x_{ij\nu} \int_0^1 \partial_\nu u_\mu(\boldsymbol{x}_i + \lambda[\boldsymbol{x}_j - \boldsymbol{x}_i]) \mathrm{d}\lambda, \tag{20}$$

hence

$$\boldsymbol{x}_{ij}'^{\,2} \simeq \boldsymbol{x}_{ij}^2 + 2x_{ij\mu}x_{ij\nu}\int_0^1 \partial_\nu u_\mu(\boldsymbol{x}_i + \lambda[\boldsymbol{x}_j - \boldsymbol{x}_i])\mathrm{d}\lambda \simeq \left(|\boldsymbol{x}_{ij}| + \frac{x_{ij\mu}x_{ij\nu}}{|x_{ij}|}\int_0^1 \epsilon_{\mu\nu}(\boldsymbol{x}_i + \lambda[\boldsymbol{x}_j - \boldsymbol{x}_i])\mathrm{d}\lambda\right)^2. \tag{21}$$

Finally,

$$|\boldsymbol{x}_{ij}'| - |\boldsymbol{x}_{ij}| \simeq \frac{x_{ij\mu}x_{ij\nu}}{|x_{ij\mu}|}\int_0^1 \epsilon_{\mu\nu}(\boldsymbol{x}_i + \lambda[\boldsymbol{x}_j - \boldsymbol{x}_i])\mathrm{d}\lambda. \tag{22}$$

We note that

$$\int_0^1 \epsilon_{\mu\nu}(\boldsymbol{x}_i + \lambda[\boldsymbol{x}_j - \boldsymbol{x}_i])\mathrm{d}\lambda = \int \mathrm{d}\boldsymbol{x}\epsilon_{\mu\nu}(\boldsymbol{x})\delta_{[\boldsymbol{x}_i,\boldsymbol{x}_j]}(\boldsymbol{x}). \tag{23}$$

The change in energy for this pair is

$$v(\boldsymbol{x}_{ij}') - v(\boldsymbol{x}_{ij}) \simeq \left(|\boldsymbol{x}_{ij}'| - |\boldsymbol{x}_{ij}|\right)v'(\boldsymbol{x}_{ij}) \simeq \frac{x_{ij\mu}x_{ij\nu}}{|x_{ij\mu}|}v'(\boldsymbol{x}_{ij})\int_0^1 \epsilon_{\mu\nu}(\boldsymbol{x}_i + \lambda[\boldsymbol{x}_j - \boldsymbol{x}_i])\mathrm{d}\lambda \tag{24}$$

$$= \int \mathrm{d}\boldsymbol{x}\epsilon_{\mu\nu}(\boldsymbol{x})\frac{x_{ij\mu}x_{ij\nu}}{|x_{ij\mu}|}v'(\boldsymbol{x}_{ij})\delta_{[\boldsymbol{x}_i,\boldsymbol{x}_j]}(\boldsymbol{x}). \tag{25}$$

Summing over the pairs,

$$U_{\text{pair}}' - U_{\text{pair}} = \int \epsilon_{\mu\nu}(\boldsymbol{x})\sigma_{\mu\nu}^{\text{pair}}(\boldsymbol{x})\mathrm{d}\boldsymbol{x}, \tag{26}$$

as we expect.

4 Average of the stress and pair correlation

6. Using that $\int \delta_{[\boldsymbol{x}_i,\boldsymbol{x}_j]}(\boldsymbol{x})\mathrm{d}\boldsymbol{x} = 1$, we easily write the volume average of the (pair) stress

$$\bar{\sigma}_{\mu\nu}^{\text{pair}} = \frac{1}{V}\int \sigma_{\mu\nu}^{\text{pair}}(\boldsymbol{x}) = \frac{1}{V}\sum_{\langle i,j\rangle}\frac{x_{ij\mu}x_{ij\nu}}{|\boldsymbol{x}_{ij}|}v'(\boldsymbol{x}_{ij}) = \frac{1}{2V}\sum_{i\neq j}\frac{x_{ij\mu}x_{ij\nu}}{|\boldsymbol{x}_{ij}|}v'(\boldsymbol{x}_{ij}). \tag{27}$$

The two-particle density is defined by

$$\rho_2(\boldsymbol{x}, \boldsymbol{x}') = \sum_{i\neq j}\delta(\boldsymbol{x} - \boldsymbol{x}_i)\delta(\boldsymbol{x}' - \boldsymbol{x}_j). \tag{28}$$

We can use it to write the pair contribution to the stress:

$$\bar{\sigma}_{\mu\nu}^{\text{pair}} = \frac{1}{2V}\int \mathrm{d}\boldsymbol{x}\mathrm{d}\boldsymbol{x}'\rho_2(\boldsymbol{x}, \boldsymbol{x}')\frac{(x_\mu' - x_\mu)(x_\nu' - x_\nu)}{|\boldsymbol{x}' - \boldsymbol{x}|}v'(\boldsymbol{x}' - \boldsymbol{x}). \tag{29}$$

We change variable to $\boldsymbol{y} = \boldsymbol{x}' - \boldsymbol{x}$:

$$\bar{\sigma}_{\mu\nu}^{\text{pair}} = \frac{1}{2V}\int \mathrm{d}\boldsymbol{x}\mathrm{d}\boldsymbol{y}\rho_2(\boldsymbol{x}, \boldsymbol{x} + \boldsymbol{y})\frac{y_\mu y_\nu}{|\boldsymbol{y}|}v'(\boldsymbol{y}). \tag{30}$$

If the system is homogeneous $\rho_2(\boldsymbol{x}, \boldsymbol{x} + \boldsymbol{y})$ does not depend on $\boldsymbol{x}$, we denote it $\rho_2(\boldsymbol{y})$ and

$$\bar{\sigma}_{\mu\nu}^{\text{pair}} = \frac{1}{2}\int \mathrm{d}\boldsymbol{y}\rho_2(\boldsymbol{y})\frac{y_\mu y_\nu}{|\boldsymbol{y}|}v'(\boldsymbol{y}). \tag{31}$$

Sometimes, the pair correlation is used instead: $\rho_2(\boldsymbol{y}) = \bar{\rho}^2 g(\boldsymbol{y})$ and

$$\bar{\sigma}_{\mu\nu}^{\text{pair}} = \frac{\bar{\rho}^2}{2}\int \mathrm{d}\boldsymbol{y}g(\boldsymbol{y})\frac{y_\mu y_\nu}{|\boldsymbol{y}|}v'(\boldsymbol{y}). \tag{32}$$

This relates the average stress and the structure of the system.

A Difference of two Dirac as a divergence

Using a test function $\phi(\boldsymbol{x})$, we can easily show that

$$\delta(\boldsymbol{x}-\boldsymbol{x}_1)-\delta(\boldsymbol{x}-\boldsymbol{x}_2)=\nabla\cdot\int_0^1\dot{\boldsymbol{\gamma}}(s)\delta(\boldsymbol{x}-\boldsymbol{\gamma}(s))\mathrm{d}s, \tag{33}$$

where $\boldsymbol{\gamma}$ is a contour with $\boldsymbol{\gamma}(0)=\boldsymbol{x}_1$, $\boldsymbol{\gamma}(1)=\boldsymbol{x}_2$.

Indeed, with such contour we have

$$\int\left[\delta(\boldsymbol{x}-\boldsymbol{x}_1)-\delta(\boldsymbol{x}-\boldsymbol{x}_2)\right]\phi(\boldsymbol{x})\mathrm{d}\boldsymbol{x}=\phi(\boldsymbol{x}_1)-\phi(\boldsymbol{x}_2) \tag{34}$$

$$=-\left[\phi(\boldsymbol{\gamma}(s))\right]_0^1 \tag{35}$$

$$=-\int_0^1\frac{\mathrm{d}}{\mathrm{d}s}[\phi(\boldsymbol{\gamma}(s))]\mathrm{d}s \tag{36}$$

$$=-\int_0^1\boldsymbol{\gamma}'(s)\cdot\nabla\phi(\boldsymbol{\gamma}(s))\mathrm{d}s. \tag{37}$$

Now we write

$$\nabla\phi(\boldsymbol{\gamma}(s))=\int\delta(\boldsymbol{x}-\boldsymbol{\gamma}(s))\nabla\phi(\boldsymbol{x})\mathrm{d}\boldsymbol{x}=-\int\phi(\boldsymbol{x})\nabla\delta(\boldsymbol{x}-\boldsymbol{\gamma}(s))\mathrm{d}\boldsymbol{x}. \tag{38}$$

Hence

$$\int\left[\delta(\boldsymbol{x}-\boldsymbol{x}_1)-\delta(\boldsymbol{x}-\boldsymbol{x}_2)\right]\phi(\boldsymbol{x})\mathrm{d}\boldsymbol{x}=\int\mathrm{d}\boldsymbol{x}\phi(\boldsymbol{x})\int_0^1\boldsymbol{\gamma}'(s)\cdot\nabla\delta(\boldsymbol{x}-\boldsymbol{\gamma}(s))\mathrm{d}s. \tag{39}$$

So that, as distributions,

$$\delta(\boldsymbol{x}-\boldsymbol{x}_1)-\delta(\boldsymbol{x}-\boldsymbol{x}_2)=\int_0^1\boldsymbol{\gamma}'(s)\cdot\nabla\delta(\boldsymbol{x}-\boldsymbol{\gamma}(s))\mathrm{d}s=\nabla\cdot\int_0^1\boldsymbol{\gamma}'(s)\delta(\boldsymbol{x}-\boldsymbol{\gamma}(s))\mathrm{d}s. \tag{40}$$

We can then specify it to $\boldsymbol{\gamma}(s)=\boldsymbol{x}_1+s(\boldsymbol{x}_2-\boldsymbol{x}_1)$, leading to

$$\delta(\boldsymbol{x}-\boldsymbol{x}_1)-\delta(\boldsymbol{x}-\boldsymbol{x}_2)=\nabla\cdot\left[(\boldsymbol{x}_2-\boldsymbol{x}_1)\int_0^1\delta(\boldsymbol{x}-\boldsymbol{x}_1-s[\boldsymbol{x}_2-\boldsymbol{x}_1])\mathrm{d}s\right]. \tag{41}$$

B Correlations of a Gaussian random variable

Here we consider a Gaussian random variable $\boldsymbol{x}\in\mathbb{R}^n$ with probability density

$$p(\boldsymbol{x})=C\exp\left(-\frac{1}{2}A_{\mu\nu}x_\mu x_\nu\right), \tag{42}$$

where $A_{\mu\nu}$ is a symmetric positive matrix, and C is the constant that ensures that the probability density is normalized, $\int p(\boldsymbol{x})\mathrm{d}\boldsymbol{x}=1$. We show that its correlations are given by

$$\langle x_\mu x_\nu\rangle=A^{-1}_{\mu\nu}. \tag{43}$$

To show this, we compute the derivatives

$$\partial_\alpha\exp\left(-\frac{1}{2}A_{\mu\nu}x_\mu x_\nu\right)=-A_{\alpha\lambda}x_\lambda\exp\left(-\frac{1}{2}A_{\mu\nu}x_\mu x_\nu\right), \tag{44}$$

$$\partial_\alpha\partial_\beta\exp\left(-\frac{1}{2}A_{\mu\nu}x_\mu x_\nu\right)=\left(A_{\alpha\lambda}x_\lambda A_{\beta\sigma}x_\sigma-A_{\alpha\beta}\right)\exp\left(-\frac{1}{2}A_{\mu\nu}x_\mu x_\nu\right). \tag{45}$$

The integral over $\boldsymbol{x}$ of these total derivatives is zero. Multiplying Eq. (45) by C and integrating over $\boldsymbol{x}$, we get for the right hand side

$$A_{\alpha\lambda}A_{\beta\sigma}\langle x_\lambda x_\sigma\rangle=A_{\alpha\beta}. \tag{46}$$

In matrix notation this means that $A\langle\boldsymbol{x}\boldsymbol{x}^{\mathrm{T}}\rangle A=A$, hence

$$\langle\boldsymbol{x}\boldsymbol{x}^{\mathrm{T}}\rangle=A^{-1}. \tag{47}$$

References

[1] J. H. Irving and John G. Kirkwood. The Statistical Mechanical Theory of Transport Processes. IV. The Equations of Hydrodynamics. *The Journal of Chemical Physics*, 18(6):817–829, 1950.