The Isotropy of the Pressure in Anisotropic Systems

A.J.Masters
Department of Chemistry
University of Manchester
Manchester M13 9PL

1. The Problem

The virial equation gives the pressure tensor, $p_{\alpha\beta}$, in terms of the equilibrium ensemble average of the microscopic stress tensor, $\sigma_{\alpha\beta}$. Thus we have

$$\begin{aligned} p_{\alpha\beta}V &= \left\langle \sigma_{\alpha\beta} \right\rangle \\ &= \left\langle \sum_i m v_{i\alpha} v_{i\beta} + \tfrac{1}{2} \sum_{i \neq j} r_{ij,\alpha} f_{ij,\beta} \right\rangle \end{aligned} \qquad (1)$$

where V is the volume of the system, m is the particle mass, $\mathbf{v}_i$ is the velocity of particle i, $\mathbf{r}_{ij}$ is the centre of mass separation between particles i and j and $\mathbf{f}_{ij}$ is the force exerted on particle i by particle j. The Greek subscripts indicate Cartesian tensor components. Eq. (1) presupposes that the system considered is classical and that the forces are pairwise additive.

The pressure tensor is thus an average of a second rank tensor. Let us consider an arbitrary second rank tensor, $A_{\alpha\beta}$, dependent on the molecular configuration. In the isotropic phase, it must be true that

$$\left\langle A_{\alpha\beta} \right\rangle = a\delta_{\alpha\beta} \qquad (2)$$

where a is a scalar constant. Thus it follows that the pressure tensor must also be isotropic, i.e.

$$p_{\alpha\beta} = p\delta_{\alpha\beta} \tag{3}$$

where p is the normal pressure.

Now let us consider an anisotropic system, in particular a nematic liquid crystal, where there is a preferred molecular alignment along a particular direction - the director, $\hat{\mathbf{n}}$. Here the average of an arbitrary second rank tensor is not isotropic. In general one has

$$\left\langle A_{\alpha\beta} \right\rangle = a\delta_{\alpha\beta} + b\hat{n}_\alpha \hat{n}_\beta \tag{4}$$

with a and b both being scalar constants. A nematic liquid crystal is a fluid, however, and experimentally one knows it cannot support an external stress. One would thus expect the pressure tensor to be isotropic. The question thus arises as to whether one can show mathematically that there is something special about the stress tensor, so that its average is indeed isotropic and that the constant, b, in eq. (4) turns out to be zero. I should point out that there is absolutely no symmetry reason for this property and, indeed, I could make no progress in this matter simply by staring at the virial expression, eq. (1), as it stood.

2. A Proposed Resolution

Let us introduce the Fourier transforms of the microscopic number and momentum densities, $n_{\mathbf{k}}$ and $p_{\mathbf{k},\alpha}$ respectively. These are given by

$$n_{\mathbf{k}} = \sum_i \exp(i\mathbf{k} \cdot \mathbf{r}_i) \tag{5a}$$

and

$$p_{\mathbf{k},\alpha} = \sum_i p_{i,\alpha} \exp(i\mathbf{k} \cdot \mathbf{r}_i) \tag{5b}$$

where $\mathbf{r}_\mathbf{i}$ is the centre of mass of particle i and $\mathbf{p}_\mathrm{i}$ is its momentum. We have the results that

$$\dot{p}_{\mathbf{k},\alpha} = ik_\beta \sigma_{\mathbf{k},\beta\alpha} \tag{6}$$

and

$$\lim_{k\to 0} \sigma_{\mathbf{k},\alpha\beta} = \sigma_{\alpha\beta}, \tag{7}$$

where the R.H.S. of eq. (7) is exactly the same quantity as appears in eq. (1). Schofield showed that for small k, [1]

$$ik_\alpha \left(\frac{\partial p_{\alpha\beta}}{\partial \rho} \right)_T = \frac{\left\langle ik_\alpha \sigma_{\mathbf{k},\alpha\beta} n_{-\mathbf{k}} \right\rangle}{\left\langle n_\mathbf{k} n_{-\mathbf{k}} \right\rangle} \tag{8}$$

where ρ is the average number density of the system and T is the temperature. Eq. (6) and the dot switching properties of stationary correlation functions allows one to rewrite eq. (8) as

$$ik_\alpha \left(\frac{\partial p_{\alpha\beta}}{\partial \rho} \right)_T = -\frac{\left\langle p_{\mathbf{k},\beta} \dot{n}_{-\mathbf{k}} \right\rangle}{\left\langle n_\mathbf{k} n_{-\mathbf{k}} \right\rangle} = \frac{ik_\beta \langle N \rangle k_B T}{\left\langle n_\mathbf{k} n_{-\mathbf{k}} \right\rangle} \tag{9}$$

where $\langle N \rangle$ is the average number of particles in the system and k_B is Boltzmann's constant. As the low k limit of $\langle n_\mathbf{k} n_{-\mathbf{k}} \rangle$ does not depend on the direction of **k**, then eq. (9) implies that

$$\left(\frac{\partial p_{\alpha\beta}}{\partial \rho}\right)_T = \lim_{k\to 0}\frac{\langle N\rangle k_B T}{\langle n_{\mathbf{k}} n_{-\mathbf{k}}\rangle}\delta_{\alpha\beta} \tag{10}$$

This is the compressibility equation of state and it shows the density derivative of the pressure tensor to be isotropic. To get the actual pressure tensor we must integrate eq. (10) with respect to density, leaving us with a result of the form

$$p_{\alpha\beta} = p\delta_{\alpha\beta} + C_{\alpha\beta}(T) \tag{11}$$

where the final term is the constant of integration. As the thermodynamic state of a nematic liquid crystal is determined simply by ρ and T, then the constant of integration can only depend on the temperature. As is well known from the virial expansion, however, there exist no density independent terms in any expression for the pressure, so clearly the constant of integration is zero and we have proved that the pressure tensor is isotropic. A rather brief account of this work appears in the appendix of reference [2].

3. Some Final Comments

The argument in the previous section, up to eq. (10) goes through for all systems at equilibrium, solids included. The argument can be generalised to deal with solids under external stresses and strains by making use not only of the zero k limit of $n_{\mathbf{k}}$ but also investigating values of **k** close to a lattice vector (at least in the case of crystals). Following though this type of approach leads eventually to a disguised expression for Hooke's law. The case of a glass can also be treated but is a little more complicated.

Finally I would like to acknowledge the contribution of Martin Whittle, who first raised the question with me as to why pressures in anisotropic systems should be isotropic and the contribution of Mike Allen, as it was in the course of collaborative work with him that the solution given above was found.

References

[1] Schofield, P., 1966, *Proc. Roy. Soc.* , **88**,149.

[2] Allen, M.P. and Masters, A.J., 1993, *Molec. Phys.*, **79**, 277.