Appendix 1

Discussion of periodic boundary conditions for mixed flows.

The Kraynik-Reinelt periodic boundary conditions (pbcs) for planar extensional flow (PEF) [KR92] have been developed [TD98, TD99, BC99, TD00, DT06] and used in several studies of atomic and molecular fluids [MDT00, MDT01, MDT03, DMT03, EBK05, BEKC05, IBE^{+}06, EBK06, DMT07, SdPG06, FST06, FTS07] at constant volume and constant temperature. Frascoli and Todd [FT07] have recently generalised the pbc scheme to systems at constant pressure and constant temperature. Kraynik and Reinelt [KR92] note that the pbcs can be generalised to systems under flows with a velocity gradient tensor $\nabla\mathbf{u}$ in two dimensions which can be diagonalised so that $\nabla\mathbf{u} = \mathsf{sds}^{-1}$. In this appendix we use this observation to obtain pbcs for homogeneous mixed flow with the velocity gradient given by,

$$\nabla\mathbf{u} = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ \dot{\gamma} & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{A-1}$$

where neither the shear nor the extension rates are zero ($\dot{\gamma} \neq 0$ and $\dot{\epsilon} \neq 0$ respectivly). The equations for the streamlines in this flow are give by,

$$x(t) = \frac{\dot{\gamma}}{\dot{\epsilon}} y(0) \sinh(\dot{\epsilon}t) + x(0) \exp(\dot{\epsilon}t) \quad \text{(A-2)}$$

$$y(t) = y(0) \exp(-\dot{\epsilon}t). \quad \text{(A-3)}$$

The development here gives details of such a scheme for mixed flow. However, we have not as yet implemented this scheme. We note without further discussion that the paper of Adler and Brenner [AB85] gives details of lattices which would be suitable for elliptical flows where the streamlines are concentric ellipses centred at the origin. The collection of pbcs: Lees-Edwards for PCF, Kraynik-Reinelt for PEF, the variation on Kraynik-Reinelt discussed here for mixed flows and development of pbcs for elliptical flows based on Adler and Brenner [AB85] would provided pbcs for all types of planar homogeneous flows [PS78, KCM77, AB85].

Reproducible lattices for mixed flow.

A key step in the Kraynik and Reinelt development of pbcs for PEF was to find lattices in $\mathbb{R}^3$ which were both spatially and temporally periodic for that flow. This condition is termed reproducibility. For mixed flows similarly reproducible lattices lead to pbcs for these flows. The points of such a lattice are given by,

$$\mathbf{R_n} = n_1 \mathbf{L}_1 + n_2 \mathbf{L}_2 + n_3 \mathbf{L}_3 \quad \text{(A-4)}$$

where $\mathbf{n} = (n_1, n_2, n_3)$ is a tuple of three integers and $\mathbf{L}_1$, $\mathbf{L}_2$ and $\mathbf{L}_3$ are three linearly independent basis vectors which span $\mathbb{R}^3$. Kraynik and Reinelt considered shear-free flows where $\nabla \mathbf{u} = \text{diag}\,(d_1, d_2, d_3) \equiv \mathsf{d}$. They stated the condition for reproducibility with the following expression,

$$\mathbf{L}_i \cdot \exp(\tau_p \mathsf{d}) = N_{i1} \mathbf{L}_1 + N_{i2} \mathbf{L}_2 + N_{i3} \mathbf{L}_3, \quad \text{(A-5)}$$

where τ_p is the time at which the lattice is reproduced and N_{ij} are elements of a 3×3 integer matrix N. This is the condition that after some time τ_p the lattice $\mathbf{R}_{\mathbf{n}}$ is mapped back on to itself.

Kraynik and Reinelt found suitable sets of basis vectors $\mathbf{L}_i$ and matrices N for PEF where $\mathsf{d} = \mathrm{diag}(+\dot{\epsilon}, -\dot{\epsilon}, 0)$. They also mention that their method gives reproducible lattices for flows with a velocity gradient which is diagonalisable, so that,

$$\nabla \mathbf{u}_{diag.} = \mathsf{s} \cdot \mathsf{d} \cdot \mathsf{s}^{-1}. \tag{A-6}$$

It is this observation that we use to find the suitable periodic boundary conditions for mixed flow with a velocity gradient given by (A-1).

With the diagonalisation given in (A-6), the homogeneous flow has the map,

$$\begin{aligned} \exp(t\ \nabla \mathbf{u}_{diag.}) &= \exp(t\ \mathsf{s} \cdot \mathsf{d} \cdot \mathsf{s}^{-1}) && \text{(A-7)} \\ &= \mathsf{s} \cdot \exp(t\ \mathsf{d}) \cdot \mathsf{s}^{-1}. && \text{(A-8)} \end{aligned}$$

Thus if the lattice with basis vectors $\mathbf{L}_i$ is reproducible under the flow $\nabla \mathbf{u} = \mathrm{diag}(d_1, d_2, d_3)$, then the lattice with basis vectors $\mathbf{L}'_i = \mathbf{L}_i \cdot \mathsf{s}^{-1}$ is reproducible under the diagonalisable flow $\nabla \mathbf{u}$. The demonstration of the reproducibility follows,

$$\begin{aligned} \mathbf{L}'_i \cdot \exp(\tau_p \nabla \mathbf{u}_{diag.}) &= \mathbf{L}'_i \cdot \mathsf{s} \cdot \exp(t\mathsf{d}) \cdot \mathsf{s}^{-1} \\ &= \mathbf{L}_i \cdot \mathsf{s}^{-1} \cdot \mathsf{s} \cdot \exp(t\mathsf{d}) \cdot \mathsf{s}^{-1} \\ &= \mathbf{L}_i \cdot \exp(t\mathsf{d}) \cdot \mathsf{s}^{-1} \\ &= (N_{i1}\mathbf{L}_1 + N_{i2}\mathbf{L}_2 + N_{i3}\mathbf{L}_3) \cdot \mathsf{s}^{-1} \\ &= N_{i1}\mathbf{L}_1 \cdot \mathsf{s}^{-1} + N_{i2}\mathbf{L}_2 \cdot \mathsf{s}^{-1} + N_{i3}\mathbf{L}_3 \cdot \mathsf{s}^{-1} \\ &= N_{i1}\mathbf{L}'_1 + N_{i2}\mathbf{L}'_2 + N_{i3}\mathbf{L}'_3. \end{aligned}$$

For the mixed flow (A-1) the diagonalisation is,

$$\nabla \mathbf{u}_{mix.} = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ \dot{\gamma} & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ \frac{\dot{\gamma}}{2\dot{\epsilon}} & -\frac{\dot{\gamma}}{2\dot{\epsilon}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 1 & -\frac{2\dot{\epsilon}}{\dot{\gamma}} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
$$\equiv \mathsf{s}_{mix.} \cdot \mathsf{d} \cdot \mathsf{s}_{mix.}^{-1} \qquad \text{(A-9)}$$

We see that the diagonal matrix d is the velocity gradient for PEF. Kraynik and Reinelt have found angles θ for which the orthonormal basis vectors $\mathbf{L}_1 = (\cos\theta, \sin\theta, 0), \mathbf{L}_2 = (-\sin\theta, \cos\theta, 0)$ and $\mathbf{L}_3 = (0, 0, 1)$ are reproducible under PEF. Thus, following the argument in the last paragraph, the vectors $\mathbf{L}'_i = \mathbf{L}_i \cdot \mathsf{s}_{mix.}^{-1}$ give a reproducible lattice under mixed flow. The basis vectors $\mathbf{L}'_i$ are given in full by,

$$\begin{aligned} \mathbf{L}'_1 &= (\cos\theta + \sin\theta, -\frac{2\dot{\epsilon}}{\dot{\gamma}}\sin\theta, 0), \\ \mathbf{L}'_2 &= (\cos\theta - \sin\theta, -\frac{2\dot{\epsilon}}{\dot{\gamma}}\cos\theta, 0), \\ \mathbf{L}'_3 &= (0, 0, 1). \end{aligned} \qquad \text{(A-10)}$$

In the simulations of PEF that we have performed in Chapter 4 and 5 the angle we used was $\theta = \arctan(\frac{\sqrt{5}-1}{2}) \approx 31.7^o$. Following Fig. 7 of [KR92] and Fig. 1 of [TD98] we have plotted the evolution of the lattice $\mathbf{R_n} = n_1\mathbf{L}_1 + n_2\mathbf{L}_2$ under PEF in Fig. A-1. As an example in Fig. A-2 we have plotted the lattice $\mathbf{R_n} = n_1\mathbf{L}'_1 + n_2\mathbf{L}'_2$ for mixed flow with $\dot{\gamma} = \dot{\epsilon}$. The lattice in both Figs. A-1 and A-2 is reproduced when $\dot{\epsilon}t = \dot{\epsilon}\tau_p = \epsilon_p = \log_e(\lambda_p) = \log_e(\frac{3+\sqrt{5}}{2}) \approx 0.9624$. This reproducible lattice combined with methods of implementation presented by Todd and Daivis [TD99] should lead directly to pbcs for mixed flow. It is useful to note that for homogeneous flows the map which transforms positions of fluid volumes is an affine transformation which implies that straight lines and planes transform to other straight lines and planes at later times. The consequence for NEMD is that under homogeneous flows a polyhedral simulation cell will remain polyhedral throughout the simulation.

Minimum lattice spacing for mixed flow.

Here we provide a method for checking that the chosen lattice for mixed flow is admissible. For this to be the case we need to choose a density for the system such that the distance between any two lattice points is never less than the diameter of an atom. This test is simplified due to the reproducibilty of the lattice, which implies that the minimum distance need only be checked for the three corners of the lattice which are not at the origin.

From the equations for the streamlines in mixed flow (A-3) we can calculate the minimum distance of a particular streamline from the origin by solving the equation,

$$\frac{d}{dt}\mathbf{r}^2 = x\dot{x} + y\dot{y} = 0 \tag{A-11}$$

From this equation the value of $y(t)$ at the minimum distance can be calculated to be,

$$y(t_{min}) = \frac{(\dot{\gamma}x(0)y(0) + \dot{\epsilon}y(0)^2)^{1/2}}{(4\dot{\epsilon}^2 - \dot{\gamma}^2)^{1/4}} \tag{A-12}$$

This can be substituted back into the equations for the streamlines to give the minimum distance. The equations for the stream lines can also be written in a non-parametric form as,

$$\dot{\gamma}y(t)^2 + 2\dot{\epsilon}x(t)y(t) = c, \tag{A-13}$$

where c is a constant. This leads to the minimum squared-distance,

$$d(t_{min.})^2 = \frac{c - \dot{\gamma}y(t_{min})^2}{2\dot{\epsilon}y(t_{min})} + y(t_{min})^2. \tag{A-14}$$

For the pbcs to be compatible under mixed flow $d(t_{min})^2$ should not be less than the square of the interatomic potential diameter for any of the vertices $(x(0), y(0))$ of the simulation cell (except the origin). We note that this analysis is applied to the case where one corner of the simulation cell is at the origin, however, the homogeneous nature of the flow means that any translation of a compatible lattice will itself be compatible.

The SLLOD equations for mixed flow

The general form of the sllod equations of motion (3.5) can be combined with the velocity gradient for mixed flow (A-1) to give the explicit equations of motion,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \dot{\epsilon}(x_i \hat{\mathbf{n}}_x - y_i \hat{\mathbf{n}}_y) + \dot{\gamma} y_i \hat{\mathbf{n}}_x, \quad \text{(A-15)}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \dot{\epsilon}(p_{xi} \hat{\mathbf{n}}_x - p_{yi} \hat{\mathbf{n}}_y) + \dot{\gamma} p_{yi} \hat{\mathbf{n}}_x - \zeta \mathbf{p}_i, \quad \text{(A-16)}$$

with the Gaussian iso-kinetic thermostat (3.6),

$$\zeta = \frac{\sum_{i=1}^{N} (\mathbf{F}_i \cdot \mathbf{p}_i - \dot{\epsilon}(p_{ix}^2 - p_{iy}^2) - \dot{\gamma} p_{xi} p_{yi})}{\sum_{i=1}^{N} \mathbf{p}_i^2}. \quad \text{(A-17)}$$

Comparing these equations with those for PEF and PCF, one sees that the flow dependent parts for mixed flow are simply the sum of the flow dependent parts for the two *pure* flows. This is a consequence of the linearity of (3.5) with respect to the velocity gradient, noting in particular that the thermostat (3.6) is a linear function of the velocity gradient.

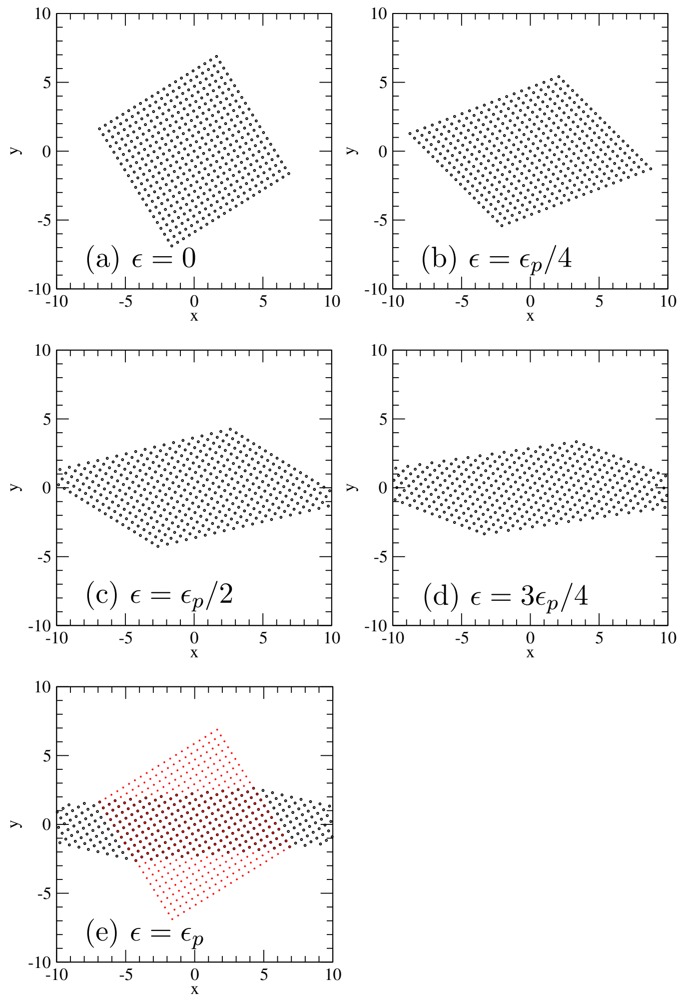

Figure A-1: Demonstration of the reproducibility of a Kraynik-Reinelt lattice under PEF. The extension is along the x-axis and compression is along the y-axis. In this example the lattice is oriented at 31.7^o to the x-axis. Figs. (a)-(e) shows the lattice at different values of the strain. In Fig. (e) we have included the initial lattice. After a period $\tau_p = \epsilon_p/\dot{\epsilon}$ the lattice is reproduced (after Fig. 1 in [TD98]).

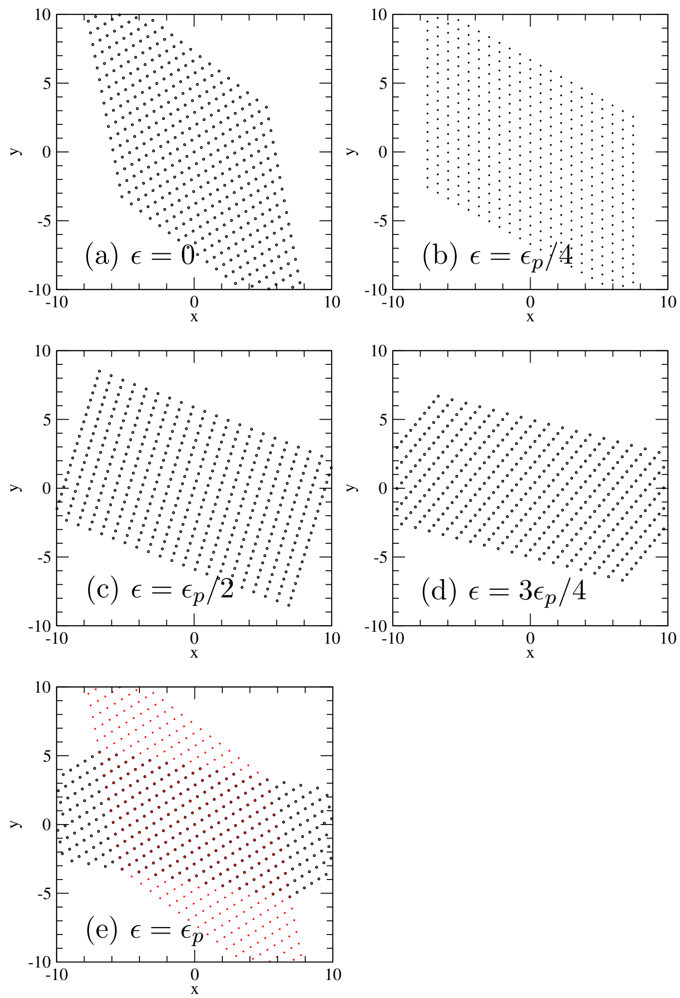

Figure A-2: The demonstration of a lattice which is reproduced under the family of mixed flows with $\dot{\epsilon} = \dot{\gamma}$. Figs. (a)-(e) present the lattice after different amounts of strain. The initial lattice is included in Fig. (e) to show that at $\epsilon = \epsilon_p$ the lattice is reproduced. The basis vectors for this lattice were calculated using (A-11) with $\theta \approx 31.7^o$.