Appendix 2. Expressions for the elements of the stability matrix for the isokinetic-isobaric ensemble.

We explicitly derive the coefficients of the stability, or Jacobian, matrix $\mathbf{T}$ defined as $\partial\mathbf{G}/\partial\mathbf{\Gamma}$, where $\mathbf{G}(\mathbf{\Gamma},t)$ is given by Eq. (3.1), for equilibrium and nonequilibrium systems in the *NpT* regime. The presence of Eqs. (1.38) and (1.41) for the NH barostat causes the dimension of the phase space to be $dN+2$, where *d* is the Cartesian dimension, *N* is the number of atoms and 2 are the extra degrees of freedom $(V,\dot{\xi})$. In general, the stability matrix is thus expressed as

$$\mathbf{T}^{NpT}=\begin{pmatrix} \frac{\partial\dot{\mathbf{r}}}{\partial\mathbf{r}} & \frac{\partial\dot{\mathbf{r}}}{\partial\mathbf{p}} & \frac{\partial\dot{\mathbf{r}}}{\partial V} & \frac{\partial\dot{\mathbf{r}}}{\partial\dot{\xi}} \\ \frac{\partial\dot{\mathbf{p}}}{\partial\mathbf{r}} & \frac{\partial\dot{\mathbf{p}}}{\partial\mathbf{p}} & \frac{\partial\dot{\mathbf{p}}}{\partial V} & \frac{\partial\dot{\mathbf{p}}}{\partial\dot{\xi}} \\ \frac{\partial\dot{V}}{\partial\mathbf{r}} & \frac{\partial\dot{V}}{\partial\mathbf{p}} & \frac{\partial\dot{V}}{\partial V} & \frac{\partial\dot{V}}{\partial\dot{\xi}} \\ \frac{\partial\ddot{\xi}}{\partial\mathbf{r}} & \frac{\partial\ddot{\xi}}{\partial\mathbf{p}} & \frac{\partial\ddot{\xi}}{\partial V} & \frac{\partial\ddot{\xi}}{\partial\dot{\xi}} \end{pmatrix} \tag{A2.1}$$

where the reduced coordinate is defined as $\mathbf{r}=\mathbf{q}/V^{1/d}$, $\mathbf{q}$ are laboratory positions and $\mathbf{p}$ are the peculiar momenta, as described in Section 4.3. If we indicate the Cartesian components with Greek letters $\alpha,\beta,...$ and the particle numbers with indexes $i,j,...$, derivations of Eqs. (4.6)-(4.7) for PSF and PEF, provide the following terms for $\dot{r}_{\beta j}$:

$$\begin{aligned} &\frac{\partial}{\partial r_{\alpha i}}\dot{r}_{\beta j}=\begin{cases}\dot{\gamma}\delta_{\alpha y}\delta_{\beta x}\delta_{ij} & \text{for shear}\\ \left(\dot{\varepsilon}\delta_{\alpha x}\delta_{\beta x}-\dot{\varepsilon}\delta_{\alpha y}\delta_{\beta y}\right)\delta_{ij} & \text{for elongation}\end{cases}\\ &\frac{\partial}{\partial p_{\alpha i}}\dot{r}_{\beta j}=\frac{\delta_{\alpha\beta}\delta_{ij}}{mV^{1/d}}\\ &\frac{\partial}{\partial V}\dot{r}_{\beta j}=-\frac{p_{\beta j}}{dmV^{(1/d+1)}}\\ &\frac{\partial}{\partial\dot{\xi}}\dot{r}_{\beta j}=0 \end{aligned} \tag{A2.2}$$

and analogously for $\dot{p}_{\beta j}$:

$$\begin{aligned}
&\frac{\partial}{\partial r_{\alpha i}}\dot{p}_{\beta j}=\frac{\partial F_{\beta j}}{\partial r_{\alpha i}}-\frac{\partial \alpha}{\partial r_{\alpha i}}p_{\beta j}\\
&\frac{\partial}{\partial p_{\alpha i}}\dot{p}_{\beta j}=-\alpha\delta_{\alpha\beta}\delta_{ij}-\frac{\partial \alpha}{\partial p_{\alpha i}}p_{\beta j}+\begin{cases}-\dot{\gamma}\delta_{\alpha y}\delta_{\beta x}\delta_{ij} & \text{for shear}\\ -\left(\dot{\varepsilon}\delta_{\alpha x}\delta_{\beta x}-\dot{\varepsilon}\delta_{\alpha y}\delta_{\beta y}\right)\delta_{ij} & \text{for elongation}\end{cases}\\
&\frac{\partial}{\partial V}\dot{p}_{\beta j}=\frac{\partial F_{\beta j}}{\partial V}-\frac{\partial \alpha}{\partial V}p_{\beta j}\\
&\frac{\partial}{\partial \dot{\xi}}\dot{p}_{\beta j}=0
\end{aligned}\qquad\text{(A2.3)}$$

where $F_{\beta j}$ is the force on component β experienced by particle j, and α is the Gaussian thermostat multiplier (see Eq. (1.33) for PSF and (1.36) for PEF). Before the expressions for the derivatives in (A2.3) are provided, let us report the elements associated with Eqs. (1.38) and (1.41):

$$\begin{aligned}
&\frac{\partial}{\partial r_{\alpha i}}\dot{V}=0\\
&\frac{\partial}{\partial p_{\alpha i}}\dot{V}=0\\
&\frac{\partial}{\partial V}\dot{V}=d\dot{\xi}\\
&\frac{\partial}{\partial \dot{\xi}}\dot{V}=dV
\end{aligned}\qquad\text{(A2.4)}$$

and

$$\begin{aligned}
&\frac{\partial}{\partial r_{\alpha i}}\ddot{\xi}=\frac{\partial p}{\partial r_{\alpha i}}\frac{V}{NQk_BT}\\
&\frac{\partial}{\partial p_{\alpha i}}\ddot{\xi}=\frac{2Vp_{\alpha i}}{dNQk_BT}\\
&\frac{\partial}{\partial V}\ddot{\xi}=\frac{\left(p-p_0\right)}{NQk_BT}+\frac{\partial p}{\partial V}\frac{V}{NQk_BT}\\
&\frac{\partial}{\partial \dot{\xi}}\ddot{\xi}=0
\end{aligned}\qquad\text{(A2.5)}$$

where p is the trace of the pressure tensor (1.6) divided by the dimensionality d, Q is the damping factor and p_0 is the target pressure. As it can be seen, formulae (A2.3) and (A2.5) contain derivatives of the force $\mathbf{F}_i$, which needs to be expressed in terms of the reduced coordinates $\mathbf{r}=\mathbf{q}/V^{1/d}$. We can introduce the constants a and b, defined as

$$a = V^{-7/d}$$
$$b = V^{-6/d} = aV$$

and obtain the expression for the WCA force in terms of $r = \left\|\mathbf{r}_i - \mathbf{r}_j\right\| = \left\|\mathbf{q}_i - \mathbf{q}_j\right\| \big/ V^{1/d}$:

$$\mathbf{F}_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \frac{24a}{r^8}\left(\frac{2b}{r^6} - 1\right)\left[\mathbf{r}_i - \mathbf{r}_j\right] \tag{A2.6}$$

It is clear that the value of (A2.6) is identical to the one that comes from the usual derivation of the potential (1.11) with respect to ordinary laboratory distances. Nonetheless, $\mathbf{F}_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ is now a function of $\mathbf{r}_i$ and of the volume *V*, and it needs to be used when calculating the terms $\frac{\partial \alpha}{\partial r_{\alpha i}}$, $\frac{\partial p}{\partial r_{\alpha i}}$ and $\frac{\partial p}{\partial V}$. Given the definition (1.6), the last derivative presents the contribution $\frac{\partial \mathbf{F}_{ij}(\mathbf{r}_i, \mathbf{r}_j)}{\partial V}$, which, for a component α, can be written as

$$\frac{\partial F_{\alpha ij}(\mathbf{r}_i, \mathbf{r}_j)}{\partial V} = -\frac{24a}{dVr^8}\left(\frac{26b}{r^6} - 7\right)\left[r_{\alpha i} - r_{\alpha j}\right] \tag{A2.7}$$

Expressions for $\frac{\partial F_{\alpha ij}(\mathbf{r}_i, \mathbf{r}_j)}{\partial r_{\beta j}}$ are analogous to those found for the usual $\frac{\partial F_{\alpha ij}(\mathbf{q}_i, \mathbf{q}_j)}{\partial q_{\beta j}}$ and are omitted here. The derivatives of the isokinetic multiplier are identical to the ones found for an *NVT* regime, except for the substitution $\frac{\partial F_{\alpha ij}(\mathbf{q}_i, \mathbf{q}_j)}{\partial q_{\beta j}} \to \frac{\partial F_{\alpha ij}(\mathbf{r}_i, \mathbf{r}_j)}{\partial r_{\beta j}}$,

$$\frac{\partial}{\partial r_{\beta j}}\alpha = \frac{\sum_{\alpha i} \partial F_{\alpha i} / \partial r_{\beta j} \cdot p_{\alpha i}}{\sum_{\alpha i} p_{\alpha i}^2}$$

$$\frac{\partial}{\partial p_{\beta j}}\alpha = \begin{cases} \dfrac{F_{\beta j} - 2\alpha p_{\beta j} - \dot{\gamma}\left(\delta_{\beta x} p_{yj} + \delta_{\beta y} p_{xj}\right)}{\sum_{\alpha i} p_{\alpha i}^2} & \text{for shear} \\ \dfrac{F_{\beta j} - 2\alpha p_{\beta j} - 2\dot{\varepsilon}\left(\delta_{\beta x} - \delta_{\beta y}\right) p_{\beta j}}{\sum_{\alpha i} p_{\alpha i}^2} & \text{for elongation} \end{cases} \tag{A2.8}$$

$$\frac{\partial}{\partial V}\alpha = \frac{\sum_{\alpha i} \partial F_{\alpha i} / \partial V \cdot p_{\alpha i}}{\sum_{\alpha i} p_{\alpha i}^2}$$

whereas the derivative of *p* respect to the component $r_{\alpha i}$ are given by

$$\frac{\partial}{\partial r_{\alpha i}} p = \frac{1}{dV^{(1-1/d)}}\left[\sum\nolimits_j F_{\alpha ij} + \sum\nolimits_{\beta j} \frac{\partial F_{\beta ij}}{\partial r_{\alpha i}}\left(r_{\beta i} - r_{\beta j}\right)\right] \tag{A2.9}$$

It is possible to write Eq. (3.2) for the tangent vectors in a compact form, which, for equilibrium, turns out to be

$$\begin{aligned}
\delta\dot{\mathbf{r}} &= \frac{\partial \dot{\mathbf{r}}}{\partial \mathbf{p}} \cdot \delta\mathbf{p} + \frac{\partial \dot{\mathbf{r}}}{\partial V}\delta V \\
\delta\dot{\mathbf{p}} &= \frac{\partial \dot{\mathbf{p}}}{\partial \mathbf{r}} \cdot \delta\mathbf{r} + \frac{\partial \dot{\mathbf{p}}}{\partial \mathbf{p}} \cdot \delta\mathbf{p} + \frac{\partial \dot{\mathbf{p}}}{\partial V}\delta V \\
\delta\dot{V} &= \frac{\partial \dot{V}}{\partial V}\delta V + \frac{\partial \dot{V}}{\partial \dot{\xi}}\delta V \\
\delta\ddot{\xi} &= \frac{\partial \ddot{\xi}}{\partial \mathbf{r}} \cdot \delta\mathbf{r} + \frac{\partial \ddot{\xi}}{\partial \mathbf{p}} \cdot \delta\mathbf{p} + \frac{\partial \ddot{\xi}}{\partial V}\delta V
\end{aligned} \tag{A2.10}$$

The dynamics of the infinitesimal displacements $\delta\mathbf{\Gamma} = \left[\delta\mathbf{r},\ \delta\mathbf{p},\ \delta V,\ \delta\dot{\xi}\right]$ can be explicitly determined by substituting the previous formulae (A2.2)-(A2.9) in the above equations. When a nonequilibrium PSF or PEF system is considered, the SLLOD terms associated with shear and elongational fields cause the emergence of the extra factor $\frac{\partial \dot{\mathbf{r}}}{\partial \mathbf{r}} \cdot \delta\mathbf{r}$ in the equation for $\delta\dot{\mathbf{r}}$ which is detailed in (A2.2), and modify the form of $\frac{\partial \dot{\mathbf{p}}}{\partial \mathbf{p}} \cdot \delta\mathbf{p}$ as pointed out in (A2.3). Further, derivatives of the thermostat multipliers with respect to $r_{\beta j}$ and $p_{\beta j}$ do depend on the type of flow. Nonetheless, it is important to note that these discrepancies between equilibrium and nonequilibrium affect *only* the components $\delta\mathbf{r}$ and $\delta\mathbf{p}$ of the tangent vectors and solely appear in the first two lines of (A2.10). The remaining elements of $\mathbf{T}$ at PSF or PEF conserve the same expressions they have at equilibrium: this is ultimately the cause for the invariant and zero conjugate pairing of the Lyapunov exponents pertaining to the degrees of freedom of the NH barostat, as discussed in Section 4.3.