

## 2.17

# NON-EQUILIBRIUM MOLECULAR DYNAMICS

Giovanni Ciccotti<sup>1</sup>, Raymond Kapral<sup>2</sup>, and Alessandro Sergi<sup>2</sup>

<sup>1</sup>*INFN and Dipartimento di Fisica, Università “La Sapienza,”  
Piazzale Aldo Moro, 2, 00185 Roma, Italy*

<sup>2</sup>*Chemical Physics Theory Group, Department of Chemistry, University of Toronto,  
Toronto, Ont. M5S 3H6, Canada*

Statistical mechanics provides a well-established link between microscopic equilibrium states and thermodynamics. If one considers systems out of equilibrium, the link between microscopic dynamical properties and non-equilibrium macroscopic states is more difficult to establish [1,2]. For systems lying near equilibrium, linear response theory provides a route to derive linear macroscopic laws and the microscopic expressions for the transport properties that enter the constitutive relations in these laws. If the system is displaced far from equilibrium, no fully general theory exists to treat such systems. By restricting consideration to a class of non-equilibrium states which arise from perturbations (linear or non-linear) of an equilibrium state, methods can be developed to treat non-equilibrium states. Furthermore, non-equilibrium molecular dynamics (NEMD) simulation methods can be devised to provide estimates for the transport properties of these systems.

Molecular dynamics is typically based on equations of motion derived from a Hamiltonian. However, often in the simulation of large complex systems, constraints are introduced to remove certain “fast” degrees of freedom from the system that are deemed to be unimportant for the phenomena under investigation. An important and prevalent example is the introduction of bond constraints to remove rapid vibrational degrees of freedom from the molecules of the system. Such constraints can be handled by the introduction of generalized coordinates and in these coordinates a Hamiltonian description of the equations of motion may be written. However, it is often more convenient to work with Cartesian coordinates with the holonomic constraints explicitly introduced in the equations of motion through Lagrange multipliers. One can treat the set of Lagrange multipliers as parameters that can be determined by

SHAKE [3] and one still has a kind of Hamiltonian description involving these parameters [4]. Alternatively, one can explicitly determine the Lagrange multipliers as functions of the phase space coordinates and in this case the equations of motion are non-Hamiltonian and are characterized by the existence of a non-zero phase space compressibility [5,6]. Consequently, such constrained systems are a special case of general non-Hamiltonian systems whose statistical mechanical formulation has been, recently, a topic of considerable interest.

The statistical mechanical methods that have been developed for non-Hamiltonian flows [7] can be used to formulate a non-equilibrium statistical mechanics of constrained molecular systems. With such a formulation in hand, a response theory can be developed to investigate linear and non-linear perturbations of equilibrium states, thus providing the link between microscopic dynamics and macroscopic non-equilibrium properties. In this chapter we show how this program can be carried out. In simulations, when external forces are applied to the system, the equations of motion must be supplemented with a thermostating mechanism to compensate for the input of energy from the external forces. The resulting thermostated equations are non-Hamiltonian in character. While, for simplicity, we do not explicitly consider the thermostat in the formulation presented below, the techniques we describe can also be extended to treat this more general situation.

## 1. Non-Hamiltonian Equations of Motion with Constraints

Consider an  $N$ -particle system with coordinates  $\mathbf{r}_i$  and momenta  $\mathbf{p}_i$  and Hamiltonian  $H_0$ ,

$$H_0 = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{r}), \quad (1)$$

where  $V(\mathbf{r})$  is the potential energy. We let phase space coordinate labels without particle indices stand for the entire set of coordinates,  $(\mathbf{r}, \mathbf{p}) = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$ . When we wish to refer to these variables collectively, we use the notation  $\mathbf{x} = (\mathbf{r}, \mathbf{p})$ .

We suppose that the system is subjected to  $\ell$  holonomic constraints

$$\sigma_\alpha(\mathbf{r}) = 0, \quad \alpha = 1, \dots, \ell. \quad (2)$$

The  $\sigma_\alpha$  could be the bond constraints mentioned above, or any other holonomic constraint such as a reaction coordinate constraint imposed in the simulation of rare reactive events [8]. The constrained equations of motion are

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \lambda_\alpha \nabla_i \sigma_\alpha(\mathbf{r}), \quad (3)$$

where  $\mathbf{F}_i = -\nabla_i V$  is the force on particle  $i$  due to the potential energy and the second term represents the constraint forces with Lagrange multipliers  $\lambda_\alpha$ . We use the Einstein summation convention on the Greek indices. Equivalently, we may write this pair of equations as single second order equation as

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i - \lambda_\alpha \nabla_i \sigma_\alpha(\mathbf{r}). \quad (4)$$

Since  $\sigma_\alpha$  is constrained at all times,  $\dot{\sigma}_\alpha = \sum_i (\mathbf{p}_i/m_i) \cdot \nabla_i \sigma_\alpha = 0$ . Typically, such equations are solved in molecular dynamics simulations using the SHAKE algorithm. However, in order to carry out the statistical mechanical treatment of such constrained systems is more convenient to formulate the problem in a form where its non-Hamiltonian character is evident. To this end we first determine an explicit expression for the Lagrange multipliers. The Lagrange multipliers can be found by differentiating the constraint  $\dot{\sigma}_\alpha = 0$  with respect to time and using Eq. (4) to yield,

$$\begin{aligned} \ddot{\sigma}_\alpha &= \frac{d}{dt} \sum_i \frac{\mathbf{p}_i}{m_i} \cdot \nabla_i \sigma_\alpha = \sum_i \ddot{\mathbf{r}}_i \cdot \nabla_i \sigma_\alpha + \sum_{i,j} \dot{\mathbf{r}}_i \dot{\mathbf{r}}_j : \nabla_i \nabla_j \sigma_\alpha \\ &= \sum_i \left( \frac{\mathbf{F}_i}{m_i} - \frac{\lambda_\beta}{m_i} \nabla_i \sigma_\beta \right) \cdot \nabla_i \sigma_\alpha + \sum_{i,j} \frac{\mathbf{p}_i}{m_i} \frac{\mathbf{p}_j}{m_j} : \nabla_i \nabla_j \sigma_\alpha = 0. \end{aligned} \quad (5)$$

Solving this equation for  $\lambda_\alpha$  we find,

$$\lambda_\alpha = \lambda_\alpha(\mathbf{x}) = \left( \sum_i \frac{\mathbf{F}_i}{m_i} \cdot \nabla_i \sigma_\beta + \sum_{i,j} \frac{\mathbf{p}_i}{m_i} \frac{\mathbf{p}_j}{m_j} : \nabla_i \nabla_j \sigma_\beta \right) (\mathbf{Z}^{-1})_{\beta\alpha}, \quad (6)$$

where

$$\mathbf{Z}_{\alpha\beta} = \sum_i \frac{1}{m_i} (\nabla_i \sigma_\alpha) \cdot (\nabla_i \sigma_\beta). \quad (7)$$

Using this explicit form of the Lagrange multiplier, the resulting equations of motion,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \lambda_\alpha(\mathbf{x}) \nabla_i \sigma_\alpha(\mathbf{r}), \quad (8)$$

are no longer in Hamiltonian form and represent a motion with the constraints as conserved quantities [5,6]. The phase space flow is compressible and the compressibility is given by

$$\begin{aligned} \kappa &= \nabla_{\mathbf{x}} \cdot \dot{\mathbf{x}} = - \sum_{i=1}^N \frac{\partial \lambda_\alpha(\mathbf{x})}{\partial \mathbf{p}_i} \cdot \nabla_i \sigma_\alpha(\mathbf{r}) \\ &= -2 \sum_i \frac{1}{m_i} (\nabla_i \dot{\sigma}_\alpha) \cdot (\nabla_i \sigma_\beta) (\mathbf{Z}^{-1})_{\beta\alpha} = - \frac{d}{dt} \ln Z, \end{aligned} \quad (9)$$

where  $Z = \det \mathbf{Z}$ .

The constrained phase space flow in Eq. (8) may be generated by the action of the Liouville operator,

$$iL_0 = \dot{\mathbf{x}} \cdot \nabla_{\mathbf{x}} = \sum_{i=1}^N \left( \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} - \lambda_a(\mathbf{x})(\nabla_i \sigma_a(\mathbf{r})) \cdot \frac{\partial}{\partial \mathbf{p}_i} \right), \quad (10)$$

on the phase space variables. More generally, the evolution of any dynamical variable,  $B(\mathbf{x})$ , is given by

$$\frac{dB(\mathbf{x}(t))}{dt} = iL_0 B(\mathbf{x}(t)), \quad (11)$$

whose formal solution is

$$B(\mathbf{x}(t)) = e^{iL_0 t} B(\mathbf{x}). \quad (12)$$

We now wish to discuss the statistical mechanics of such a system. The existence of a phase space compressibility has implications for the nature of the phase space flow and the computation of statistical properties [6,7]. The phase space volume element at time  $t_0$ ,  $d\mathbf{x}_{t_0}$  transforms into  $d\mathbf{x}_t = J(\mathbf{x}_t; \mathbf{x}_{t_0})d\mathbf{x}_{t_0}$  at time  $t$ , where  $J(\mathbf{x}_t; \mathbf{x}_{t_0}) = \det \mathbf{J}$  and the matrix  $\mathbf{J}$  has elements  $J_{ij} = \partial \dot{x}_t^i / \partial x_{t_0}^j$ . Using the fact that  $J = \det \mathbf{J} = \exp(\text{Tr} \ln \mathbf{J})$  one may derive an equation of motion by differentiating this expression for  $J$  to find,

$$\begin{aligned} \frac{dJ(\mathbf{x}_t; \mathbf{x}_{t_0})}{dt} &= \left( \text{Tr} \frac{d\mathbf{J}}{dt} \mathbf{J}^{-1} \right) J = \left( \sum_{i,j} \frac{\partial \dot{x}_t^i}{\partial x_{t_0}^j} \frac{\partial x_{t_0}^j}{\partial x_t^i} \right) J \\ &= \left( \sum_i \frac{\partial \dot{x}_t^i}{\partial x_t^i} \right) J = \kappa(\mathbf{x}_t) J(\mathbf{x}_t; \mathbf{x}_{t_0}). \end{aligned} \quad (13)$$

Integrating this equation and using the explicit expression for  $\kappa$  given above, one may show that the Jacobian takes the form,  $J(\mathbf{x}_t; \mathbf{x}_{t_0}) = Z(\mathbf{r}_{t_0})/Z(\mathbf{r}_t)$ . Consequently, we see that  $Z(\mathbf{r}_t) d\mathbf{x}_t = Z(\mathbf{r}_{t_0}) d\mathbf{x}_{t_0}$  and  $d\boldsymbol{\mu}(\mathbf{r}, \mathbf{p}) = Z(\mathbf{r}) d\mathbf{r} d\mathbf{p}$  is the invariant measure for the phase space flow.

Next we consider the time evolution of the phase space distribution function  $f(\mathbf{x})$ , where  $\int_{V_\Omega} d\boldsymbol{\mu}(\mathbf{x}) f(\mathbf{x}) = \int_{V_\Omega} d\mathbf{x} Z(\mathbf{r}) f(\mathbf{x}) \equiv \int_{V_\Omega} d\mathbf{x} \rho(\mathbf{x})$  is the fraction of systems in the phase space volume  $V_\Omega$ . The phase space flow is conserved so that  $\rho(\mathbf{x}) = Z(\mathbf{x}) f(\mathbf{x})$  satisfies the continuity equation,

$$\frac{\partial \rho(\mathbf{x}, t)}{\partial t} + \nabla_{\mathbf{x}} \cdot (\dot{\mathbf{x}} \rho(\mathbf{x}, t)) = 0, \quad (14)$$

and, therefore,

$$\frac{\partial \rho(\mathbf{x}, t)}{\partial t} = -(\dot{\mathbf{x}} \cdot \nabla_{\mathbf{x}} + \nabla_{\mathbf{x}} \cdot \dot{\mathbf{x}}) \rho(\mathbf{x}, t) = -(iL_0 + \kappa) \rho(\mathbf{x}, t). \quad (15)$$

We now want to derive the evolution equation for  $f(\mathbf{x}, t)$ . To this end we first note that we may again use the identity  $Z = \det \mathbf{Z} = \exp(\text{Tr} \ln \mathbf{Z})$  and the fact that  $Z$  depends only on the coordinates to compute

$$\begin{aligned} iL_0 Z &= \sum_i \frac{\mathbf{p}_i}{m_i} \cdot \nabla_i Z = \sum_i \frac{\mathbf{p}_i}{m_i} \cdot (\nabla_i Z_{\alpha\beta})(\mathbf{Z}^{-1})_{\beta\alpha} Z \\ &= \sum_j \frac{1}{m_j} [(\nabla_j \dot{\sigma}_\alpha) \cdot (\nabla_j \sigma_\beta) + (\nabla_j \sigma_\alpha) \cdot (\nabla_j \dot{\sigma}_\beta)] (\mathbf{Z}^{-1})_{\beta\alpha} Z = -\kappa Z, \end{aligned} \quad (16)$$

where we have used Eq. (9) and the fact that  $\mathbf{Z}$  is a symmetric matrix to relate the expression in the penultimate equality to the compressibility. Then, inserting the definition  $\rho(\mathbf{x}) = Z(\mathbf{x})f(\mathbf{x})$  into Eq. (15) and using the result  $iL_0 Z = -\kappa Z$  we find the Liouville equation for  $f(\mathbf{x})$ ,

$$\frac{df(\mathbf{x}, t)}{dt} = \frac{\partial f(\mathbf{x}, t)}{\partial t} + iL_0 f(\mathbf{x}, t) = 0. \quad (17)$$

The equations of motion (8) have  $H_0$ ,  $\sigma_\alpha$  and  $\dot{\sigma}_\alpha$  as constants of the motion. Consequently, the equilibrium density is given by

$$f_{\text{eq}}(\mathbf{x}) = \Omega(E)^{-1} \delta(H_0 - E) \prod_\alpha \delta(\sigma_\alpha) \delta(\dot{\sigma}_\alpha), \quad (18)$$

where  $\Omega(E)$  is a normalizing factor and  $E$  is the energy of the microcanonical system.

In non-equilibrium statistical mechanics the average value of a dynamical variable at time  $t$  is given by the integral over the phase space measure of the phase space probability density times the dynamical variable,

$$\bar{B}(t) = \int d\mu(\mathbf{x}) B(\mathbf{x}) f(\mathbf{x}, t) = \int d\mu(\mathbf{x}) B(\mathbf{x}) e^{-iL_0 t} f(\mathbf{x}). \quad (19)$$

We may transfer the action of the evolution operator to the dynamical variable. To do this we first use the following identity for any phase space functions  $A(\mathbf{x})$  and  $B(\mathbf{x})$ , which is obtained by integrating by parts:

$$\begin{aligned} \int d\mathbf{x} B(\mathbf{x}) iL_0 A(\mathbf{x}) &= \int d\mathbf{x} \left( \left( -iL_0 + \sum_i \frac{\partial \lambda_\alpha(\mathbf{x})}{\partial \mathbf{p}_i} \cdot (\nabla_i \sigma_\alpha) \right) B(\mathbf{x}) \right) A(\mathbf{x}) \\ &= - \int d\mathbf{x} ((iL_0 + \kappa) B(\mathbf{x})) A(\mathbf{x}). \end{aligned} \quad (20)$$

The last equality was obtained using

$$\sum_i \frac{\partial \lambda_\alpha(\mathbf{x})}{\partial \mathbf{p}_i} \cdot (\nabla_i \sigma_\alpha) = -\kappa. \quad (21)$$

Making use of this result we may also show that

$$\begin{aligned}
\int d\boldsymbol{\mu}(\mathbf{x}) B(\mathbf{x}) iL_0 A(\mathbf{x}) &= \int d\mathbf{x} Z(\mathbf{r}) B(\mathbf{x}) iL_0 A(\mathbf{x}) \\
&= - \int d\mathbf{x} ((iL_0 + \kappa)(Z(\mathbf{r}) B(\mathbf{x}))) A(\mathbf{x}) \\
&= - \int d\mathbf{x} (iL_0 B(\mathbf{x})) Z(\mathbf{r}) A(\mathbf{x}), \tag{22}
\end{aligned}$$

where the last equality follows from the fact that  $iL_0(ZA) = -\kappa ZA + ZiL_0A$ , again using  $iL_0Z = -\kappa Z$ . Thus, expanding the propagator  $\exp(-iL_0t)$  in Eq. (19) as power series, integrating by parts term by term, using the above identities and finally resumming, we obtain,

$$\bar{B}(t) = \int d\boldsymbol{\mu}(\mathbf{x}) (e^{iL_0t} B(\mathbf{x})) f(\mathbf{x}) = \int d\boldsymbol{\mu}(\mathbf{x}) B(\mathbf{x}(t)) f(\mathbf{x}). \tag{23}$$

Thus, we have the result

$$\int d\boldsymbol{\mu}(\mathbf{x}) B(\mathbf{x}) e^{-iL_0t} f(\mathbf{x}) = \int d\boldsymbol{\mu}(\mathbf{x}) (e^{iL_0t} B(\mathbf{x})) f(\mathbf{x}), \tag{24}$$

which shows that when the scalar product is defined with respect to the measure  $d\boldsymbol{\mu}(\mathbf{x})$ , the Liouville operator  $L_0$  is self-adjoint. Alternatively, we may write the right hand side of Eq. (24) and then integrate by parts, using the properties discussed above, to obtain the equivalent formulas,

$$\begin{aligned}
\bar{B}(t) &= \int d\mathbf{x} B(\mathbf{x}) \rho(\mathbf{x}, t) = \int d\mathbf{x} B(\mathbf{x}) e^{-(iL_0 + \kappa)t} \rho(\mathbf{x}) \\
&= \int d\mathbf{x} (e^{iL_0t} B(\mathbf{x})) \rho(\mathbf{x}) = \int d\boldsymbol{\mu}(\mathbf{x}) (e^{iL_0t} B(\mathbf{x})) f(\mathbf{x}). \tag{25}
\end{aligned}$$

This result shows that if the scalar product is defined with respect to integration over the phase space coordinates, and not the invariant measure, the adjoint of  $iL_0$  is  $-(iL_0 + \kappa)$  and the operator is not self-adjoint.

The development we have presented contains the standard Hamiltonian description of statistical mechanics if the constraints are not present. In this case the terms involving the explicit forms of the Lagrange multipliers no longer appear and the equations of motion adopt a Hamiltonian form. The metric factor  $Z(\mathbf{r}) = 1$  and consequently  $d\mathbf{x}_t = d\mathbf{x}_{t_0}$  and the Liouville operator is self-adjoint with respect to this simple metric.

We may now use this Liouville formulation of the dynamics of constrained systems to carry out an analysis of how the system responds when external forces are applied to the system.

## 2. Response Theory

We next examine how the constrained non-Hamiltonian system responds to external time dependent forces. In the presence of such external forces the equations of motion take the general form,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{C}_i^r(\mathbf{x})\mathcal{F}(t), \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \lambda_a(\mathbf{x}, t)\nabla_i\sigma_a(\mathbf{r}) + \mathbf{C}_i^p(\mathbf{x})\mathcal{F}(t). \quad (26)$$

We write this set of equations compactly as

$$\dot{\mathbf{x}} = \mathbf{G}(\mathbf{x}, t), \quad (27)$$

where we have indicated the explicit time dependence in  $\lambda_a(\mathbf{x}, t)$  and  $\mathbf{G}(\mathbf{x}, t)$  arising from the external force. Since the Lagrange multipliers must be determined in the presence of the external forces, they acquire explicit time dependence. In the general case we are considering, the external forces are not assumed to be derived from a generalized potential; i.e., there is no function  $\mathcal{V}(\mathbf{r}, \mathbf{p})$  such that  $\mathbf{C}_i^r = (\partial\mathcal{V}/\partial\mathbf{p}_i)$  and  $\mathbf{C}_i^p = -(\partial\mathcal{V}/\partial\mathbf{r}_i)$ . We do assume that  $\mathbf{C}^T(\mathbf{x}) = (\mathbf{C}^r, \mathbf{C}^p)$ , where T stands for the transpose, satisfies the incompressibility condition,  $\nabla_{\mathbf{x}} \cdot \mathbf{C} = 0$ . This latter condition guarantees that, even in the presence of the external forces, the compressibility arises only from the Lagrange multipliers, which impose the constraints, and is still given by

$$\kappa(t) = \nabla_{\mathbf{x}} \cdot \dot{\mathbf{x}} = - \sum_{i=1}^N \frac{\partial\lambda_a(\mathbf{x}, t)}{\partial\mathbf{p}_i} \cdot \nabla_i\sigma_a(\mathbf{r}). \quad (28)$$

The Liouville operator that generates these equations of motion is  $iL(t) = \dot{\mathbf{x}} \cdot \nabla_{\mathbf{x}} = \mathbf{G}(\mathbf{x}, t) \cdot \nabla_{\mathbf{x}}$ , or, more explicitly,

$$\begin{aligned} iL(t) = & \sum_{i=1}^N \left( \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial\mathbf{r}_i} + (\mathbf{F}_i - \lambda_a(\mathbf{x}, t)(\nabla_i\sigma_a(\mathbf{r}))) \cdot \frac{\partial}{\partial\mathbf{p}_i} \right) \\ & + \sum_{i=1}^N \left( \mathbf{C}_i^r \cdot \frac{\partial}{\partial\mathbf{r}_i} + \mathbf{C}_i^p \cdot \frac{\partial}{\partial\mathbf{p}_i} \right) \mathcal{F}(t). \end{aligned} \quad (29)$$

We compute the response of the system to the external force by measuring the average value of a dynamical variable  $B(\mathbf{x})$  as (cf. Eq. (25))

$$\bar{B}(t) = \int d\mathbf{x} B(\mathbf{x}) \rho(\mathbf{x}, t), \quad (30)$$

where  $\rho(\mathbf{x}, t)$  again satisfies the continuity Eq. (14) which now takes the form,

$$\frac{\partial\rho(\mathbf{x}, t)}{\partial t} = -(\dot{\mathbf{x}} \cdot \nabla_{\mathbf{x}} + \nabla_{\mathbf{x}} \cdot \dot{\mathbf{x}})\rho(\mathbf{x}, t) = -(iL(t) + \kappa(t))\rho(\mathbf{x}, t). \quad (31)$$

The compressibility  $\kappa(t)$  now also depends explicitly on time since the Lag-range multipliers appear in its expression. If we integrate Eq. (31) from

some initial time  $t_0$  to time  $t$  and solve the resulting integral equation by iteration we obtain,

$$\begin{aligned} \rho(\mathbf{x}, t) = & \rho(\mathbf{x}, t_0) - \int_{t_0}^t dt_1 (iL(t_1) + \kappa(t_1))\rho(\mathbf{x}, t_0) + \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 (iL(t_1) \\ & + \kappa(t_1))(iL(t_2) + \kappa(t_2))\rho(\mathbf{x}, t_0) + \dots . \end{aligned} \quad (32)$$

The formal solution of Eq. (32) can be written as

$$\rho(\mathbf{x}, t) = U^\dagger(t, t_0)\rho_0(\mathbf{x}), \quad (33)$$

where  $\rho_0(\mathbf{x}) = \rho(\mathbf{x}, t_0)$  and the propagator  $U^\dagger(t, t_0)$  is defined by

$$U^\dagger(t, t_0) = \mathcal{T} \exp \left[ - \int_{t_0}^t d\tau (iL(\tau) + \kappa(\tau)) \right], \quad (34)$$

where  $\mathcal{T}$  is the time-ordering operator.

For any two phase space functions  $A(\mathbf{x})$  and  $B(\mathbf{x})$  we have the analog of Eq. (20):

$$- \int d\mathbf{x} B(\mathbf{x})(iL(t) + \kappa(t))A(\mathbf{x}) = \int d\mathbf{x} (iL(t)B(\mathbf{x}))A(\mathbf{x}). \quad (35)$$

Consequently, we may substitute the series solution for  $\rho(\mathbf{x}, t)$  into Eq. (32) and integrate by parts term by term, using Eq. (35), to obtain,

$$\begin{aligned} \bar{B}(t) = & \int d\mathbf{x} B(\mathbf{x})\rho(\mathbf{x}, t) \\ = & \int d\mathbf{x} \left( B(\mathbf{x}) + \int_{t_0}^t dt_1 iL(t_1)B(\mathbf{x}) \right. \\ & \left. + \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 iL(t_1)iL(t_2)B(\mathbf{x}) + \dots \right) \rho_0(\mathbf{x}). \end{aligned} \quad (36)$$

This series defines the evolution operator  $U(t, t_0)$ ,

$$U(t, t_0) = \mathcal{T} \exp \left[ \int_{t_0}^t d\tau iL(\tau) \right], \quad (37)$$

which is the formal solution of the equation of motion,

$$\frac{dU(t, t_0)}{dt} = iL(t)U(t, t_0). \quad (38)$$

The propagator  $U(t, t_0)$  is the adjoint of  $U^\dagger(t, t_0)$ . As a result of these considerations we may write,

$$\bar{B}(t) = \int d\mathbf{x} B(\mathbf{x}) U^\dagger(t, t_0) \rho_0(\mathbf{x}) = \int d\mathbf{x} (U(t, t_0) B(\mathbf{x})) \rho_0(\mathbf{x}). \quad (39)$$

This formula provides a means to determine the non-equilibrium macroscopic value of the dynamical variable  $B(\mathbf{x})$  by considering its evolution under the fully perturbed dynamics and taking the phase space average over the arbitrary initial preparation of the system described by  $\rho_0(\mathbf{x})$ .

If the initial distribution is taken to be the equilibrium distribution in the absence of the perturbing field,  $\rho_{\text{eq}}(\mathbf{x}) = Z(\mathbf{r}) f_{\text{eq}}(\mathbf{x})$ , then the problem has a well-defined structure. Inserting the initial equilibrium distribution into Eq. (39) we find

$$\begin{aligned} \bar{B}(t) &= \int d\mathbf{x} (U(t, t_0) B(\mathbf{x})) \rho_{\text{eq}}(\mathbf{x}) \\ &= \int d\boldsymbol{\mu}(\mathbf{x}) (U(t, t_0) B(\mathbf{x})) f_{\text{eq}}(\mathbf{x}) \equiv \langle U(t, t_0) B(\mathbf{x}) \rangle_{\text{eq}}, \end{aligned} \quad (40)$$

where the measure  $d\boldsymbol{\mu}(\mathbf{x})$  is that for the unperturbed system discussed in the previous section. From this equation we see that, for systems initially at equilibrium, non-equilibrium properties may be obtained from the equilibrium ensemble average of the observable evolved under the full perturbed dynamics due to the external force. This equation expresses some fundamental features of non-equilibrium statistical mechanics. It is an expression of Onsager's regression hypothesis that relates the decay of macroscopic observables to the regression of fluctuations about the equilibrium state [9] and has been exploited in NEMD simulations to take dynamical averages out of equilibrium [10].

In the limiting case where the equations of motion are Hamiltonian in form and the external perturbation arises from a potential  $V_I(t) = A(\mathbf{x}) \mathcal{F}(t)$ , Eq. (40) reduces to the microcanonical version of Kubo's linear response result [11] in the limit of weak perturbations. To see this we note that the perturbed Liouville operator in Eq. (29) reduces to the following usual form for this simple Hamiltonian case:

$$\begin{aligned} iL(t) &= \sum_{i=1}^N \left( \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) + \mathcal{F}(t) \sum_{i=1}^N \left( \frac{\partial A(\mathbf{x})}{\partial \mathbf{p}_i} \cdot \frac{\partial}{\partial \mathbf{r}_i} - \frac{\partial A(\mathbf{r})}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) \\ &\equiv iL_0 + iL_I(t). \end{aligned} \quad (41)$$

Using the decomposition of  $iL(t)$  into unperturbed and perturbed parts and the expression  $U_0(t, t_0) = \exp(-iL_0(t - t_0))$  for the propagator of the

unperturbed system, we may write Eq. (38) in the form of a Dyson equation for  $U(t, t_0)$ :

$$U(t, t_0) = U_0(t, t_0) + \int_{t_0}^t d\tau U_0(\tau, t_0) iL_I(\tau) U(t, \tau). \quad (42)$$

If we then insert this expression for  $U(t, t_0)$ , truncated to first order in the external force, into Eq. (40), we obtain

$$\bar{B}(t) = \langle B(\mathbf{x}) \rangle_{\text{eq}} + \int_{t_0}^t d\tau \int d\mathbf{x} (U_0(t, \tau) B(\mathbf{x})) \dot{A}(\mathbf{x}) \frac{df_{\text{eq}}(\mathbf{x})}{dH_0} \mathcal{F}(\tau), \quad (43)$$

where we have used the fact that  $f_{\text{eq}}(\mathbf{x}) = \Omega(E)^{-1} \delta(H_0 - E)$  is a function of the phase space coordinates through the Hamiltonian. Finally, using the identity  $g(z) \delta'(z - a) = -g'(a) \delta(z - a)$ , and the fact that the microcanonical partition function is related to the entropy by  $\Omega(E) = \exp(S(E)/k_B)$ , we have  $df_{\text{eq}}(\mathbf{x})/dH_0 = -\beta f_{\text{eq}}(\mathbf{x})$ . Thus, we obtain the standard result

$$\Delta \bar{B}(t) = - \int_{t_0}^t d\tau \langle (U_0(t, \tau) B(\mathbf{x})) \dot{A}(\mathbf{x}) \rangle_{\text{eq}} \mathcal{F}(\tau). \quad (44)$$

Here  $\Delta \bar{B}(t)$  is the deviation from the equilibrium average value,  $\Delta \bar{B}(t) = \bar{B}(t) - \langle B(\mathbf{x}) \rangle_{\text{eq}}$ .

However, the linear response of constrained systems to perturbations, either with Hamiltonian or non-Hamiltonian structure, is not simple. The external forces enter in the Lagrange multipliers that appear in the non-Hamiltonian equations of motion as well as in the explicit forces that couple the system to the external fields. Consequently, the form of the perturbation in the Liouville operator is complicated and unfamiliar terms appear in the linear response formulas. In addition, the equilibrium distribution function in Eq. (18) does not depend solely on the Hamiltonian but contains delta function contributions from the conserved constraint variables. As a result, some of the standard manipulations that are often carried out in linear response theory to obtain the response as a physically interesting correlation function in Eq. (43), such as those that give  $df_{\text{eq}}(\mathbf{x})/dH_0 = -\beta f_{\text{eq}}(\mathbf{x})$ , may no longer be carried out. For instance, even if the perturbation is of the form of  $V_I(t)$  given above, the linear response of the constrained system is not simple because the form of the equilibrium density precludes a reduction to that in Eq. (44).

These technical difficulties with the linear response derivation do not detract from the computational utility of Eq. (40) which forms the starting point for investigating the linear or non-linear response of either Hamiltonian or non-Hamiltonian systems by NEMD. Below, we discuss how such simulations may be carried out.

### 3. Simulation of Non-Equilibrium Systems

The dynamical response of a system subjected to the general time-dependent external force in Eq. (26) and initially in an equilibrium state of the unperturbed system can be computed from Eq. (40). To do this one simply samples phase space configurations along an equilibrium trajectory of the unperturbed system. For independent initial configurations extracted from this trajectory, one evolves the dynamical variable  $B(\mathbf{x})$  using Eq. (26) under the full perturbed dynamics for a time  $t$ . The ensemble average over these trajectory segments yields  $\bar{B}(t)$ . The method based on Eq. (40) is called the *dynamical approach* to non-equilibrium molecular dynamics.

In carrying out such NEMD simulations, one necessarily needs perturbation strengths that are huge on the macroscopic scale in order to produce a detectable response. Such large perturbation strengths are needed to yield a response that is larger than the statistical noise. From such a simulation it is difficult to obtain information in the region of linear behavior. Consequently, an extrapolation to small perturbation strengths is required in order to compare the numerical results with those of linear response theory. For example, consider the mobility of an ion with mass  $m$  immersed in a fluid. In the absence of an external field the average ion velocity is zero and its variance is  $k_B T/m$ . The typical velocity of the ion is  $(k_B T/m)^{1/2}$  and sampling of 100 independent configurations will yield an estimate of the average value zero by  $(k_B T/m)^{1/2}/10$ , which is still a large number. If we wish to apply an external force to push the ion and to compute its drift velocity, the drift velocity should be significantly larger than the noise,  $\langle v_{\text{ion}} \rangle_{\text{neq}} \gg 10^{-1} (k_B T/m)^{1/2}$ . In order to fulfill this condition a huge field strength is required and one can no longer guarantee that the linear regime is being investigated.

A solution to this problem was obtained by using the subtraction technique [12], a method that permits one to decrease the noise of the response. If we consider evolution under  $U_0(t, t_0)$ , the propagator of the unperturbed system, then, since the equilibrium distribution is stationary under this evolution we have  $U_0^\dagger(t, t_0) f_{\text{eq}}(\mathbf{x}) = 0$  and  $\langle U_0(t, t_0) B(\mathbf{x}) \rangle_{\text{eq}} = 0$ . Therefore we may write Eq. (40) in the form,

$$\bar{B}(t) = \langle (U(t, t_0) B(\mathbf{x}) - U_0(t, t_0) B(\mathbf{x})) \rangle_{\text{eq}} \quad (45)$$

The dynamical variable inside the parentheses has the same average value as that in Eq. (40) but the variance is significantly different. This is easily seen for a time-impulsive perturbation at time  $t \rightarrow t_0^+$ :

$$\begin{aligned} & \text{Var} [U(t, t_0) B(\mathbf{x}) - U_0(t, t_0) B(\mathbf{x})] \\ &= \text{Var} [U(t, t_0) B(\mathbf{x})] + \text{Var} [U_0(t, t_0) B(\mathbf{x})] \\ & \quad - 2\text{Cov} [U(t, t_0) B(\mathbf{x}), U_0(t, t_0) B(\mathbf{x})]. \end{aligned} \quad (46)$$

Using  $\text{Cov}[X, Y] = (\text{Var}[X]\text{Var}[Y])^{1/2}\gamma$ , with the correlation coefficient  $|\gamma| \leq 1$  and noticing that for  $t$  close to  $t_0$  the correlation coefficient of the two microscopic fluxes is equal to  $1 + \mathcal{O}(\mathcal{F})$ , one finds from Eq. (46) that the leading term of the variance of the difference between the two fluxes is

$$\begin{aligned} & \text{Var} [U(t \rightarrow t_0^+, t_0)B(\mathbf{x}) - U_0(t \rightarrow t_0^+, t_0)B(\mathbf{x})] \\ &= (\text{SD} [U(t \rightarrow t_0^+, t_0)B(\mathbf{x})] - \text{SD} [U_0(t \rightarrow t_0^+, t_0)B(\mathbf{x})])^2 + \mathcal{O}(\mathcal{F}) \\ &= \mathcal{O}(\mathcal{F}), \end{aligned} \quad (47)$$

where SD stands for the standard deviation. This result applies only for  $t \approx t_0$  and the variance will generally grow exponentially as  $t$  increases. In many situations, though, the desired results can be obtained using a time range compatible with this divergence of the variance.

A simple illustration of the subtraction technique is provided by the mobility of a charged particle in an atomic fluid of Lennard–Jones particles. In this case the system has no constraints and we may use the simpler limiting forms of the equations presented above. The interaction between the charged particle and the neutral bath atoms is given by the Lennard–Jones plus a charge induced dipole term  $V_D(r) = V_{LJ}(r) - \frac{1}{2}\alpha_P e^2 r^{-4}$ , where  $\alpha_P$  is the atomic polarizability and  $e$  the electric charge. (See Ref. [12] for details.) To calculate the mobility of the ion we take  $B(\mathbf{x}) = \mathbf{v}_c$ , the velocity of the ion, and use Eq. (45). The molecular dynamics runs are broken into *segments* and two trajectories of the particles are computed in each segment, starting from the same initial configuration: one trajectory evolves in the absence of the external force, and a constant force  $\mathcal{F}$  of order  $1 \text{ eV cm}^{-1}$  is applied to the charged particle in the other trajectory. The drift velocity of the charged particles  $\mathbf{u}_D$  induced by the applied field is computed as a function of time simply by calculating the difference of the particle’s velocity in the perturbed and unperturbed trajectories, averaged over all segments of the run. One obtains,

$$\mathbf{u}_D \equiv \bar{\mathbf{v}}_c(t) = \langle [U(t, 0)\mathbf{v}_c - U_0(t, 0)\mathbf{v}_c] \rangle_{\text{eq}}. \quad (48)$$

The mobility constant  $\mu$  is given by  $\mathbf{u}_D(\infty) = \mu\mathcal{F}$  at vanishingly small  $\mathcal{F}$ . The force applied in Ref. [12] was about  $10^{-7}$  of the mean Lennard–Jones force. The calculation of the drift velocity induced by such a small external field in a simulation run of realistic length is made possible only by the subtraction technique. The results for the mobility agree well with experimental data for argon and with calculations using the Green–Kubo formula.

As a second illustration of the subtraction technique to simple systems, we consider the calculation of the shear-rate dependence of the viscosity of a Lennard–Jones fluid [13,14]. To simulate the response of the equilibrium system, at  $t = 0$  a fictitious external impulsive field is applied which induces

a planar Couette flow (the so-called SLLOD perturbation [15, 16]). The equations of motion are

$$\dot{\mathbf{r}}_i = \mathbf{p}_i/m_i + \mathbf{r}_i \cdot \nabla \mathbf{u}, \quad (49)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u}, \quad (50)$$

where  $\mathbf{F}_i$  is the total force acting on atom  $i$  with mass  $m_i$  and the velocity gradient  $\nabla \mathbf{u}$  has been chosen to yield a planar Couette flow in the  $x$  direction, with shear along  $y$ :

$$\nabla \mathbf{u} = \begin{bmatrix} 0 & 0 & 0 \\ h_0 \delta(t) & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad (51)$$

where  $h_0$  is a constant related to the shear rate  $\dot{\epsilon}$ . The velocity gradient, induced in the MD cell by the application of the chosen external field, has to be accommodated at the boundaries by applying the appropriate generalization of the periodic boundary conditions known in the literature as Lees–Edwards boundary conditions [17, 18]. The transient behavior of the off-diagonal element  $S_{xy}$  of the stress tensor of the perturbed system was simulated over a time interval  $t$  in order to determine the viscosity coefficient,  $\eta$ ,

$$\eta = \lim_{t \rightarrow \infty} \eta(t) = \lim_{t \rightarrow \infty} \lim_{h_0 \rightarrow 0} h_0^{-1} \int_0^t d\tau \langle U(\tau, 0) S_{xy} - U_0(\tau, 0) S_{xy} \rangle_{\text{eq}}. \quad (52)$$

In Fig. 1 we show the time dependent friction coefficient  $\eta(t)$  calculated by the subtraction technique for a low shear rate ( $\dot{\epsilon} < 0.02$ ). One see that good agreement between the non-equilibrium molecular dynamics simulation and linear response theory is found for low shear rates. In Ref. [13] it is also shown that, for shear rates below  $10^{12} \text{ s}^{-1}$ , the viscosity, considered as a function of the shear rate, does not differ significantly from its limiting value. It is only at rates higher than  $10^{12} \text{ s}^{-1}$  (a rather high perturbation!) that it starts to depend on the shear rate. Moreover, the dependence is well represented by an analytical power series truncated to the fourth order.

Non-equilibrium molecular dynamics has also been used to investigate transport properties of polyatomic systems using Cartesian coordinates with imposed holonomic constraints. Liquid butane has been the subject of a number of studies [19, 20] and the subtraction technique was used in [20] to compute the shear viscosity of this molecular system. In this calculation the symmetric part of the molecular stress tensor for a polyatomic fluid in a volume  $V$  is determined from the center of mass positions and velocities of the butane molecules:

$$S_{xy}^s = -\frac{1}{V} \sum_I \left[ \frac{1}{M} P_{Ix} P_{Iy} + \frac{1}{2} (F_{Ix} R_{Ix} + F_{Iy} R_{Iy}) \right]. \quad (53)$$

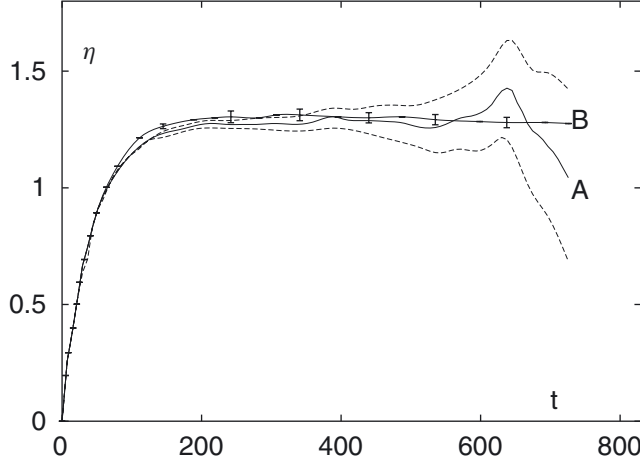


Figure 1. Curve A: time dependent friction coefficient  $\eta(t)$  for a Lennard–Jones atomic fluid, calculated by the subtraction technique at low shear rate ( $\dot{\epsilon} < 0.02$ ); curves above and below indicate the uncertainties. Curve B:  $\eta(t)$  from the Green–Kubo expression,  $\eta(t) = (V/k_B T) \int_0^t ds \langle S_{xy}(s)S_{xy}(0) \rangle_{\text{eq}}$ ; errors are shown as vertical bars.

Here  $M$ ,  $\mathbf{R}_I$ ,  $\mathbf{P}_I$  are, respectively, the mass, the center of mass coordinate and the total linear momentum of molecule  $I$ , while  $\mathbf{F}_I$  is the total force acting on the center of mass of the molecule; the sum runs over all molecules in the system. The shear viscosity coefficient  $\eta$  can be directly obtained from the *constitutive law* [21],

$$\mathbf{S}^s - p\mathbf{I} = 2\eta\nabla\mathbf{u}, \quad (54)$$

where  $p$  is the hydrostatic pressure and  $\mathbf{u}$  is the local velocity field corresponding to a pure deformational flow ( $\nabla \cdot \mathbf{u} = 0$ ). The equations of motion for such a polyatomic system can be written [15] (denoting the atomic coordinates and momenta of the  $n$  atoms of molecule  $I$  by  $(\mathbf{r}_I, \mathbf{p}_I) = (\mathbf{r}_{1I}, \mathbf{r}_{2I}, \dots, \mathbf{r}_{nI}, \mathbf{p}_{1I}, \mathbf{p}_{2I}, \dots, \mathbf{p}_{nI})$ ) as

$$\dot{\mathbf{r}}_{kI} = \frac{\mathbf{p}_{kI}}{m_k} + \mathbf{R}_I \cdot \nabla\mathbf{u}, \quad (55)$$

$$\dot{\mathbf{p}}_{kI} = \mathbf{F}_{kI} - \frac{m_k}{M} \nabla\mathbf{u} \cdot \mathbf{P}_I - \lambda_{\alpha I} \nabla_{kI} \sigma_{\alpha I}(\mathbf{r}_I), \quad (56)$$

where  $\mathbf{F}_{kI}$  is the force acting on atom  $k$  of molecule  $I$ , the tensor  $\nabla\mathbf{u}$  is the homogeneous velocity gradient (possibly time dependent),  $\sigma_{\alpha I}(\mathbf{r}_I)$  are the constraints acting on molecule  $I$  with their associated Lagrange multipliers

$\lambda_{\alpha I}$ . The perturbed equations of motion (55)–(56), are known as the DOLLS [22] tensor equations and can be derived from a Hamiltonian perturbation,

$$H_I = \sum_I \mathbf{R}_I \mathbf{P}_I : (\nabla \mathbf{u})^T, \quad (57)$$

where  $(\nabla \mathbf{u})^T$  is the transpose of  $\nabla \mathbf{u}$ .

The calculation of the shear viscosity by the subtraction technique proceeds as in the previous application. An impulsive external force derived from a shear shear gradient of the form

$$\nabla \mathbf{u} = \begin{bmatrix} 0 & (h_0/2)\delta(t) & 0 \\ (h_0/2)\delta(t) & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (58)$$

is applied to the equilibrium system at  $t = 0$ . Notice that, due to the choice of a symmetric velocity gradient tensorial perturbation, Eq. (58), no distinction exists, in this case, between the DOLLS tensor equations, used in this application, and the SLLDS equations employed in Ref. [13]. The viscosity is then computed from the analog of Eq. (52) using the symmetric part of the stress tensor,  $S_{xy}^s = (S_{xy} + S_{yx})/2$ . Since the molecular constraints do not act on the centers of mass of the molecules no technical difficulties are encountered as a result of their presence. The viscosity obtained using this method has been compared with the corresponding Green–Kubo formula and with the available experimental data. Although the equivalence between the Green–Kubo and NEMD methods is not evident in present molecular case, the authors find a remarkable agreement between the results of the two methods, while the known experimental value is about half of the computed values. There are many possible reasons for this discrepancy (and the authors correctly point them out), however, at this stage, we cannot exclude a theoretical inconsistency.

## 4. Outlook

Non-equilibrium molecular dynamics is a field with a long history. For atomic systems the problem has been formulated completely and a variety of applications have been studied (see Ref. [18] for a review, as well as other chapters in this book). In this chapter we have shown that there are new issues that need to be considered when molecular systems with constraints are studied. In order to make molecular dynamics simulations practical, most complex molecular systems are treated by imposing constraints to remove certain degrees of freedom from the problem. It is therefore important to formulate a response theory for such constrained systems in order to be able to compute non-equilibrium properties. We have shown that it is possible to carry out

this program for systems with constraints in the context of a non-Hamiltonian formulation of the equations of motion. The general expression for the response (Eq. (40)) is simple and is in a form that permits direct application of the subtraction method to determine small responses. The passage to the linear regime and determination of the analogs of standard Green–Kubo expressions for transport properties involve subtle issues that deserve further study. We have not included a thermostat in the formulation presented here. In practice it is necessary to thermostat the system when external forces are applied to it to study the response. Such thermostats may also be implemented naturally in the context of a non-Hamiltonian framework.

## References

- [1] D.J. Evans and G.P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids.*, Academic Press, New York, 1990.
- [2] G. Ciccotti, D. Frenkel, and I.R. McDonald, *Simulations of Liquids and Solids*, 3rd edn., North-Holland, Amsterdam, 1987.
- [3] J.P. Ryckaert, G. Ciccotti, and H.J.C. Berendsen, “Numerical-integration of cartesian equations of motion of a system with constraints—molecular-dynamics of *n*-alkanes,” *J. Comp. Phys.*, 23, 327–341, 1977.
- [4] T.O. White, G. Ciccotti, and J.P. Hansen, “Brownian dynamics with constraints,” *Mol. Phys.*, 99, 2023–2036, 2001.
- [5] S. Melchionna, “Constrained systems and statistical distributions,” *Phys. Rev. E*, 61, 6165–6170, 2000.
- [6] M.E. Tuckerman, Y. Liu, G. Ciccotti, and G.L. Martyna, “Non-Hamiltonian molecular dynamics: generalizing Hamiltonian phase space principles to non-Hamiltonian systems,” *J. Chem. Phys.*, 115, 1678–1702, 2001.
- [7] M.E. Tuckerman, C.J. Mundy, and G.L. Martyna, “On the classical statistical mechanics of non-Hamiltonian systems,” *Europhys. Lett.*, 45, 149–155, 1999.
- [8] G. Ciccotti, R. Kapral, and A. Sergi, “Simulating reactions that occur once in a blue moon,” In: S. Yip and H. Metiu (eds.), *Encyclopedia of Materials Modeling*, 2004.
- [9] L. Onsager, “Reciprocal relations in irreversible processes. I,” *Phys. Rev.*, 37, 405–426, 1931. “Reciprocal relations in irreversible processes. II,” *Phys. Rev.*, 38, 2265–2279, 1931.
- [10] G. Ciccotti, G. Jacucci, and I.R. McDonald, “Thought experiments by molecular dynamics,” *J. Stat. Phys.*, 21, 1–22, 1979.
- [11] R. Kubo, M. Toda, N. Hashitsume, M. Toda, and R. Kubo, *Statistical Physics II: Nonequilibrium Statistical Mechanics*, 2nd edn., Springer, Berlin, 1995.
- [12] G. Ciccotti and G. Jacucci, “Direct computation of dynamical response by molecular-dynamics—mobility of a charged Lennard–Jones particle,” *Phys. Rev. Lett.*, 35, 789–792, 1975.
- [13] J.P. Ryckaert, A. Bellemans, G. Ciccotti, and G.V. Paolini, “Shear-rate dependence of the viscosity of simple fluids by nonequilibrium molecular dynamics,” *Phys. Rev. Lett.*, 60, 128–131, 1988.
- [14] J.P. Ryckaert, A. Bellemans, G. Ciccotti, and G.V. Paolini, “Evaluation of transport coefficients of simple fluids by MD: comparison of Green–Kubo and nonequilibrium approaches for shear viscosity,” *Phys. Rev. A*, 39, 259–267, 1989.

- [15] A.J.C. Ladd, "Equations of motion for non-equilibrium molecular-dynamics simulations of viscous-flow in molecular fluids," *Mol. Phys. Rep.*, 53, 459–463, 1984.
- [16] D.J. Evans and G.P. Morriss, "Non-Newtonian molecular-dynamics," *Comp. Phys. Rep.*, 1, 297–343, 1984.
- [17] A.W. Lees and S.F. Edwards, "The computer study of transport processes under extreme conditions," *J. Phys. C*, 5, 1921–1972, 1972.
- [18] G. Ciccotti, C. Pierleoni, and J.P. Ryckaert, "Theoretical foundation and rheological application of non-equilibrium molecular dynamics," In: M. Mareschal and B.L. Holian (eds.), *Simulations of Complex Hydrodynamic Phenomena*, NATO ASI Series B 292. Plenum Press, New York, 1992.
- [19] R. Edberg, D.J. Evans, and G.P. Morriss, "Conformational dynamics in liquid butane by nonequilibrium molecular dynamics," *J. Chem. Phys.*, 87, 5700–5708, 1987.
- [20] G. Mareschal, J-P. Ryckaert, and A. Bellemans, "The shear viscosity of n-butane by equilibrium and non-equilibrium molecular dynamics," *Mol. Phys.*, 61, 33–49, 1987.
- [21] S.R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam, 1962.
- [22] W.G. Hoover, D.J. Evans, R.B. Hickman, A.J. Ladd, W.T. Ashurst, and B. Moran, "Lennard-jones triple-point bulk and shear viscosities. Green-Kubo theory, hamiltonian mechanics, and nonequilibrium molecular dynamics," *Phys. Rev. A*, 22, 1690–1697, 1980.