A stochastic thermopotentiostat for molecular dynamics simulations

F. Deißenbeck,1 C. Freysoldt,1 M. Todorova,1 J. Neugebauer,1 and S. Wippermann1,*

1Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

(Dated: March 19, 2020)

We derive a stochastic approach to sample the canonical ensemble at constant temperature and applied electric potential. Our proposed thermopotentiostat is the electrical analog to the Langevin thermostat. It is free of simulation artefacts, avoiding any spurious energy transfer between kinetic and electric degrees of freedom. Our approach can be straightforwardly applied in the context of ab initio molecular dynamics calculations. Using thermopotentiostat molecular dynamics simulations, we explore the interfacial dielectric properties of nano-confined water.

Molecular dynamics (MD) has become an indispensible tool to efficiently simulate the behaviour of macroscopic systems, using models with finite size and reduced complexity. At finite size, however, intensive quantities, that are controlled at the macroscale, are no longer constant but fluctuating. These local fluctuations impact kinetics significantly and must be explicitly taken into account in finite simulation cells. Temperature fluctuations are widely recognized as one of the most important examples of this kind. Consequently, significant effort has been directed at developing thermostats [1–12] with the dual purpose of (i) efficiently sampling the canonical ensemble and (ii) enabling direct control of the temperature.

Fluctuations, however, are inherent to any thermodynamic degree of freedom, including the pressure [13] and the electric potential. Electrically triggered processes involving electron transfer reactions, such as electrochemical reactions, field desorption, and quantum transport, depend on localized mechanisms and are strongly affected by the local fluctuating charge density and electric field. Accurately describing these processes requires a level of theory beyond MD with fast, but simple interatomic potentials. With the advent of robust techniques to apply electric fields in density-functional calculations [14–25], it is now possible, in principle, to study such systems using ab initio molecular dynamics (AIMD). Compared to classical MD, however, system sizes are much more restricted. Therefore, it is of particular importance to incorporate charge and electric field fluctuations explicitly and actively control the applied potential by a potentiostat. The first approach of this kind was suggested by Bonnet et al. [19], introducing an empirically motivated potentiostat with a fictitious momentum of the instantaneously applied potential coupled to Nose-Hoover dynamics. It relies, however, on a continuum description of the counter charge. In analogy to thermostats, multiple valid approaches towards potential control are conceivable, each featuring distinct advantages and disadvantages. For different temperature control schemes, these are revealed by the general theory of thermostats [6, 9, 12]. A corresponding general theory for potentiostats has not yet been devised.

In this Letter, we introduce a general theory of potentiostats and derive a new stochastic approach to potential control that is the electric equivalent of the Langevin thermostat. Our approach samples the canonical NVTΦ or NpTΦ ensemble at constant temperature and applied potential. It is free of simulation artefacts, avoiding any spurious energy transfer between kinetic and electric degrees of freedom. It can be fully integrated with Langevin dynamics [8] for the kinetic degrees of freedom or the BDP thermostat [9, 10]. The necessity for an explicit energy functional, that is differentiable with respect to the total charge, is completely avoided. The approach is straightforward to implement in any standard density functional code, and it is fully consistent with the modern theory of polarization [14, 15], the generalized dipole correction [23] and the computational counter electrode [24].

To derive the approach we consider a dielectric placed between two electrodes, which are connected to a voltage source with potential difference Φ and an internal resistance R, cf. Fig. 1a. Φ is the instantaneous voltage measured directly across the electrodes and C₀ is the bare capacitance of the electrodes in vacuum without the dielectric. The system is described by momenta \( p_i \), coordinates \( q_i \) and the electrode charge \( n \). We define a Hamiltonian \( H(p_i, q_i, n) = K(p_i) + V(q_i) + E(q_i, n) \), where \( K(p_i) \) is the kinetic energy and \( V(q_i) \) is the potential energy. \( E(q_i, n) \) denotes the total electrostatic potential energy, stored in the capacitance. For the kinetic degrees of freedom, the canonical distribution can be sampled by equations of motion in the form

\[
dp_i = \left( \frac{\partial V}{\partial q_i} + \frac{\partial E}{\partial q_i} \right) dt + g_idt, \tag{1}
\]

\[
dq_i = \frac{1}{m_i} p_i dt. \tag{2}
\]

Eqs. 1, 2 are Hamiltonian with an added correction force \( g_i \), cf., for example, Ref. [10]. We define \( E(q_i, n) = \frac{(n + \rho_p)^2}{2C_0} \) so that

\[
\frac{d\Phi}{dt} = \frac{1}{C_0} \left[ \frac{dn}{dt} + \frac{dp_p}{dt} \right], \tag{3}
\]
where \( \rho_p \) is the polarization bound charge at the electrode surface due to the polarization of the dielectric [26]. Previous studies, using, e.g., the modern theory of polarization, introduced either (i) a constant electric field [15, 20] or (ii) a constant dielectric displacement [16, 20, 21, 24] as electrostatic boundary condition. This means that either (i) \( d\Phi/dt \) or (ii) \( dn/dt \) is set to zero (cf. Eq. 3). The former is equivalent to a short circuit with zero impedance, implying an instantaneous fluctuating counter charge \( dn = -d\rho_p \) on the electrodes that cancels out any macroscopic electric field fluctuations exactly. The latter represents an open circuit, where the charge is constant, but the potential is fluctuating with \( d\Phi = d\rho_p/C_0 \). Note that boundary conditions (i) and (ii) both represent constant-energy Hamiltonian dynamics.

In order to obtain an equation of motion for the full potential dynamics, we equate the current flowing through the capacitance \( dn/dt \) to the current \(- (\Phi - \Phi_0)/R\) flowing in reverse through the voltage source and its internal resistivity \( R \) (Kirchhoff’s 2nd law):

\[
\begin{align*}
\frac{d\Phi}{dt} &= \frac{1}{C_0} d\rho_p + f dt \\
f dt &= -\frac{1}{RC_0} (\Phi - \Phi_0) dt + \tilde{\Phi} dW_t
\end{align*}
\]  

\( \tilde{\Phi} \) and \( dW_t \) are a fluctuation term and a Wiener noise, respectively. Note that the role of \( g_t \) and \( f \) is conceptually similar. In Hamiltonian dynamics, the total energy \( H \) is conserved, so that in Eqs. 1, 2 the term \( g_t \) alone is responsible for energy exchange with the surroundings and the system’s thermalization. Similarly, in Eq. 4 the term \( f \) is responsible for energy exchange with the voltage source \( \Phi_0 \).

Since the first term in Eq. 5 is dissipative, the fluctuation-dissipation theorem (FDT) [27] requires an associated fluctuation. Johnson [28] and Nyquist [29] recognized that a resistor on a transmission line creates electric fluctuations at its leads. In conjunction with the capacitance \( C_0 \), the resistance \( R \) in our system forms an RC low pass. Thereby, the variance of \( \Phi \) is

\[
\sigma_\Phi^2 = \frac{k_B T}{C_0}.
\]

It is now straightforward to construct a suitable fluctuation term \( \tilde{\Phi} \). The energy loss in Eq. 5 due to the dissipation by the resistance \( R \) must be exactly equal, on average, to the energy gained through the fluctuations in \( \tilde{\Phi} \), while the variance, and also the frequency spectrum of the fluctuations, are determined by the FDT. Thereby, the applied electric field itself is fluctuating and has a finite temperature. In analogy to the Langevin [7, 8] and BDP [9, 10] thermostats, we recognize that Eq. 5 formally represents a stochastic differential equation known as the Ornstein-Uhlenbeck process

\[
\begin{align*}
dx &= -k x dt + \sqrt{D} dW_t.
\end{align*}
\]  

The expectation value and variance of the Ornstein-Uhlenbeck process are given by [30]:

\[
\langle x(t) \rangle = x_0 e^{-kt} \quad \text{(8)}
\]

\[
\text{var}[x(t)] = \left( \text{var}[x_0] - \frac{D}{2k} \right) e^{-2kt} + \frac{D}{2k} \quad \text{(9)}
\]

With \( \tau_\Phi := RC_0, \ k := \tau_\Phi^{-1} \) and \( D/2k := \sigma_\Phi^2 \) we write:

\[
f dt = -\frac{1}{\tau_\Phi} (\Phi - \Phi_0) dt + \sqrt{\frac{2}{2kT} \frac{k_B T}{C_0}} dW_t \quad \text{(10)}
\]

In the limit \( \tau_\Phi \to 0 \) the system is instantly potentialized, recovering the microcanonical ensemble at constant electric field. For \( \tau_\Phi \to \infty \) the microcanonical ensemble at constant dielectric displacement is recovered. Far from equilibrium, the deterministic part in Eq. 10 dominates, leading to equilibration with a relaxation time of \( \tau_\Phi \). Close to equilibrium, the stochastic term dominates, correctly sampling the canonical ensemble. Note that the fluctuation term in Eq. 10 depends only on the geometry of the simulation cell and is independent of the dielectric properties of the system. Instead, dielectric screening is accounted for within the deterministic part by means of the polarization bound charge, which responds to the stochastic fluctuations.

In practical simulations, integration is performed using a discrete time step. The Ornstein-Uhlenbeck process has an analytical solution [31, 32] that can be obtained from Itô calculus [30]. Analogously, Eq. 10 also features an analytical solution to use as an exact propagator for the potential, with

\[
f(t) = \Phi_0 + (\Phi - \Phi_0) e^{-\frac{t}{\tau_\Phi}} + N \sqrt{\frac{k_B T}{C_0}} (1 - e^{-\frac{t}{\tau_\Phi}}), \quad \text{(11)}
\]

where \( N \) is a Gaussian random number with \( \langle N \rangle = 0 \) and \( \langle N^2 \rangle = 1 \).

We note that the empirically motivated potentialistat suggested by Bonnet et al. [19] fits seamlessly into the general theory presented here. Bonnet et al. introduced a
fictitious electronic momentum $P_n$ and mass $M_n$. These are used to perform Nosé-Hoover dynamics on the charge $n$, with

$$
\dot{n} = \frac{P_n}{M_n}
$$

(12)

$$
dP_n = (\Phi - \Phi_0)dt + P_n d\xi.
$$

(13)

$P_n^2/(2M_n)$ enters the Nosé-Hoover equation of motion for $\xi$ as a fictitious kinetic energy. From our scheme, it now becomes apparent that these quantities are not fictitious, but indeed have a clear physical interpretation. With $P_n := -Rn$ and $M_n := R^2n/(\Phi - \Phi_0)$ Eq. 12 is identical to Ohm’s law. The fictitious kinetic energy $P_n^2/(2M_n)$ then becomes the electrostatic potential energy $n(\Phi - \Phi_0)/2$. Inserting $P_n$ and $M_n$ into Eq. 13 yields:

$$
dn = -\frac{1}{\tau_\Phi}C_0(\Phi - \Phi_0)dt - nd\xi
$$

(14)

Multiplying with $C_0$ and setting $\dot{n} = C_0 \dot{\Phi}$, our Eq. 5 can be recast as

$$
dn = -\frac{1}{\tau_\Phi}C_0(\Phi - \Phi_0)dt + \dot{\Phi}dW_t.
$$

(15)

Comparing Eqs. 14 and 15, we see that the deterministic $d\xi$ in Bonnet et al.’s potentiostat substitutes for the stochastic term in Eq. 15.

In order to test our proposed scheme, we performed classical MD simulations [33] of liquid TIP3P water confined between two parallel electrodes. Our thermopotentiostat controls either directly the electrode charge, or the applied electric field. In a first principles context, the former approach applies to the use of a computational counter electrode [20], while the latter is suitable for the modern theory of polarization [14]. Further numerical details are provided in the supplementary information.

We first investigated the effect of our potential control scheme on the temperature of an NVE ensemble. Straightforward approaches to adjust the potential with a relaxation time are always dissipative, cf. left hand term Eq. 10. Conceptually, this type of potentiostat is the electrical analog to Berendsen et al.’s velocity rescaling thermostat [3], where $dK = -\gamma^{-1}(K - \bar{K})dt$. The Berendsen thermostat suffers from a simulation artefact known as the “flying ice-cube effect” [12]. As it dissipates the difference between the instantaneous and mean kinetic energy, it dissipates temperature fluctuations until the instantaneous kinetic energy becomes constant. As a result, all particles eventually share the same velocity, and, in resemblance of the Maxwell demon, disordered thermal motion has been converted into ordered translational motion. Analogously, the Ohm’s law potentiostat dissipates thermal potential fluctuations. In absence of a thermostat, it is cooling the NVE ensemble significantly, cf. Fig. 1b.

Note that the potentiostat affects only vibrational modes that couple to the total dipole moment. A thermostat, in contrast, acts indiscriminately on all modes. Thereby, even if a thermostat is used to replenish the energy dissipated by the potentiostat, a spurious energy transfer is induced that can drive the ensemble out of equilibrium. A canonical potentiostat as proposed here, in contrast, will prevent a priori any unphysical energy transfer between kinetic and electric degrees of freedom. In fact, the potentiostat alone must be able to control the kinetic temperature by means of its fluctuating electric field, even in the absence of a thermostat. We checked the validity of our approach by performing the same simulation as described above, without a thermostat, but using the full Eq. 11. As shown in Fig. 1b, the spurious energy transfer is completely eliminated and the temperature correctly fluctuates around the target temperature $T = 350$ K set in Eq. 11.

Using the potentiostat to apply a voltage allows us now to directly measure the static dielectric constant $\varepsilon_\perp$ and compare it to the value obtained from calculations for the variance of the dipole moment fluctuations, using Kirkwood-Fröhlich theory [34]. The variance of the dipole fluctuations depends on the electrostatic boundary conditions. In linear response, $\varepsilon$ is calculated either from the susceptibility at $\Phi = 0$ or the polarizability at $n = 0$, respectively [20]:

$$
\varepsilon = 1 + \frac{\langle M^2 \rangle_{\Phi=0}}{3\Omega k_B T \epsilon_0} \left[ 1 - \frac{\langle M^2 \rangle_{n=0}}{3\Omega k_B T \epsilon_0} \right]^{-1}
$$

(16)

$\Omega$ is the unit cell volume. Here, the volume is calculated as the unit cell area times the electrode separation $d$. In our setup, $\varepsilon_\parallel$ is calculated from the left hand side of Eq. 16, whereas for $\varepsilon_\perp$ we use the right hand side of Eq. 16 and constant charge boundary conditions in that direction. For an electrode separation of $d = 2$ nm we obtain $\varepsilon_\parallel = 55.3$. This value is smaller than the isotropic $\varepsilon_{\text{bulk}} = 73.2$ of TIP3P water at 350 K, since the $d = 2$ nm simulation cell is rather small, containing only 282 water molecules. For $d = 4$ nm and $d = 8$ nm we find $\varepsilon_\parallel = 70.4$ and $\varepsilon_\parallel = 72.0$, respectively. Interestingly, in agreement with a recent experimental study [35], we observe that $\varepsilon_\perp$ is strongly reduced compared to $\varepsilon_{\text{bulk}}$. 

![Figure 2. $\varepsilon_\perp$ of TIP3P water for an electrode separation of $d = 2$ nm as a function of applied potential, calculated using the NVT$\Phi$ ensemble. Kirkwood-Fröhlich theory at $n = 0$ and zero field extrapolation (orange line) yield $\varepsilon_\perp = 6.24$ and $\varepsilon_\perp = 6.16$, respectively. Inset: zero field extrapolation for $d = 8$ nm.](image-url)
We now proceed to compute \( \epsilon_\perp := \langle C \rangle_{\Phi=\Phi_0}/C_0 \), using our thermopotentiostat MD approach. The total instantaneous capacitance \( C \) and the bare capacitance \( C_0 \) without the dielectric are straightforwardly obtained from thermopotentiostat simulations, thereby avoiding any ambiguity in the definition of the volume \( \Omega \) in the presence of adsorbates, thermal motion of the electrode surface or in the context of explicit electronic structure calculations. At \( d = 2 \) nm and \( \Phi_0 < 10 \) V, \( \epsilon_\perp \) is a linear function of \( \Phi \) within our statistical error bars, cf. Fig. 2. To compare to the Kirkwood \( \epsilon_\perp \), we perform a linear fit and extrapolate to \( \Phi_0 = 0 \), as indicated by the orange line in Fig. 2. We find \( \epsilon_\perp = 6.16 \) in close agreement with the value of 6.24 derived from the dipole fluctuations at \( n = 0 \). The inset in Fig. 2 shows an enlarged plot of the low voltage region for \( d = 8 \) nm, where the Kirkwood expression and zero field extrapolation result in \( \epsilon_\perp = 20.09 \) and \( \epsilon_\perp = 20.13 \), respectively.

Fig. 3a shows \( \epsilon_\perp \) as a function of electrode separation, derived from Kirkwood theory and compared to our thermopotentiostat MD. As suggested previously by Zhang et al. [36], the dielectric constant remains anisotropic up to tens of nanometers. Qualitatively, our simulations are in excellent agreement with the measurements by Fumagalli et al. [35]. The origin of the decreasing \( \epsilon_\perp \) with decreasing \( d \) can be traced to the local dielectric properties of water close to the interface. A detailed discussion based on the theory of local polarization fluctuations [37] will be presented by Ruiz-Barragan et al. [38]. Here, in analogy to the constant charge simulations in Ref. [39], we compute the electric field profile induced by the thermopotentiostat’s displacement field \( D_\perp \) as

\[
\Delta E_\perp(z) = \epsilon_\perp^{-1}[D_\perp - m_\perp(z) + m_\perp,0(z)],
\]

where the local polarization density \( m_\perp(z) \) is obtained from the dielectric’s charge density by \( m_\perp(z) = -\int_0^z \rho(z')dz' \) and subscript 0 denotes zero external field. The local dielectric profile is then extracted from the linear response relation \( \Delta E_\perp \approx \epsilon_0 \epsilon_\perp^{-1}D_\perp \).

Fig. 3b shows \( \epsilon_\perp^{-1}(z) \) for \( d = 8 \) nm. At the position of the electrode surface, \( \epsilon_\perp^{-1} \) drops sharply and intersects the water bulk value at \( \sim 3 \) Å above the surface. With further increasing \( z \), \( \epsilon_\perp^{-1} \) assumes negative values for interfacial water and then approaches the bulk water value in an oscillatory fashion. At a normal distance of \( \sim 9 \) Å, \( \epsilon_{\text{bulk}} \) is recovered. This behaviour reflects the density modulation and layered structure of water found close to interfaces, cf. Fig. 3b lower part, and the inherent non-locality of the dielectric properties of water [41–43].

We now divide the dielectric profile into three regions: (i) a hydrophobic gap between electrode and surface with a thickness of \( d_\parallel = 2 \) Å, (ii) the first two interfacial water layers with a thickness of \( d_n = 5.5 \) Å and (iii) the remaining approximately bulk-like region, cf. Fig. 3b. Based on spectroscopic data, the existence of a hydrophobic gap was also suggested by Niu et al. [40]. The effective dielectric constant of each region is obtained by integrating over the dielectric profile according to \( \epsilon_\perp^{-1} = d^{-1} \int_{z_i}^{z_2} \epsilon_\perp^{-1}(z)dz \), yielding \( \epsilon_\parallel = 1.2 \) and \( \epsilon_n = 17.3 \) for the hydrophobic gap and interfacial water regions, respectively. We describe our system as a simple plate capacitor with multiple dielectrics, cf. inset in Fig. 3a, with \( \epsilon_\perp(d) = d/[2d_\parallel/\epsilon_\perp + 2d_n/\epsilon_n + (d - 2(d_\parallel + d_n))/\epsilon_{\text{bulk}}] \) shown as the orange dashed line in Fig. 3a. Thereby, from a single explicit data point at \( d = 8 \) nm, \( \Phi_0 = 4 \) V, we accurately obtain the whole range of \( \epsilon_\perp(d) \).

Fitting \( \epsilon_n \) instead to Fumagalli et al.’s measurements, assuming a hydrophobic gap of constant size with \( d_\parallel = 2 \) Å, the optimum fit is obtained for \( \epsilon_n = 2.85 \), which is significantly lower than what we obtain from our thermopotentiostat simulations. Alternatively, assuming \( \epsilon_n = 17.3 \) for interfacial water to be independent of the specific electrode surface, a fit with identical accuracy is obtained for \( d_\parallel = 4 \) Å. We propose that these pronounced differences in the size of the hydrophobic gap and the dielectric properties of interfacial water encode chemical information about the surface: the size of the hydrophobic gap depends on the specific surface and, in contrast to experiment, our model electrode is perfectly inert towards hydrogen. Hence it is incapable of directly

![Image](https://via.placeholder.com/150)
guiding the orientation of water. Our model electrode, thereby, affects the interfacial water orientation only by
the reduced dimensionality at the interface and the elec-
trode charge.

We finally note that the calculation of dielectric pro-
files from polarization fluctuations [37] requires hundreds
of nanoseconds of statistical sampling. In contrast, our
proposed direct approach according to Eq. 17 converges
within a few nanoseconds. In addition, for distances be-
yond \(\sim 10 \text{ Å} \) water already becomes bulk-like. Therefore,
using our thermopotentiostat MD in conjunction with fi-
nite field density-functional techniques moves these types
of calculations within range of first principles simulations.

In conclusion, we devised a new stochastic thermopotent-
tiostat to sample the canonical ensemble under an ap-
plied electric bias from a general theory of thermopoten-
tiostats. Introducing thermal fluctuations to the elec-
tric field and electrode charge, our approach satisfies the
fluctuation-dissipation theorem exactly and thereby pre-
vents any spurious energy transfer between kinetic and
electric degrees of freedom. Our approach is straightforward to implement in the context of \textit{ab initio} molecular
dynamics simulations, using the modern theory of po-
larization or an explicit computational counter electrode or
indeed any simulation scheme that can be coupled to
an external electric field. To demonstrate the efficiency
of our approach we calculated the dielectric properties
of nano-confined water. Based on these calculations we
showed that the presence of interfaces leads to a strongly
anisotropic dielectric response, persisting for distances exceeding 100 nm. In conjunction with \textit{ab initio} MD, we expect our thermopotentiostat to open the door to-
wards accurate and efficient simulations of electrochemi-
cally triggered processes.

We thank L. Fumagalli for providing the raw experi-
mental data from Ref. [35] and D. Marx for discus-
sions. This work is supported by the German Fed-
eral Ministry of Education and Research (BMBF) within
the NanoMatFutur programme, grant no. 13N12972.
Funded by the Deutsche Forschungsgemeinschaft (DFG,
German Science Foundation) under Germany’s Excel-
ence Strategy – EXC 2033 – project no. 390677874. Su-
percomputer time provided by NERSC Berkeley, project
no. 35687, is gratefully acknowledged.

[1] L. Woodcock, Chem. Phys. Lett. 10, 257 (1971)
[2] H. Andersen, J. Chem. Phys. 72, 2384 (1980)
[3] H. Berendsen, J. Postma, W. van Gunsteren, A. DiNola,
J. Haak, J. Chem. Phys. 81, 3684 (1984)
[4] S. Nosé, J. Chem. Phys. 81, 511 (1984)
[5] W. Hoover, Phys. Rev. A 31, 1695 (1985)
[6] G. Martyna, M. Klein, M. Tuckerman, J. Chem. Phys.
97, 2635 (1992)
[7] T. Schneider, E. Stoll, Phys. Rev. B 17, 1302 (1978)
[8] M. Allen, D. Tildesley, \textit{Computer Simulation of Liquids},
Oxford University Press, NY (1991)
[9] G. Bussi, D. Donadio, M. Parinello, J. Chem. Phys. 126,
014101 (2007)
[10] G. Bussi, M. Parinello, Comp. Phys. Comm. 179, 26
(2008)
[11] B. Leimkuhler, E. Noorizadeh, F. Theil, J. Stat. Phys.
135, 261 (2009)
[12] E. Braun, S. Moosavi, B. Smit, J. Chem. Theory Comput.
14, 5262 (2018)
[13] S. Feller, Y. Zhang, W. Pastor, B. Brooks, J. Chem.
Phys. 103, 4613 (1995)
[14] R. Resta, Rev. Mod. Phys. 66, 899 (1994)
[15] M. Stengel, N. Spaldin, Phys. Rev. B 75, 205121 (2007)
[16] M. Stengel, N. Spaldin, D. Vanderbilt, Nature Physics 5,
304 (2009)
[17] A. Lozovoi, A. Alavi, J. Kohanoff, R. Lynden-Bell, J.
Chem. Phys. 115, 1661 (2001)
[18] I. Tavernelli, R. Vuilleumier, M. Sprik, Phys. Rev. Lett.
88, 213002 (2002)
[19] N. Bonnet, T. Morishita, O. Sugino, M. Otani, Phys.
Rev. Lett. 109, 266101 (2012)
[20] C. Zhang, M. Sprik, Phys. Rev. B 94, 245309 (2016)
[21] T. Sayer, M. Sprik, C. Zhang, J. Chem. Phys. 150,
041716 (2019)
[22] Q. Wan, L. Yang, M. Pander, S. Tecklenburg, A. Erbe,
F. Gygi, G. Galli, S. Wippermann (in preparation)
[23] M. Ashton, A. Mishra, C. Freysoldt, J. Neugebauer,
Phys. Rev. Lett. (under review)
[24] S. Surendralal, M. Todorova, M. Finnis, J. Neugebauer,
Phys. Rev. Lett. 120, 246801 (2018)
[25] O. Magnussen, A. Groß, J. Am. Chem. Soc. 141, 4777
(2019)
[26] L. Landau, E. Lifshitz, \textit{Electrodynamics of continuous
medium}, Pergamon Press, Oxford (1984)
[27] H. Callen, T. Welton, Phys. Rev. 83, 34 (1951)
[28] J. Johnson, Phys. Rev. 32, 97 (1928)
[29] H. Nyquist, Phys. Rev. 32, 110 (1928)
[30] C. Gardiner, \textit{Stochastic Methods}, Springer, Berlin (2009)
[31] D. Gillespie, Am. J. Phys. 64, 225 (1996)
[32] D. Gillespie, Phys. Rev. E 54, 2084 (1996)
[33] S. Plimpton, Fast Parallel Algorithms for Short-Range
Molecular Dynamics, J. Comp. Phys. 117, 1-19 (1995),
https://lammps.sandia.gov
[34] M. Sharma, R. Resta, R. Car, Phys. Rev. Lett. 98,
247401 (2007)
[35] L. Fumagalli et al., Science 22, 1339 (2018)
[36] C. Zhang, F. Gygi, G. Galli, J. Phys. Chem. Lett. 4, 2477
(2013)
[37] H. Stern, S. Feller, J. Chem. Phys. 118, 3401 (2003)
[38] S. Ruiz-Barragan, D. Munoz-Santiburcio, S. Körning, D.
Marx (in preparation)
[39] P. Loche, A. Wolde-Kidan, A. Schlaich, D. Bonthuis, R.
Netz, Phys. Rev. Lett. 123, 049601 (2019)
[40] F. Niu, R. Schulz, A. Castaneda Medina, R. Schmid, A.
Erbe, PCCP 19, 13585 (2017)
[41] P. Bopp, A. Kornyshew, G. Sutmann, Phys. Rev. Lett.
76, 1280 (1996)
[42] A. Kornyshew, S. Leikin, G. Sutman, Electrochimica
Acta 42, 849 (1997)
[43] D. Cherepanov, Phys. Rev. Lett. 93, 266104 (2004)
Supplementary Information for  
*A Stochastic thermopotentiostat for finite systems*

F. Deißenbeck,\(^1\) C. Freysoldt,\(^1\) M. Todorova,\(^1\) J. Neugebauer,\(^1\) and S. Wippermann\(^1\)\(^,*\)

\(^1\)Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

**NUMERICAL DETAILS**

Water is described by the TIP3P \(^1\) potential. The electrodes are modeled as single sheets of fixed atoms, where interactions with water are described by the TIP3P O-O pair potential. We do not include any pair potential for the electrode atoms and the hydrogen atoms of the water molecules. The electrode thereby affects the orientation of interfacial water only by the reduced dimensionality at the interface and by the electrode charge. Periodic boundary conditions are applied in \(x\) and \(y\) direction; non-periodic boundary conditions are used along the direction of the electrode surface normal. Simulations were carried out either in the NVE ensemble or the NVT ensemble at \(T = 350\) K, using a time step of 40 atomic units (\(\approx 0.97\) fs). All ensembles were first equilibrated without a field for 1 ns using the Langevin thermostat and subsequently for another 2 ns using the BDP thermostat. Sampling time was 4 ns. Coulomb long-range interactions were treated by a particle-particle particle mesh solver \(^3\) with a precision of \(10^{-5}\). All calculations were performed for rigid water in order to enable the use of a longer time step. Bond lengths and angles were constrained using the SHAKE algorithm \(^4, 5\).

**SPECTRAL CONSIDERATIONS**

An oscillating electric dipole radiates energy, leading to a radiation resistance. This radiation resistance gives rise to a fluctuating electric field as given by Planck’s radiation law. In analogy to a one-dimensional version of Planck’s radiation law, a resistor on a transmission line creates electric fluctuations at its leads. This was first recognized by Johnson \(^6\) and Nyquist \(^7\), and generalized later by Callen and Welton in terms of the fluctuation-dissipation theorem (FDT) \(^8\).

Classically, per frequency interval \(d\nu\), the variance of the fluctuating voltage at a resistance \(R\) is given by \(\sigma^2 \nu d\nu = 4k_B T R d\nu\). In conjunction with the capacitance \(C_0\), the resistance \(R\) in our system forms an RC low pass, thereby avoiding the “UV catastrophe” even in the classical case. The variance of \(\Phi\) is obtained by integrating the noise spectral density over the bandwidth of the RC low pass:

\[
\sigma^2 \nu = 4k_B T R \frac{1}{2\pi} \int_0^\infty \frac{1}{1 + (\omega RC_0)^2} d\omega = \frac{k_B T}{C_0} \tag{S1}
\]

In this case, the FDT determines also the frequency spectrum of the fluctuations. In absence of a dielectric, the variance of the voltage fluctuations given by Eq. S1 is distributed in frequency space according to the spectral density function of the ideal fully relaxed Ornstein-Uhlenbeck process

\[
S_\nu(\nu) = \frac{2c\nu^2}{1 + (2\pi\nu)^2}, \tag{S2}
\]

with \(c = 2k_B T/(\tau_\Phi C_0)\). In Fig. S1 we show the spectral density of the variance of the potential fluctuations for the \(d = 8\) nm cell. Below the cutoff frequency \((2\pi\tau_\Phi)^{-1}\), the slope of the spectral density is zero (white noise region), whereas it is -2 above \((1/f^2)\) noise region), cf., e.g., Ref. \(^9\) for a detailed discussion. Comparing the expressions for the Nose-Hoover potentiostat and our Langevin potentiostat

\[
dn = -\frac{1}{\tau_\Phi} C_0 (\Phi - \Phi_0) dt - nd\xi \tag{S3}
\]

\[
dn = -\frac{1}{\tau_\Phi} C_0 (\Phi - \Phi_0) dt + \tilde{n}dW_t, \tag{S4}
\]

it becomes clear that Eq. S3 approximates the spectrum required by the FDT with a single discrete frequency. For poorly ergodic systems, as is the case here, it is generally recognized that a single frequency is insufficient. Using a Nose-Hoover chain as proposed by Bonnet et al. \(^10\), the spectrum is then approximated by a set of discrete frequencies. For water in particular, which has a rather discrete spectrum itself with large phonon gaps, it is advantageous to utilize a continuous spectrum. By design, Eq. S4 satisfies the required spectrum exactly. Compared to the reversible integrator proposed by Martyna et al. \(^11, 12\) or a self-consistent solution of the Nose-Hoover equations of motion, Eq. S4 is straightforward to integrate since it has an analytical propagator.

**FIG. S1.** Spectral density plot of the variance of the potential fluctuations.
[1] W. Jorgensen et al., J. Chem. Phys. 79, 926 (1983)
[2] G. Bussi, D. Donadio, M. Parinello, J. Chem. Phys. 126, 014101 (2007)
[3] Hockney, Eastwood, Computer Simulations Using Particles, Adam Hilger, NY (1989)
[4] J.-P. Ryckaert, G. Ciccotti and H. J. C. Berendsen, J. Comp. Phys. 23, 327-341 (1977)
[5] H. Andersen, J. Comp. Phys. 52, 24-34 (1983)
[6] J. Johnson, Phys. Rev. 32, 97 (1928)
[7] H. Nyquist, Phys. Rev. 32, 110 (1928)
[8] H. Callen, T. Welton, Phys. Rev. 83, 34 (1951)
[9] D. Gillespie, Am. J. Phys. 64, 225 (1996)
[10] N. Bonnet, T. Morishita, O. Sugino, M. Otani, Phys. Rev. Lett. 109, 266101 (2012)
[11] G. Martyka, M. Klein, J. Chem. Phys. 97, 2635 (1992)
[12] M. Tuckerman, Y. Liu, G. Cicotti, G. Martyna, J. Chem. Phys. 115, 1678 (2001)