1 SUPPLEMENTARY MATERIAL

1.1 Content
In addition to this PDF, we provide the raw data for all plots shown in this work in the form of a spreadsheet in open-document format (PBE-DATA.ods).

1.2 Theory and implementation
Let us begin with a review of the theoretical framework of the D4 model as this will provide the context for the introduction of the new features. The underlying concept of D4 and its predecessors is to model the dispersion energy based on atomic pairwise dispersion coefficients $C_{6}^{jk}$, which are obtained from a Casimir–Polder integration of the respective atomic polarizabilities $\alpha_{i}^{\text{eff}}(i\omega)$

$$C_{6}^{jk} = \frac{3}{\pi} \int_{0}^{\infty} d\omega \alpha_{i}^{\text{eff}}(i\omega) \alpha_{j}^{\text{eff}}(i\omega).$$  \hspace{1cm} (1)

Note that electronic units are used throughout in this work. To account for the influence of the chemical environment, the atomic polarizabilities used in the D4 model are not fixed at the values of the isolated atoms $\alpha(i\omega)$, but depend (i) on geometric parameters captured by the atomic coordination number (CN$_j$, as in D3), as well as (ii) on effective atomic charges ($z_j$, new in D4) obtained via an electronegativity-equilibration (EEQ) scheme. The idea behind the introduction of this charge scaling is to allow for a more “natural” behavior of the effective polarizabilities, i.e., to render atoms with negative partial charge more polarizable and vice versa.

In practice, the geometry and charge dependence of the polarizabilities is implemented using an interpolation based on a set of molecular reference systems. To do this efficiently and avoid an interpolation in two dimensions, the atomic polarizabilities of all reference systems are, in a first step, rescaled to match the effective charge of the atom under consideration of $z_j$ via

$$\tau_{i}^{\text{ref}}(i\omega) = \alpha_{i}^{\text{ref}}(i\omega) \zeta(\zeta, z_{j}^{\text{ref}}),$$ \hspace{1cm} (2)

where $\zeta$ describes an empirical relation between the polarizability of an atom and its effective charge. Its analytical form

$$\zeta(\zeta, z_{j}^{\text{ref}}) = \exp\left(\beta \left[ 1 - \exp \left( \gamma \left( 1 - \frac{z_{j}^{\text{ref}}}{z_j} \right) \right) \right]\right),$$ \hspace{1cm} (3)

with $\beta$ as a global parameter set to 3 and $\gamma$ as the chemical hardness taken from Ref. [2] is discussed in more detail in Ref. [1]. The calculation of the necessary effective charges $z$ done with an EEQ model is described in section 1.3.

In a second step, the effective polarizability of the atom $j$ is obtained via interpolation from the charge-scaled reference polarizabilities using a Gaussian weighting based on the coordination number (CN)

$$\alpha_{i}^{\text{eff}}(i\omega) = \sum_{i, \text{ref}=1}^{N_{\text{ref}}} \tau_{i}^{\text{ref}}(i\omega) W_{j}^{\text{ref}}(\text{CN}_{i}^{\text{ref}}, \text{CN}_{j}).$$ \hspace{1cm} (4)

However, to use this CN-based approach in periodic systems, a different formula for the CN is used compared to the molecular implementation to avoid CN-divergences. The expression for the CN in periodic systems reads

$$\text{CN}_{j} = \sum_T \sum_{j'} \frac{R_{j}^{\text{EN}}}{2} \left( 1 + \text{erf} \left( -k_{0} \left( \frac{\mathbf{T}^{\text{en}} - R_{ij}^{\text{cov}}}{R_{ij}^{\text{cov}}} \right) \right) \right) \hspace{1cm} (5)$$

where $T = t_1a_1 + t_2a_2 + t_3a_3$ denotes the translation vector with $a_1$, $a_2$, and $a_3$, being the lattice vectors ($t_1$, $t_2$, and $t_3 \in \mathbb{Z}$). The primed sum over $j$ indicates that the case $i = j$ is omitted for $T = 0$. Within the definition of the CN, we apply Pauling elec-
tronegativities (EN) as well as the inter-nuclear distance \( R_{ij} \) of the pair \( ij \), and the covalent atomic radii \( R^{\text{cov}}_{ij} = R_{ij}^{\text{cov}} + R_{ij}^{\text{SOV}} \). Note that the CN has become EN-dependent to differentiate between covalent and ionic bonding (e.g., differentiate \( F_2 \) from HF). The parameters in equation (5) \((k_0 = 7.5, k_1 = 4.1, k_2 = 19.09, \) and \( k_3 = 254.56 \)) were taken from Ref. [1].

This charge and geometry dependent calculation of atomic polarizabilities from molecular reference systems, which may be described as an atom-in-molecule approach to polarizabilities, presumes the additivity of atomic polarizabilities, which is reflected in the following equation

\[
\alpha_i^{\text{ref}}(\omega) = \frac{1}{m} \left[ \alpha_X^{\text{hom}}(\omega) - \frac{n}{l} \alpha_X^{\text{homo}}(\omega) \zeta(X \cdot \xi) \right].
\]

(6)

Here, \( \alpha_X^{\text{hom}}(\omega) \) is the molecular polarizability of one I-reference, \( \alpha_X^{\text{homo}}(\omega) \) refers to the homonuclear compound (e.g., \( \alpha_{\text{H}_2}^{\text{homo}}(\omega) \) as dihydrogen) and \( m, n, \) and \( l \) are the particular stoichiometric coefficients. All \( I \) atoms inside the reference molecules and the \( X \) atoms in the homonuclear compounds are electronically equal and thus symmetry equivalent. By exploiting this symmetry equivalence, the approximation of additive polarizabilities is justified. Furthermore, the charge scaling of all \( X \) atoms in the respective reference system is directly incorporated. This more general scheme has no disadvantages compared to the hydrogenated reference systems used in the D3 model. With it, any diatomic molecular polarizabilities, e.g., dihalide molecular polarizabilities (chlorine or fluorine) and oxygen molecular polarizabilities can be used in the subtraction scheme of equation (5) as briefly discussed in Ref. [6].

This generalization of the approach opens up the possibility to provide specialized \( C_6 \) dispersion coefficients, which is exploited here to properly describe interactions in ionic solids.

1.3 Periodic electronegativity equilibration model

For the generation of atomic partial charges \( q_i \) under periodic boundary conditions, a classical geometry dependent EEQ charge model is developed in the present work. For this purpose, a cyclic cluster model (CCM) is implemented which applies periodic boundary conditions to a cluster that uses a non-primitive unit cell of a solid, a surface, or an infinite chain by directly employing cyclic Born-ván-Kármán boundary conditions. The environment of each atom is replaced by a notional cyclic arrangement of cluster atoms, where the interaction zone of each atom within the cyclic cluster is described by a Wigner-Seitz cell, constructed by the translation vectors of the unit cell and centered at the atom. The cluster is constructed as a supercell of the primitive unit cell, so that a repetition of this unit cell of \( N_1, N_2, \) and \( N_3 \) cells along the lattice vectors \( \mathbf{a}_1, \mathbf{a}_2, \) and \( \mathbf{a}_3 \) leads to a total cell number of \( N = N_1 \cdot N_2 \cdot N_3 \). In the CCM, the WSCs are stoichiometrically and symmetrically constructed to ensure local electroneutrality. This is guaranteed by the fact that each WSC central atom \( i \) is surrounded by \( \Xi_i \) neighbours \( j \) with an inverted partial charge. When setting up the cluster, the number of all neighbours of each WSC central atom is determined and weighting factors \( w_{ij} = 1/\Xi_i \) for the respective neighbours are assigned, accordingly. Since the CCM is a finite-size method, the clusters used can also carry a net charge without running into convergence problems occurring within the employed Ewald sums. In contrast to a supercell model, no summation over special \( \mathbf{k} \)-points has to be carried out. Instead, a discrete number of \( \mathbf{k} \)-points is contained implicitly by placing them equally distributed in space.

\[
\{ \mathbf{k} \} = \prod_{j}^{\mathbf{N}_j} \mathbf{b}_j \quad g_j = 0, \ldots, N_j^{-1}
\]

(7)

Here, we introduce the reciprocal lattice vectors \( \mathbf{b} \). The periodic charge density \( \rho(r) \) of the system is supposed to be a superposition of spherically symmetric Gaussian functions centered at the atoms position, each normalized to the corresponding nuclear charge \( q_i \), given by the following expression

\[
\rho_i(r) = \sum_{j=1}^{q_i} \frac{q_j}{a_i^2 \pi^{3/2}} \exp \left( -\frac{r - \mathbf{R}_i - \mathbf{T}_j}{a_i^2} \right).
\]

(8)

Here, the atomic van der Waals radii \( a_i \) are introduced. By choosing such atomic charge densities the total isotropic electrostatic (IES) energy is amenable by the following expression given in matrix notation

\[
E_{\text{IES}} = \mathbf{q}^T \left( \frac{1}{2} \mathbf{A} \cdot \mathbf{q} - \mathbf{X} \right).
\]

(9)

The interaction matrix \( \mathbf{A} \) contains all periodic Coulomb interactions, which are developed in Ewald sums by splitting the Coulomb operator into short-range and long-range contributions (Ewald splitting parameter \( \xi = \sqrt{\pi/V}^{1/3} \)). Here, the previously determined weighting factors \( w_{ij} \) (as obtained from the CCM) are applied for all off-diagonal elements

\[
A_{ij}^{\text{rec}} = \frac{4\pi}{V} \sum_{\mathbf{k} \neq 0} \cos (\mathbf{k} \cdot (\mathbf{R}_{ij} + \mathbf{T})) \exp \left( -\frac{k^2}{4\xi^2} \right) w_{ij}^{\text{rec}}
\]

\[
A_{ii}^{\text{rec}} = \frac{4\pi}{V} \sum_{\mathbf{k} \neq 0} \exp \left( -\frac{k^2}{4\xi^2} \right) \frac{1}{k^2}
\]

\[
A_{ij}^{\text{dir}} = \sum_{j=1}^{\mathbf{q}_j} \left( \text{erf}(\gamma_j \mathbf{R}_{ij} + \mathbf{T}) - \frac{\text{erf}(\xi \mathbf{R}_{ij} + \mathbf{T})}{\mathbf{R}_{ij} + \mathbf{T}} \right) w_{ij}^{\text{dir}}
\]

\[
A_{ii}^{\text{dir}} = \sum_{j=1}^{\mathbf{q}_j} \frac{\text{erf}(\gamma_j \mathbf{T}) - \text{erf}(\xi \mathbf{T})}{\mathbf{T}} w_{ij}^{\text{dir}}
\]

\[
A_{ii}^{\text{self/back}} = J_i + \frac{2\gamma_i}{\sqrt{\pi}} - \frac{\pi}{\xi^2 V}
\]

Furthermore, we define \( \gamma_j \) to be equal to \( (a_i^2 + a_j^2)^{-1/2} \). The Lagrangian is constructed under the constraint that the sum of the atomic charges conserves the total charge of the cluster, i.e.,

\[
L = E_{\text{IES}} + \lambda \left( \sum_q q_k - q_{\text{cluster}} \right)
\]

(11)

with \( \frac{\partial L}{\partial q} = 0 \) and \( \frac{\partial L}{\partial \lambda} = \sum q_i - q_{\text{cluster}} = 0 \), which leads to a set of \((N + 1)\) linear equations. The right-hand side (RHS) of this set of equations is given by \( X_i = -\chi_i \), where \( \chi_i \)
consists of the fitted atomic electronegativity \( \text{EN}_i \) which is shifted according to the following expression
\[
\chi_i = \text{EN}_i - \Omega_i.
\] (12)

The molecular EEQ model uses for this shift the square root of a modified error function CN as described in Ref. [1]. Since high coordination numbers can be reached very quickly in a periodic system, artificial polarity reversals can occur. An instructive example is displayed in figure 1, where the polarity between cations and anions within the sodium chloride crystal is reversed (i.e., sodium formally becomes anionic and chlorine cationic). This is an arti-

![Fig. 1 Functional dependence on the sodium partial charge \( q(\text{Na}) \) with increasing CN(\text{Na}) using the molecular EEQ model within the sodium chloride crystal.](image)

fact of the definition of the CN, which depends on the covalent radius \( R_{ij}^{\text{cov}} \) of the respective atom. As a result, the atom with the larger covalent radius also gets a higher CN (here \( R_{\text{Na}}^{\text{cov}} = 3.5 \) Bohr and \( R_{\text{Cl}}^{\text{cov}} = 2.5 \) Bohr) and thus a higher EN shift resulting in non-

physical polarity changes. In order to avoid such artifacts, the procedure is modified for periodic boundary conditions. Here, \( \Omega_i \) is used which includes the global parameter \( \gamma = 8 \) and is given as
\[
\Omega_i = \kappa_i \left( \log \left( \frac{1 + \exp(\gamma)}{1 + \exp(\gamma - \text{CN}_i)} \right) \right)^{1/2}.
\] (13)

This classical charge model requires overall five empirical parameters \( \{U_{ij}, A_{ij}, \text{EN}_i, \kappa_i, R_{ij}^{\text{cov}}\} \) per element and achieves for molecules across the entire periodic table of elements an average deviation of about 0.04 e\(^-\) (0.03 e\(^-\) for organic molecules) with respect to PBE0 based Hirshfeld charges.[1]

By using the definition of the Lagrangian given in equation 11 the analytical charge gradients is derived as
\[
\frac{\partial \mathbf{q}}{\partial \mathbf{R}_j} = A^{-1} \left[ -\frac{\partial (A \cdot \mathbf{q})}{\partial \mathbf{R}_j} + \frac{\partial \mathbf{X}}{\partial \mathbf{R}_j} \right]
\] (14)

where the inverse of the indefinite \((N+1)\) matrix has been ob-


### 1.4 Dispersion energy

The periodic DFT-D4 energy expression is constructed as follows
\[
E_{\text{disp}}^{\text{D4}} = E_{\text{disp}}^{(6,8)} + E_{\text{disp}}^{(9), \text{ATM}}.
\] (15)

The left part of equation 15 corresponds to the pairwise dispersion energy which is given by
\[
E_{\text{disp}}^{(6,8)} = -\frac{1}{2} \sum_i \sum_j \sum_{n=6.8} s_n \frac{C_{ij}^{(n)}}{R_{ij}^{(n)}} f_{\text{damp}}(R_{ij}) \cdot
\] (16)

Here, the primed sum over \( j \) indicates that the case \( i = j \) is omit-
ted for \( T = 0 \). In equation 16, \( s_n \) scales the individual multi-
polar contributions—\( s_6 \) and \( s_8 \) for the dipole–dipole and dipole–quadrupole term—and \( f_{\text{damp}}^{(n)} \) denotes the rational Becke–Johnson (BJ) damping function (denoted as BJ-damping (BJD) in the following) which is used to couple this approach to standard DFAs.

\[
f_{\text{BJD}}^{(n)}(R_{ij}) = \frac{R_{ij}^{(n)}}{R_{ij}^{(n)} + (a_1 R_{ij}^{(n)} + a_2)^{(n)}}
\] (17)

Equation 17 incorporates the DFA-specific parameters \( a_1 \) and \( a_2 \) and the cutoff-radii defined as
\[
R_{0,\text{BJD}}^{ij} = (a_1 R_{0}^{ij} + a_2).
\] (19)

The simplest way to include three-body effects uses the well-
known Axilrod–Teller–Muto63 (ATM) term (cf., right side of equation 15) which is defined as the sum over \( ijk \) energy contributions each defined by
\[
E_{ijk}^{ij} \approx C_{ij}^{jk} \left( 3 \cos \theta_i \cos \theta_j \cos \theta_k + 1 \right) \left( R_{ij} R_{jk} R_{ki} \right)^{3/2}
\] (20)

Here, \( \theta_i, \theta_j, \) and \( \theta_k \) are the internal angles of the triangle formed by \( R_{ij}, R_{jk}, \) and \( R_{ki} \) while \( C_{ij}^{jk} \) is the triple-dipole constant given by
\[
C_{ij}^{jk} \approx \sqrt{C_i^{ij} C_j^{jk} C_k^{ij}}.
\] (21)

The \( C_{ij}^{jk} \) coefficients are derived from \( C_6 \) coefficients which are obtained from charge-neutral atomic polarizabilities (i.e., neutral atoms with \( z_j = Z_j \)). The finally used three-body dispersion energy expression is as follows
\[
E_{\text{disp}}^{(9), \text{ATM}} = -k \sum_i \sum_j \sum_k \sum_{n=6.8} f_{\text{damp}}^{(9)}(R_{ij} R_{k}) E_{ijk}^{9, \text{ATM}}.
\] (22)
where the sum is over all atom triples $ijk$ applied with a zero-
damping scheme proposed by Chai and Head-Gordon\textsuperscript{10}
\begin{align}
  f_{damp}^{(9)}(\bar{R}_{ijk_{\nu}}) = \frac{1}{1 + 6 (\bar{R}_{ijk_{\nu}})^{-16}},
\end{align}

To avoid multiple counting of three-body interactions the factor $k$
is set to $\frac{1}{2}$ if atoms $i$, $j$, $k$ are within the reference cell and to $\frac{1}{4}$
in all other cases. As previously, the primed sum over $j$ indicates
that the case $i = j$ is omitted for $T = 0$, the double primed sum
over $k$ indicates that the case $j = k$ is omitted for $T = T'$ and $i = k$
is omitted for $T = 0$. Equation \textsuperscript{23} includes the averaged inter-
atomic distance
\begin{align}
  \bar{R}_{ijk_{\nu}} = \left( R_{ij} R_{j\nu} R_{\nu k} / R_{0,ij} R_{0,j\nu} R_{0,\nu k} \right)^{1/3},
\end{align}

which incorporates $\rho_{ij\nu}^{(i)jk_{\nu}(k)}$ (cf. equation \textsuperscript{19}). Since dispersion
interactions are much faster decaying (leading order term \(\propto R^{-6}\))
than, e.g., Coulomb interactions we employ for this energy con-
tribution a real-space cutoff within the periodic implementation.
Furthermore, analytical gradients are available for the dispersion
energy expression in equation \textsuperscript{15}.

\subsection{1.5 Theory of the Quasi-harmonic approximation}

In order to account for thermodynamic properties to crystals,
the knowledge of phonon modes is required over the complete first
Brillouin zone (FBZ) of the system. The easiest way to account
for ZPVE contributions include harmonic lattice dynamics where
each k-point in the FBZ is associated with 3M harmonic oscillators
(\textit{i.e.} phonons) which are labeled by a phonon band index
$n \in \{1, \ldots, 3N\}$ and whose energy levels are given by the usual
harmonic expression as
\begin{align}
  e_{m}^{n,k} = \left( m + \frac{1}{2} \right) \omega_{k},
\end{align}

where $m$ is an integer, $\omega_{k} = 2\pi\nu_{k}$, and $N$ is the number of
atoms per primitive cell. The overall vibrational canonical parti-
tion function of a crystal at a given temperature $T$ is given as
\begin{align}
  Q_{vib}(T) &= \prod_{k=1}^{3N} \prod_{m=1}^{\infty} \sum_{n=0}^{\infty} \exp \left( - \frac{e_{m}^{n,k}}{k_{B}T} \right),
\end{align}

where $k_{B}$ is Boltzmann’s constant. From this expression it is
straightforward to obtain harmonic expressions to the internal
green energy given as
\begin{align}
  \delta(T) &= k_{B}T^{2} \left( \frac{\partial \log(Q_{vib})}{\partial T} \right) = \sum_{k} \hbar \omega_{k} \left( \frac{1}{2} + \frac{1}{\exp(\hbar \omega_{k}/k_{B}T) - 1} \right). \tag{27}
\end{align}

However, the harmonic approximation has its limitations like zero
thermal expansion, temperature independence of elastic
constants and bulk modulus, equality of constant-pressure and
constant-volume specific heats, as well as infinite thermal conduc-
tivity and phonon lifetimes.\textsuperscript{11} To overcome such drawbacks,
the simplest way includes quasi-harmonic quantities in the sense
of the quasi-harmonic approximation (QHA).\textsuperscript{12,13} According to

\begin{align}
  F_{QHA}(T, V) &= U_{0}(V) + F_{vib}^{QHA}(T, V), \tag{28}
\end{align}

where $U_{0}(V)$ is the zero-temperature internal energy of the crystal
without any vibrational contribution (similar to volume con-
strained geometry optimizations) and the vibrational part is given
by
\begin{align}
  F_{vib}^{QHA}(T, V) &= \sum_{k} \hbar \omega_{k}(V) + k_{B}T \left[ \ln \left( 1 - \exp \left( - \frac{\hbar \omega_{k}(V)}{k_{B}T} \right) \right) \right], \tag{29}
\end{align}

where the first part refers to the zero-point energy of the system. The
equilibrium volume at a given temperature $T$ is obtained by
minimizing $F_{QHA}(T, V)$ with respect to volume $V$ while keeping $T$
constant.

\subsection{1.6 Technical details}

All molecular dynamic dipole polarizabilities $\alpha(\iota,a)$ were cal-
culated using time-dependent density functional theory (TD-
DFT).\textsuperscript{16,17} A variant of the PBE0 hybrid functional was used,
with a Fock-exchange admixture of 37.5% (dubbed PBE38). This
method has already proved its accuracy and robustness in previous
works.\textsuperscript{18,19} The atomic orbital (AO) basis sets used in the
TD-DFT calculations are of def2-QZVPP\textsuperscript{20,21} quality closely
representing the complete basis set (CBS) limit for this prop-
erty. The following ECPs are used: ecp-2-sdf (unpublished,
Stuttgart group) covering 2 core electrons, ecp-10-sdf (unpub-
lished, Stuttgart group) covering 10 core electrons, ecp-18-sdf
(unpublished, Stuttgart group) covering 18 core electrons, ecp-
36-sdf (unpublished, Stuttgart group) covering 36 core electrons,
ecp-54-sdf (unpublished, Stuttgart group) covering 54 core electrons,
ecp-60-sdf (unpublished, Stuttgart group) covering 60 core electrons,
ecp-54-sdf (unpublished, Stuttgart group) covering 54 core electrons,
ecp-54-sdf (unpublished, Stuttgart group) covering 54 core electrons,
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ecp-60-sdf (unpublished, Stuttgart group) covering 60 core electrons,
ecp-60-sdf (unpublished, Stuttgart group) covering 60 core electrons,
sdf; for d-block elements we used: Sc/ecp-10-mdtf, Y/ecp-28-mwf, for halogen we applied Cl/ecp-10-sdf and F/ecp-2-sdf and for oxygen we applied O/ecp-2-sdf).

1.7 Computational details

1.7.0.1 BJ-damping parameter For consistency we add the BJ-damping parameter that are used in this work.

**Table 1** Applied BJ-damping parameter of different DFAs as extracted from Ref. [1]

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<th>$a_1$</th>
<th>$a_2$</th>
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1.7.0.2 X23: Solid state volumina For the determination of the 23 molecular crystal structure volumes we applied the VASP 6.0.8 software package. All PBE PAW calculations used an 800eV plane-wave cutoff (convergence criteria: energy difference $\propto 10^{-6}$). The DFT conjugated gradient method has been used within the optimization where all atomic positions and the cell has been relaxed. For all calculations standard pseudopotentials have been used.

1.7.0.3 ICE10: QHA calculations Quasi-harmonic approximation calculations have been performed for eight different ice polymorphs. For this purpose the QHA implementation within the CRYSTAL17 code has been applied in combination with HSE-3c. Here, four different volumina have been used (steps of 2.5%) for which overall ten different temperatures have been applied (ranging from 10 K to 100 K applying 10 K steps). $V_0$ has been extracted from Helmholtz free energy calculations at a pressure of 0 GPa.

1.7.0.4 Timings for the cyclohexanedione crystal A self-consistent field (SCF) calculation has been performed for the cyclohexanedione crystal using the PBE/800eV setup in VASP 6.0.8 (convergence criteria: energy difference $\propto 10^{-6}$). The converged wave function has been used to determine the pure timing arising from each dispersion correction. For SCAN-rVV10 and vdW-DF2 we applied an PW cutoff of 800eV. For all calculations standard pseudopotentials have been used.

1.7.0.5 Salt polarizabilities Salt polarizabilities have been calculated for several alkalai halides. For D3 and D4 we use polarizabilities from the DFTD3 and DFTD4 standalone programs. For other dispersion corrections we have calculated polarizabilities using VASP 6.0.8 with a PBE/800eV setup using standard pseudopotentials.

2 References

Notes and references

