# Multimode Propellant Discovery: A Computational High-throughput Screening Paradigm

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The emergence of multimode propulsion (MMP) architectures in in-space propulsion shows great promise for improving the future of spacecraft mission design. However, seeking an ideal propellant requires traversing a complex chemical design space that satisfies optimal chemical and electric propulsion requirements. To this end, we propose a computational, high-throughput screening framework founded upon software developed by the Materials Project and accurate, polarizable molecular dynamics (MD) force fields to discover new MMP propellants. We highlight the metric space within the scope of this framework and present a case study of a candidate ionic liquid propellant mixture composed of HAN and HEHN to inform important paths for the future.

## I. Introduction

Tuning chemical structure for target engineering applications presents a complex, high-dimensional problem. Moreover, unlike smooth, convex optimization spaces, the chemical design space consists of discrete inputs (e.g., add/remove  $CH_2$  group) that translate nonlinearly to desired outputs (e.g., thermophysical properties). Consequently, the time required to discover materials with desirable properties through trialand-error greatly hinders technology development cycles. To this end, a number of research communities have implemented high-throughput screening (HTS) protocols to automate rapid evaluation of candidate

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materials. For instance, modern HTS methods for drug design can screen  $10^4 - 10^5$  compounds per week to identify "hits", or compounds of biological relevance.<sup>1–4</sup>

Despite the success of wet lab-based screening (e.g. autonomous experimentation), synthesis and replicating complex testing conditions are time and cost intensive. Thus, the advent of *in silico* HTS has greatly accelerated material discovery for lithium-ion battery cathodes, <sup>5-9</sup> hydrogen storage, <sup>10-16</sup> carbon capture, <sup>17-21</sup> and dielectric materials.<sup>22</sup> In 2011, the Materials Genome Initiative (MGI) for Global Competitiveness<sup>23</sup> made evident this need for deploying novel materials "at least twice as fast [and] at a fraction of the cost" through integrated computational tools.<sup>24</sup> One successful component of the MGI is the Materials Project<sup>25</sup> (www.materialsproject.org), an open-source, collaborative, and multi-institutional database composed of first-principles-based structural and energetic property calculations for over 150,000 solid-state materials, i.e., the "Google of material properties".<sup>26</sup> The Materials Project can be accessed by a user-friendly website or programmatically via an API and is supported by an extensive software ecosystem for organizing, executing, and analyzing high-throughput simulations of materials properties. Recent high-profile forays into materials science by large tech companies have built on the Materials Project stack. The pervasive impact of the Materials Project has led to novel machine learning methods,<sup>27</sup> modular, user-friendly software packages,<sup>28-30</sup> and accelerated innovation and technological development across scientific domains.<sup>31,32</sup>

In this paper, we leverage the successes of the Materials Project and the advancements in computational HTS methods to introduce a streamlined framework for identifying novel propellants for in-space propulsion applications. Historically, in-space propulsion has kept chemical and electric propulsion modes separate, resulting in a concomitant separation between the highest performing chemical and electric propellants. On one hand, high-thrust chemical propulsion systems require highly exothermic propellants that exhibit hypergolic properties and compatibility with heterogeneous catalysts, and hence are typically nitrogen or alcohol-rich compounds (e.g., hydrazine,  $N_2H_4$ ).<sup>33–35</sup> On the other hand, electric propulsion has relied on inert gases like xenon, krypton, or argon for propellants due to their low ionization energies and high atomic mass.<sup>36,37</sup> Despite this contrast, recent progress in propellant chemistry and thruster architectures has enabled the emergence of multimode propulsion (MMP) concepts, in which combined chemical-electric systems share propellant and/or thruster hardware.<sup>38</sup> As outlined by Rovey et al.,<sup>38</sup> the MMP paradigm extends the operating envelope of numerous space mission concepts in their "flexibility, adaptability, and responsiveness" while reducing dry mass cost through shared propulsion resources.

The primary research challenge with MMP technologies is the competing trade-offs between chemical and electric propulsion propellants, let alone the complexities involved in their individual trade-spaces irrespective of MMP. Concretely, of the number of candidate MMP propellants explored, herein we focus on a promising category of materials, ionic liquids (ILs), which have already shown spaceflight heritage in chemical and electric propulsion systems independently.<sup>39–41</sup> ILs are room temperature organic salts composed of cation-anion pairs that exhibit desirable properties (e.g., low vapor pressures,<sup>42</sup> high thermal stabilities,<sup>43</sup> high ionic conductivities,<sup>44</sup> low toxicity<sup>45</sup>) for propulsion. Seeking an ideal MMP propellant, however, is obstructed by the immense chemical space of ILs: cation and anion combinations can yield up to 10<sup>6</sup> possible ILs. Thus, traversing the vast compositional space for the design and discovery of novel MMP propellants is ripe for novel and advanced computational approaches.

With this motivation in mind, the objective of this work is to reduce the chemical design space of IL MMP propellants by proposing a robust, computational framework to accurately quantify key thermophysical parameters via first-principles calculations. To this end, the paper is outlined in three main sections. In Section II, we discuss the valuable insights learned from past chemical, electric, and multimode propulsion studies to develop design principles and guide property calculations of interest. Then, in Section III, we outline the novel, computational HTS framework composed of the software stack drawn from the Materials Project and molecular dynamics (MD) simulation methods. Finally, in Section IV we share results of a case study for a set of binary protic ionic liquid (PIL) mixtures to highlight the insights and future opportunities with such a computational paradigm. We emphasize the motivation of this work exists at the intersection of MMP technology development and fundamental IL science exploration. Computational high-throughput screening of ILs will impact fields beyond electric and in-space propulsion, as ILs are readily used as battery electrolytes,  $^{46-49}$  in water desalination,  $^{50}$  and even in carbon capture.

## II. Related Work

## A. Key Multimode Performance Parameters

We begin this section by reviewing the multimode rocket equation introduced in previous studies by Berg,<sup>52,53</sup> Donius,<sup>54,55</sup> and Rovey et al.<sup>38</sup> Given the separate nature of chemical and electric propulsion (CP and EP, respectively) modes, the "EP fraction",  $f_{EP}$ , is commonly defined as shown in Equation 1:

$$f_{EP} = \frac{\Delta V_{elec}}{\Delta V},\tag{1}$$

where the EP mode contribution towards the total delta-V is quantified. Consequently, the multimode rocket equation  $^{38,52-55}$  is defined by Equation 2,

$$\frac{n_f}{n_o} = e^{-(\Delta V/I_{sp,mm}g_o)} \tag{2}$$

where the initial and final mass is  $m_o$  and  $m_f$ , respectively, and the effective multimode specific impulse is

$$I_{sp,mm} = \left[\frac{1 - f_{EP}}{I_{sp,chem}} + \frac{f_{EP}}{\eta_v I_{sp,elec}}\right]^{-1},\tag{3}$$

where the chemical and electric specific impulse are given by  $I_{sp,chem}$  and  $I_{sp,elec}$ , respectively, and "mission planning efficiency" is  $\eta_v$ , for which typical Earth orbiting missions, these values range from 0.45 to 0.65.<sup>38,56,57</sup> The coupling of optimal electric propulsion specific impulse with chemical mode specific impulse has been previously discussed;<sup>53,56</sup> nonetheless, Equation 3 highlights holistically how multimode performance is inherently linked to propellant properties. Concretely, by linking (to reduced order) specific impulse and exhaust velocity ( $u_e = I_{sp}g_o$ ), CP performance can be evaluated by neglecting pressure thrust and assuming isentropic expansion, resulting in Equation 4,

$$I_{sp,chem} = \sqrt{2g_o \frac{\bar{R}}{\bar{M}} \frac{\gamma}{\gamma - 1} T_o \left[ 1 - \left(\frac{p_e}{p_o}\right)^{\frac{\gamma - 1}{\gamma}} \right]},\tag{4}$$

where  $\bar{R}$  is the universal gas constant,  $\gamma$  is the specific heat ratio,  $\bar{M}$  is the ejected propellant species, molecular weight,  $T_o$  is the combustion chamber temperature, and  $p_o$  and  $p_e$  are combustion chamber and exit pressures. In contrast, most state-of-the-art EP systems use electrostatic acceleration of charged particles based on the electric potential energy of the power source, resulting in Equation 5

$$I_{sp,elec} = \frac{1}{g_o} \sqrt{2V_B \frac{q}{m_i}},\tag{5}$$

where  $V_B$  is the beam voltage, and  $q/m_i$  is the charge-to-mass ratio of some particle *i*. In the case of electrospray thrusters, an exemplary ionic liquid-based EP system, the charge-to-mass ratio is ubiquitously linked to the emitted current,  $I_{em}$ , which has been shown to be theoretically and experimentally linked to physical liquid properties by the proportionality in Equation 6:

$$\frac{q}{m_i} \propto \frac{I_{em}}{\rho Q} \propto \frac{1}{\rho} \sqrt{\frac{\gamma K}{\epsilon Q}},\tag{6}$$

where propellant density,  $\rho$ , surface tension,  $\gamma$ , electrical conductivity, K, dielectric constant,  $\epsilon$ , and flow rate, Q, contribute to the overall EP performance. The implications of Equations 4-6 are clear: the liquid properties that contribute to MMP performance differ fundamentally between modes, where  $I_{sp,chem}$  depends on chemical potential energy while  $I_{sp,elec}$  depends on bulk-phase static, electrical, and transport properties.

#### B. Candidate Ionic Liquid MMP Propellants

Unsurprisingly, insights from Section II.A have led to a natural demarcation in the nature of ionic liquid propellants for either chemical or electric propulsion applications. For instance, ILs used successfully in CP systems are often categorically energetic ILs (EILs) due to their high heats of combustion, hypergolic behavior, relatively high thermal stability, low toxicity, and low vapor pressures.<sup>63</sup> Accordingly, many examples of EIL compounds are characteristically nitrogen rich, where azide, dinitramide, dicyanamide, and

nitrocyanamide and ammonium, aminotriazole, and aminotetrazole are all examples of anions and cations, respectively.<sup>64-66,66-70,70-73</sup> CP propellant blends, or mixtures, include other constituents that ultimately tune performance-driving properties. These include, for instance, ammonium dinitramide (ADN)-based monopropellants like FLP-106<sup>74</sup> and LMP-103S<sup>75</sup> and hydroxylammonium nitrate (HAN)-based formulas like AF-M315E<sup>76</sup> and SHP163.<sup>39</sup> In parallel, the development of electric propulsion systems, like electrospray thrusters, depend on highly mobile and structurally compact cation/anion pairs. Hence, significant research has been done for [EMIM][BF4],<sup>77</sup> [EMIM][TFSI],<sup>78</sup> [BMIM][DCA],<sup>79</sup> and other similar ILs. While chemical and electric propellants fundamentally differ, a number of studies have begin char-

While chemical and electric propellants fundamentally differ, a number of studies have begun characterizing combinations of the two. For example, such mixtures include  $[\text{EMIM}][\text{EtSO}_4][\text{HAN}]^{80-82}$  and  $[\text{EMIM}][\text{EtSO}_4][\text{AN}]$ ,<sup>81</sup> in which the linear burn rate, synthesis procedures, and catalytic compability were assessed. While other HAN-based mixtures have also been explored,<sup>83,84</sup> the general availability of fundamental studies of relevant systems is relatively unexplored. Nonetheless, across the literature, it is clear that mixture chemistry presents added bulk-phase complexity that is not easily rationalized by individual components.<sup>85</sup> Furthermore, solubility and phase behavior is often a rather subtle balance of hydrophilic and hydrophobic domains present in the IL, resulting in the reportedly non-intuitive mixing behavior among many "double salt ILs" (DSILs).<sup>86</sup> Thus, these previous insights further substantiate the importance of high-throughput simulation methods to support experimental campaigns to better understand design principles for MMP propellants.

## III. Approach: Computational High-throughput Screening

#### A. First-principles-based Computational Methods

#### 1. Molecular Dynamics and Force Field Selection

The overall high-throughput screening framework relies on the use of accurate, first-principles-based molecular dynamics (MD) simulations. Unlike the current Materials Project database, where solid-state properties are computed using density functional theory (DFT) calculations, the desired bulk-phase, liquid properties in this work demand extensive statistical sampling and hundreds to thousands of molecules in each simulation to properly obtain short- and long-range behavior. To this end, we use modern MD practices within the overarching framework.

The crux of any MD simulation is in the force field, or the functional form that characterizes the interatomic potential. Classical MD force fields account for bonded (i.e., bonds, angles, dihedrals) and nonbonded (i.e., 12-6 Lennard Jones and Coulomb potentials) terms via a series of empirical or first-principles-based parameters. We highlight that for ILs, force field selection is a significant challenge given the complex behavior of charged molecules in a condensed-phase system. For the purposes of this computational framework, we approach force field selection with two prominent categories in mind: polarizable and nonpolarizable force fields.

We emphasize that the workflow proposed offers modular and interchangeability between available force fields. Previous nonpolarizable force fields used for ILs include OPLS-AA,<sup>87</sup> AMBER,<sup>88</sup> and recently, machine learning-based force fields like espaloma.<sup>89</sup> While a number of thermophysical properties have been accurately reproduced via nonpolarizable force fields, we emphasize the need for polarizable force fields like APPLE&P,<sup>90</sup> CL&Pol,<sup>91,92</sup> or SAPT-FF,<sup>93</sup> in which the molecular response to local electric fields is explicitly modeled through induced atomic dipoles. Based on significant literature,<sup>94</sup> nonpolarizable force fields systematically miss a number of key static and transport properties crucial for the proposed metric space in this work. The inconsistent macroscopic properties predicted by nonpolarizable force fields is rigorously explained by the requirement that ionic liquids, being electrolytes, satisfy electroneutrality and screening conditions.<sup>95</sup> Electroneutrality requires the following constraint on the ion-ion, radial distribution functions

$$\sum_{\mu} \int_0^\infty 4\pi r^2 \rho_{\mu} q_{\mu} g_{\nu\mu}(r) d\mathbf{r} = -q_{\nu} \tag{7}$$

where  $\mu$  and  $\nu$  are cations or anions, and  $g_{\nu\mu}(r)$  is the ion-ion radial distribution function (RDF). In essence, Equation 7 illustrates that a tagged ion must be surrounded by an equal and opposite "charge cloud" to ensure electroneutrality.

Also, being an electrolyte, the ionic liquid is expected to exhibit perfect electrostatic screening, at least in

the asymptotic limit. This condition is quantified by the asymptotic requirement of the dielectric response, which in Fourier-space is  $\lim_{k\to\infty}\epsilon(k)^{-1}=0$ . This behavior is analogous to perfect conductors (e.g. metals) that screen electric fields instantaneously, usually quantified by  $\epsilon^{-1}=0$  without a lengthscale specification. Utilizing statistical mechanical linear response theory, this screening requirement is translated to conditions imposed on the pairwise correlation functions of the ionic liquid, or their Fourier space analogues, structure factors. These screening requirements are known as the second-moment Stillinger-Lovett sum rule or "perfect screening condition"  $^{96-101}$ , which takes the general form

$$\frac{4\pi}{k_B T} \lim_{|\mathbf{k}| \to 0} \frac{S_{zz}(\mathbf{k})}{\mathbf{k}^2} = 1 - \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty}},\tag{8}$$

where  $\epsilon_{\infty}$  is the infinite frequency dielectric response.  $S_{zz}$  is the charge-correlation structure factor,

$$S_{zz}(\mathbf{k}) = \frac{1}{V} \langle \hat{\rho}_Z(\mathbf{k}) \hat{\rho}_Z(-\mathbf{k}) \rangle, \tag{9}$$

where  $\langle \cdots \rangle$  denotes an ensemble average, **k** is the wavevector, and

$$\hat{\rho}_Z(\mathbf{k}) = \sum_{i=1}^N q_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \tag{10}$$

is the Fourier component of the microscopic charge density, where  $q_i$  is the partial atomic charge,  $\mathbf{r}_i$  is the position of the atom *i*, and *N* is the total number of atoms in the system.

It is expected that ionic liquids and electrolytes at equilibrium should obey Equation 8, at least away from a phase transition or critical point. The interpretation of  $S_{zz}$  is instrumental to understanding ILs: the Coulomb interaction length-scales that govern bulk-phase arrangement of ions are directly quantified by the charge correlation structure factor. The key difference in simulations of polarizable and non-polarizable force fields is the right hand side of Equation 8, since polarizable force fields have  $\epsilon_{\infty} \neq 1$  while non-polarizable force fields have  $\epsilon_{\infty} = 1$ . McDaniel and Yethiraj have shown that the differences in this fundamental limit on the structure factors propagates to substantial deviations in ion structuring, on both sub-nanometer and nanometer lengthscales as predicted by polarizable vs non-polarizable force fields.<sup>102</sup> Thus for simulations of ionic liquids, correct prediction of  $S_{zz}$  and its asymptotic limit are instrumental to the force field's predictive capability of macroscopic and transport properties.<sup>94, 102</sup> We will later comment on the importance of  $S_{zz}$ in understanding relevant solvation and miscibility behavior in ionic liquids.

#### B. Software Pipeline and Infrastructure

#### 1. Materials Project Software Stack and Base Libraries

Running high-throughput simulations requires setting up diverse sets of simulations, managing their execution on high performance computers (HPC), and analyzing and organizing the simulation output. The Materials Project stack provides a sophisticated framework for managing these high-throughput campaigns, which can quickly become messy and burdensome when run on the scale of tens or hundreds of thousands of simulations. For example, running a molecular dynamics simulation requires assembling a set of force field parameters, synthesizing them into a single input file, using Packmol<sup>103</sup> to generate an initial configuration, executing the job on HPC, and running analysis scripts. Traditionally, each step would be performed manually, at best linked together by bespoke analysis scripts, essentially precluding high-throughput approaches. For this reason, MD has acquired a reputation for being difficult, time-consuming, and tedious. Instead, implemented in the Materials Project stack, ~80 lines of Python code can execute the end-to-end MD workflow.

## 2. Basic Input and Output Operation

Pymatgen<sup>28</sup> and Atomate2,<sup>30</sup> building on the Open Force Field stack,<sup>104</sup> implement utilities for configuring molecular dynamics systems from simple user inputs. The minimal input is a Python dictionary specifying the structure (as a SMILES string) and count for each molecule. Users can select the force field, partial charges, initial geometries, and metadata as needed. Atomate2 evolves the system in OpenMM<sup>105</sup> with pre-set and custom workflows while tracking the trajectory and state. Here, the user can configure various simulation parameters such as temperature, pressure, time step, etc. While running, the positions of all

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Figure 1: Overarching computational high-throughput screening framework

atoms in the system are recorded in a trajectory file (by default, a '.dcd') along with other state variables such as the system energy, volume, and pressure. Emmet automatically calculates a wide variety of properties from the system output using MDAnalysis<sup>106</sup> and SolvationAnalysis.<sup>107</sup> Users can easily upload these to a MongoDB database for easy querying, access, and sharing. The full workflow is detailed in Figure 1. Each package is designed to be extensible for new simulations, new workflows, and new analyses.

## C. Defining Metrics

In this section, we highlight the utility of MD as a method to accumulate important properties of IL shortand long-range structure, electrostatics, and dynamics. It is important to note that classical MD simulations report equilibrium properties and cannot directly quantify energetic properties like ignition time delays or enthalpies of combustion. Moreover, from a material discovery standpoint, hypergolic behavior is notably difficult to predict.<sup>108</sup> However, as will be shown in Section IV (*vida infra*), hydrogen bonding behavior can be characterized by the following structural analyses, a primary indicator of proton transfer reactions relevant in protic ILs (PILs).<sup>109–111</sup>

To this end, we aim to acquire a database of simulated properties for a range of IL mixtures with varying concentrations and temperature conditions. For instance, typical MD simulations calculate time-averaged properties to characterize local and long-range structure. These include radial distribution functions (RDFs), g(r), which provides the average number density of particles around a reference as a function of radial position. The coordination number, N(r), is proportional to the integral of the g(r) by Equation 11

$$N(r) = \int_0^r 4\pi \tilde{r}^2 \hat{\rho} g(\tilde{r}) d\tilde{r}, \qquad (11)$$

where  $\hat{\rho} = N/V$  is the average number density of the observed atom (in Å<sup>-3</sup>). The g(r) provides detailed information of pairwise correlations that compliment experimental X-ray or neutron scattering structure factors, which can also be computed via MD simulations.<sup>102</sup> Similar distribution functions that quantify

conformation diversity or angular arrangement near coordination sites can be acquired by dihedral and angular distribution functions, (ADFs and DDFs), respectively.

Along with structural properties, thermophysical, electrostatic, and transport properties are also of significant interest for MMP performance evaluation. Unlike molecular solvents, ILs have large liquid cohesive energies due to strong Coulombic interactions between cation/anion pairs, giving rise to their unique thermophysical and transport properties. The liquid cohesive energy,  $E_{coh}$  can be computed by Equation 12

$$E_{cohesive}(T) = \frac{1}{N_{ionpair}} E_{liquid}(T) - E_{cation}(T) - E_{anion}(T).$$
(12)

While  $E_{coh}$  cannot be determined experimentally due to the challenge of gas phase ion binding, enthalpy of vaporization can be computed by Equation 13,

$$\Delta H_{vap}(T) = \frac{1}{N_{ionpair}} \left[ E_{vapor}(T) - E_{liquid}(T) \right] + RT.$$
(13)

The charge correlation structure factor  $S_{zz}$  provides rigorous characterization of the electrical properties of the ionic liquid. Analysis of  $S_{zz}(k)$  (and its dynamic analogue,  $S_{zz}(k,t)^{95}$ ) provides information on electrostatic screening,<sup>102</sup> solvation behavior,<sup>112</sup> and miscibility.<sup>113</sup> For instance, McDaniel and Verma<sup>113</sup> show that the  $S_{zz}$  of *pure* ILs can unambiguously classify them into hydrophobic and hydrophilic categories based on signatures in the ~1 Å<sup>-1</sup> wavevector region.

Furthermore, transport properties are also made accessible by MD simulations. The Einstein relation for the self-diffusion coefficient is given by Equation 14

$$D_s = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle \left| \bar{r}(t) - \bar{r}(0) \right|^2 \rangle, \tag{14}$$

where the bracketed quantity is the mean squared displacement (MSD). The diffusion-viscosity relationship is often related by the Stokes-Einstein equation that yields the proportionality,  $D_s \propto T/\eta$ , where  $\eta$  is the bulk viscosity. The shear viscosity can be computed via MD simulations directly, however, and is given as a function of the elements of the pressure tensor,  $P_{\alpha\beta}$ ,<sup>114</sup>

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle, \tag{15}$$

where  $k_B$  is the Boltzmann constant, T is the temperature, and V is the system volume. Similarly, the total ionic conductivity is defined by Equation 16,<sup>115</sup>

$$\sigma = \lim_{t \to \infty} \frac{1}{6tVk_BT} \sum_{i,j}^{n} \langle (q_i[r_i(t) - r_i(0)]) \cdot (q_j[r_j(t) - r_j(0)]) \rangle,$$
(16)

where charges q and positions r are used to sum over all combinations of cations, i, and anions, j. Moreover, the total ion conductivity in Equation 16 can be decomposed to capture correlations in the motion of species i and j by the self ( $\alpha = \beta$ ) and distinct ( $\alpha \neq \beta$ ) terms in Equation 17,

$$\sigma^{\alpha\beta} = \lim_{t \to \infty} \frac{1}{6tVk_BT} \left\langle \sum_{i \in \alpha} \left( q_i [r_i(t) - r_i(0)] \right) \cdot \sum_{j \in \beta} \left( q_j [r_j(t) - r_j(0)] \right) \right\rangle.$$
(17)

In summary, the MMP propellant property predictions within the scope of this work are provided below:

- 1. Characterization of Local Structure
  - radial distribution function (RDF), g(r)
  - running coordination numbers, N(r)
  - angular distribution function (ADF)
  - dihedral distribution function (DDF)
  - X-ray and neutron scattering structure factors

- 2. Static and Transport Properties
  - density,  $\rho$
  - liquid cohesive energy,  $E_{coh}$
  - enthalpy of vaporization,  $\Delta H_{vap}$

  - self-diffusion coefficients,  $D, D_+, D_-$
  - viscosity,  $\eta$
  - conductivity,  $\sigma$

# IV. A Case Study: Binary [HAN][HEHN] Mixtures

Herein, we present a case study based on our work in Parmar et al.<sup>116</sup> to showcase a series of exemplary results representative of that sought after in our overarching, high-throughput framework. In particular, we investigate mixtures of two, task-specific ILs, HAN ( $NH_3OH^+ \cdot NO_3^-$ ) and HEHN ( $HOCH_2CH_2N_2H_4^+ \cdot NO_3^-$ ); in a propellant blend, HAN and HEHN compliment each other as an ionic oxidizer and fuel, respectively. For computational methods and verification, we refer the reader to Parmar et al.<sup>116</sup> As shown in Figure 2, four [HAN][HEHN] systems at 25, 50, and 75% HAN by weight and neat HEHN for comparison were simulated using polarizable MD. Each simulation cell has a length of ~30 – 40 Å.



Figure 2: Equilibrium snapshots of bulk-phase [HAN][HEHN] liquid mixtures with varying mole fractions,  $\chi$ , of [HAN]. Red, blue, and green colored molecules correspond to hydroxyethylhydrazinium cation (HEH<sup>+</sup>), nitrate anion (NO<sub>3</sub><sup>-</sup>), and hydroxylammonium cation (HA<sup>+</sup>), respectively.

#### A. [HAN][HEHN] Density and Mixture Compatibility

Among the properties studied, density and excess molar volumes as a function of mole fraction are discussed first, as shown in Figure 3. As shown in Eq. 18,  $V_m^E$  is effectively the difference in the actual mixture molar volume and the individual constituent molar volumes,

$$V_m^E = \frac{\chi_{\text{HAN}} M_{\text{HAN}} + \chi_{\text{HEHN}} M_{\text{HEHN}}}{\rho_{[\text{HAN}][\text{HEHN}]}} - \frac{\chi_{\text{HAN}} M_{\text{HAN}}}{\rho_{\text{HAN}}} - \frac{\chi_{\text{HEHN}} M_{\text{HEHN}}}{\rho_{\text{HEHN}}},\tag{18}$$

where  $\chi$ , M, and  $\rho$  are the mole fractions, molar masses, and densities of the constituents in the subscripts, respectively.<sup>86</sup> As expected, the density as a function of mole fraction,  $\rho(\chi)$ , displays an inverse relationship with increasing  $\chi_{\text{HEHN}}$ ; or rather, at larger values of  $\chi_{\text{HAN}}$ , the system experiences stronger cation-anion Coulombic attraction given the compact, polar nature of the HA<sup>+</sup> cation. As a result, introducing HAN into the mixture can effectively increase the density by up to ~20%. We highlight that, while density predictions from classical MD are typically ancillary, in the context of MMP propellant assessment, they have significant implications from a performance standpoint. For instance, as addressed by Freudenmann and Ciezki,<sup>117</sup> AF-M315E—a propellant blend predominantly composed of HAN, HEHN, and water—outperforms hydrazine in its density specific impulse by ~50%. Through Figure 3a, this is directly rationalized by MD simulations: the compact HA<sup>+</sup> and the bulky HEH<sup>+</sup> cations compliment each other structurally, ultimately enabling a relatively stable, condensed-phase mixture at varied concentrations. Nonetheless, Figure 3a highlights how  $\rho(\chi)$  is nonlinear and that to tune a single performance parameter like  $\rho I_{sp}$  requires a subtle balance of molecular components.

Moreover, an *a priori* estimation of [HAN][HEHN] miscibility would suggest that, given both species are polar, mixtures therein should be compatible; Figure 3b suggests otherwise. The relatively large and positive excess molar volumes indicate that certain concentration regimes may undergo non-ideal mixing behavior, such as phase separation. Similar studies of excess molar volumes of ILs attribute non-idealities to the substantial difference in molecular weight and volume of the uncommon ion (i.e.,  $34.04 \text{ g mol}^{-1}$  for HA<sup>+</sup> vs.  $77.11 \text{ g mol}^{-1}$  for HEH<sup>+</sup>).<sup>118,119</sup> Evidently, the relationship between concentration and phase behavior is complex. Thus, we highlight the importance of both high-throughput software infrastructure and available experimental data to support exploration of a wider range of mixtures beyond simple, binary systems.



Figure 3: (3a) Simulation results for density as a function of HEHN and HAN mole fraction at room temperature (the 50 – 50% [HAN][HEHN] was conducted at 293 K to match the experimental measurement while every other "room temperature" calculation was at 298 K). Density of pure HAN ( $\chi_{\text{HEHN}} = 0.0$ ) is based on an experimental reference value of  $1.68 \text{ g cm}^{-3}$  for anhydrous HAN,<sup>120</sup> for which no temperature value was reported but is expected to be near the HAN melting point, 44–48 °C.<sup>121</sup> 3b) Calculated excess molar volume of [HAN][HEHN] mixture. Experimental comparison includes three-ion DSIL mixtures of 1-ethyl-3-methyl-imidazolium (EMIM) cations with ethylsulfate (EtSO<sub>4</sub>) and bis(trifluoromethylsulfonyl)imide (TFSI), EMIM with tetrafluoroborate (BF<sub>4</sub>) and TFSI, and nitrate anions (NO<sub>3</sub>) with ethylammonium (N<sub>0022</sub>) cations. Associated Redlich-Kister curve fits as a function of mole fraction are provided for systems with sufficient data points (dashed lines).

#### B. Fundamental Electrostatic and Transport Behavior

It is well known that ions in ILs and electrolytes more generally arrange based on either hard-packing or electrostatic screening.<sup>95</sup> The charge-neutrality sum rule introduced in Equation 8 indicates that in the limit as  $r \to \infty$ , the sum of the charge for a given species should approach unity, i.e.,  $|-q_{sum}^{\nu}| = 1$ . Figure 4a shows this behavior, where the cation and anion species result in charge oscillations up to 15 Å for both the neat HEHN and the 50 – 50% [HAN][HEHN] systems. These charge oscillations are macroscopically indicative of concentric spheres of alternating charge that determine the long-range liquid behavior. In the case of neat HEHN, the HEH<sup>+</sup> introduces charge delocalization that manifests in its increased length-scale of  $q_{sum}^{HEH^+}$  (red curves) relative to  $q_{sum}^{HA^+}$  (green curves).

The power of analyzing ILs through Figure 4a is highlighted by its connection to transport properties, like the self-diffusion coefficient introduced in Equation 14,  $D_s$ , and shown in Figure 4b. As Roy et al.<sup>122</sup> describe, the anti-correlated charge oscillations along with the strong cohesive energies of ILs result in a "disordered lattice" behavior of the bulk-phase; macroscopically, this results in relatively small self-diffusion

coefficients on the order of  $10^{-13} - 10^{-10}$ ; compared to literature values of common ILs, this is relatively small.<sup>123,124</sup> While limited experimental data is available for [HAN][HEHN] mixtures, the small self-diffusion coefficients are supported by the remarkably high viscosities of similar liquids, i.e., 147 cP for 2-HEH (2-hydroxyethylhydrazine).<sup>125</sup> As will be further discussed in Section C, the slow dynamics and low ion mobility present in bulk-phase [HAN][HEHN] is connected to the Coulombic interactions characterized by strong hydrogen bonds.



Figure 4: (4a) Charge oscillations (Eq. 7) in a neat HEHN (solid lines) and 50 - 50% [HAN][HEHN] (dashed lines) system. (4b) Self-diffusion coefficients calculated for each species in comparison to Gutowski et al.<sup>126</sup>

#### C. Behavior of Hydrogen Bonding

Finally, we present the importance of hydrogen bonding elucidated by simulation results. While extensive discussion is provided in Parmar et al.,<sup>116</sup> here we summarize the implications of numerous distribution functions (i.e., radial, angular, spatial) on the protic nature of HEHN and [HAN][HEHN] systems. Figures 5a and 5b show combined distribution functions (CDFs) in which the x- and y-axes are radial and angular distribution functions (ADFs and RDFs), respectively. The RDFs show average coordination distances below 2.0 Å of the HEH<sup>+</sup> amine (5a) and hydroxyl (5b) hydrogen with the nitrate oxygen; the ADFs show the hydrogen bond angle between ~ 150 and 180° of the O…H…N (5a) or O…H…O (5b) coordination sites. The CDFs largely convey the geometric conditions of hydrogen bonding, or a "point along the proton transfer coordinate."<sup>127</sup> The dense, red region in the top left corner of the CDFs suggest that relative to previously reported hydrogen bonds, the strength and linear directionality can be classified as "moderately" strong "ionic" bonds.<sup>127,128</sup> The spatial distribution function (SDF) in Figure 5c shows ocean blue isosurfaces of dense regions where the nitrate anion's oxygen atoms coordinate: the amine and hydroxyl coordination sites.

Figure 5 provides holistic information regarding the inherent, thermal decomposition behavior expected in combustion environments. The complex chemical kinetics related to HAN and HEHN have been hardly studied. However, the first step in the decomposition mechanism for HAN and HEHN are Eqs. 19 and 20, respectively:<sup>129,130</sup>

$$NH_3OH^+ + NO_3^- \longrightarrow NH_2OH + HNO_3$$
 (19)

$$\text{HEHN} \longrightarrow \text{HEH} + \text{HNO}_3 \tag{20}$$

While preliminary neutral, gas-phase insights may qualitatively connect classical MD results to thermal decomposition pathways,<sup>131–135</sup> it is apparent that a high-throughput infrastructure will enable exploration of a wider range of concentrations and mixtures to understand what factors enhance or suppress hydrogen bonding.



Figure 5: (5a and 5b) Combined distribution functions (CDFs) of O···H RDFs and O···H···N (5a) or O···H···O (5b) ADFs for bulk-phase 50 - 50% [HAN][HEHN] mixture. (5c) Spatial distribution functions (SDFs) in [HAN][HEHN]] mixtures around the HEH<sup>+</sup> cation. Ocean blue isosurfaces indicate preferential positioning of the nitrate oxygen with respect to the cation reference frame. Reprinted with permission from J. Phys. Chem. B 2023, 127, 40, 8616–8633. Copyright 2024 American Chemical Society.

## V. Conclusions

Herein, we present the first computational high-throughput screening framework for multimode propulsion propellant discovery. The maturity of Materials Project software infrastructure and high performance computing resources presents an interesting case to explore ionic liquids fundamentally over a vast chemical design space. Moreover, the mixture chemistry and temperature-dependence involved with designing and characterizing macroscopic behavior of propellants adds a layer of complexity appropriate for large scale, parallelized simulations. Through the case study of [HAN][HEHN] mixtures, we show properties that inform design considerations based on first-principles. The goal of this work is to invite the MMP and IL community at large to generate a database of material properties to support the next-generation of IL discovery and participate in modeling efforts towards the proposed framework for propellant discovery.

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