Dependence of the self-diffusion coefficient on the q-gap value in fluids

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Intensive studies are currently focused on the properties of liquids and their collective dynamics, yet the microscopic mechanisms linking these collective modes to diffusion processes remain poorly understood. Using *in silico* studies of model fluids and liquid metals, we show for the first time a linear relationship between the self-diffusion coefficient and the q-gap width, accompanied by a non-diffusive region across 3D systems. These findings open new avenues for studying fluid dynamics, providing a unified framework for linking microscopic transport properties with collective excitations.

INTRODUCTION

The excitation spectra describe the propagation of mechanical waves in medium and make it possible to determine the energy distribution in the phonon system at various frequencies and wave vectors. These spectra arise from correlated many-body dynamics and manifest as distinct branches in dispersion relations – longitudinal acoustic modes governing density fluctuations and transverse modes reflecting shear resistance. The analysis of collective excitation spectra offers valuable insights into various phenomena and associated properties, such as elastic, thermodynamic, and transport characteristics in crystals, condensed matter, and strongly coupled plasmas [1–3].

Despite considerable progress in understanding collective excitations in crystalline structures using lattice dynamics theory, applying these frameworks to disordered systems (e.g., liquids and amorphous materials) faces major theoretical difficulties. Unlike crystalline solids, liquids are characterized by the absence of small parameter related to anharmonicity [4]. Hence, traditional analytical approaches based on the assumption of small atomic fluctuations about fixed equilibrium positions are inapplicable. In recent studies, collective excitations have gained significant attention in the context of fluid thermodynamics and collective dynamics [4–19]. One of the distinct features of excitation spectra in fluids is the q-gap – a discontinuity in transverse excitation dispersion curves arising from their instability at long wavelengths. This specific property characterizes the ability to maintain the propagation of transverse waves in liquids which is for significant importance for various applied industries, including biotechnology, chemical physics, and soft materials.

The definition of q-gap was first formulated within the framework of Maxwell-Frenkel approach [20] as $q_g = 1/2c\tau$, where c is the transverse sound velocity and τ is the Maxwell relaxation time. Originally identified in dusty plasmas [21], q-gap have since been extensively studied by molecular dynamics simulations of classical liquids [5, 7, 22–28] and other liquid systems [9, 29–31] and experiments in liquid metals and colloidal suspensions [31–35]. Additionally, the similarity between vibrational modes at high frequency/wave-vector in liquids and solids have been experimentally verified [36–40]. The recent paper [41] reviews the emergence of gapped momentum states across diverse physical systems, ranging from ordinary liquids to holographic models, discussing their origin, implications, and theoretical approaches. The review underscores the importance of q-gap in characterizing collective behavior across these systems, particularly in distinguishing between vibrational and diffusive regimes. Recent work [7] establishes a correlation between the q-gap width and the system's heat capacity, implying its potential influence on other thermodynamic properties, including the self-diffusion coefficient. However, this topic remains little studied.

In this work we establish a correlation between the self-diffusion coefficient D and the q-gap width in classical liquids through molecular dynamics simulations of Lennard-Jones, Yukawa, Embedded atom model (EAM for iron) and machine-learning-based (ML-IAP for liquid aluminum) potentials across 2D and 3D configurations. Analysis of velocity current spectra using two-oscillator model reveals a universal linear dependence of D on q-gap width across all investigated interaction potentials in 3D cases. We demonstrate that 3D systems exhibit discontinuous growth of D during melting due to crystalline lattice breakdown and metastable cluster formation, while 2D systems show smooth transitions consistent with Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) melting scenario. The observed temperature-dependent expansion of the q-gap and emergence of solid-like transverse modes for $q > q_g$ confirm its role as a critical parameter separating vibrational and diffusive regimes.

METHODS

We considered model fluids of particles interacting via the Lennard-Jones and Yukawa pair potentials, as well as liquid aluminum described by a machine-learning interatomic potential (ML-IAP) [42] and liquid iron modeled using Embedded Atom Model (EAM) with parameters reported in Ref. [46]. Further details of the simulation

procedures can be found in the supplementary material.

Fluids in states near the freezing line were considered. Chosen states for each system are represented in supplementary material. The reduced LJ units are used for Lennard-Jones and Yukawa systems throughout the paper.

To obtain excitation spectra of the fluids, we studied the velocity current spectra [48]

$$C_{L,T}(\mathbf{q},\omega) = \int dt\, e^{i\omega t}\, \mathrm{Re}\langle j_{L,T}(\mathbf{q},t) j_{L,T}(-\mathbf{q},0)\rangle, \quad (1)$$

where $\mathbf{j}(\mathbf{q},t) = N^{-1}\sum_s^N \mathbf{v}_s(t)\exp(i\mathbf{q}\mathbf{r}_s(t))$ is the velocity current; $\mathbf{v}_s(t) = \dot{\mathbf{r}}_s(t)$ is the velocity of particle s; $\mathbf{j}_L = \mathbf{q}(\mathbf{j}\cdot\mathbf{q})/q^2$ and $\mathbf{j}_T = (\mathbf{j}\cdot\mathbf{e}_\perp)\mathbf{e}_\perp$ are longitudinal and transverse components of velocity current, respectively (here $\mathbf{e}_\perp$ is unit vector, normal to the $\mathbf{q}$) and the brackets $\langle \ldots \rangle$ denote ensemble average. The isotropy of simple fluids allows us to average $C_{L,T}(\mathbf{q},\omega)$ across all wavevector $\mathbf{q}$ directions:

$$C_{L,T}(q,\omega) = \frac{1}{N_q}\sum_{|\mathbf{q}|=q}^{N_q} C_{L,T}(\mathbf{q},\omega), \quad (2)$$

where N_q is the number of directions used for averaging.

Further, to obtain dispersion relations $\omega_{L,T}(q)$ the values of $C_{L,T}(q,\omega)$ were investigated by two-oscillator model [5]

$$C(q,\omega) \propto \frac{\Gamma_L}{(\omega-\omega_L)^2+\Gamma_L^2} + \frac{\Gamma_L}{(\omega+\omega_L)^2+\Gamma_L^2} + \frac{(d-1)\Gamma_T}{(\omega-\omega_T)^2+\Gamma_T^2} + \frac{(d-1)\Gamma_T}{(\omega+\omega_T)^2+\Gamma_T^2}, \quad (3)$$

where d is the space dimension.

The self-diffusion coefficient D was calculated using mean-squared displacement of particles:

$$\mathrm{MSD}(t) = N^{-1}\sum_s^N (\mathbf{r}_s(t)-\mathbf{r}_s(0))^2, \quad (4)$$

$$D = \lim_{t\to\infty}\frac{\mathrm{MSD}(t)}{2dt}, \quad (5)$$

where d, as clarified earlier, is the space dimension. The calculated mean squared displacement dependencies for the investigated systems are illustrated in the supplementary material.

RESULTS

The fluids were studied at the same densities (κ for Yukawa), but under different temperatures (Γ for Yukawa).

To obtain the excitation spectra, velocity current spectra was calculated in a certain range of wavenumber values. The resulting velocity current spectra for the considered systems are presented in the supplementary material.

The q-gap values were obtained by calculating the dispersion relations $\omega_{L,T}(q)$ and fitting them using Eq. (4). The supplementary material. contains representative examples of the low-frequency terms $\omega_T(q)$ for the systems examined in this study.

The dependencies of the self-diffusion coefficient, calculated using particle MSD given by Eq. (5), on the q-gap width for the considered systems are shown in Figure 1 for both three- and two-dimensional cases.

The plots display values corresponding to the q-gap along with their approximations. A clear linear relationship between the coefficient D and the q-gap width is observed for three-dimensional cases and, notably, it does not pass through the origin, which corresponds to a crystalline state with zero values of D and q-gap. Thus, the obtained dependencies indicate a nonlinear growth of the self-diffusion coefficient D with increasing q-gap in 3D classical fluids during melting. However, in this work, we were unable to analyze systems with $q_g < q_0$ (values of q_0 are given in Table in supplementary material), so clarifying the behavior of $D(q_g)$ in the melting region requires further investigation.

In contrast, this effect does not manifest in two-dimensional systems, where the given dependencies exhibit a smooth increase from the origin. However, a nonlinear dependence is observed for the 2D Yukawa system (Fig. 1(d)). To analyze this behavior, we employed a fit based on Eq.(6).

$$D \propto q_g^{-\lambda_D/\sqrt{n}}. \quad (6)$$

We also investigated the dependency of the self-diffusion coefficient on the slope $\mathrm{d}D/\mathrm{d}q_g$ and observed an intriguing behavior, as shown in Figure 2. It appears that this universal relationship might be described by the theoretical fit (7):

$$D \approx 7.4\exp\left[30\left(\frac{\mathrm{d}D}{\mathrm{d}q_g}\right)\right]\cdot 10^{-4} \quad (7)$$

Furthermore, the extended Lennard-Jones (LJ) and Yukawa systems were analyzed, and a comparison of $D(q_g)$ with the original systems is provided in the supplementary material.

DISCUSSION

The distinction between 3D and 2D systems, as we assume, appears from fundamental differences in the melting scenarios. In three-dimensional systems, first-order

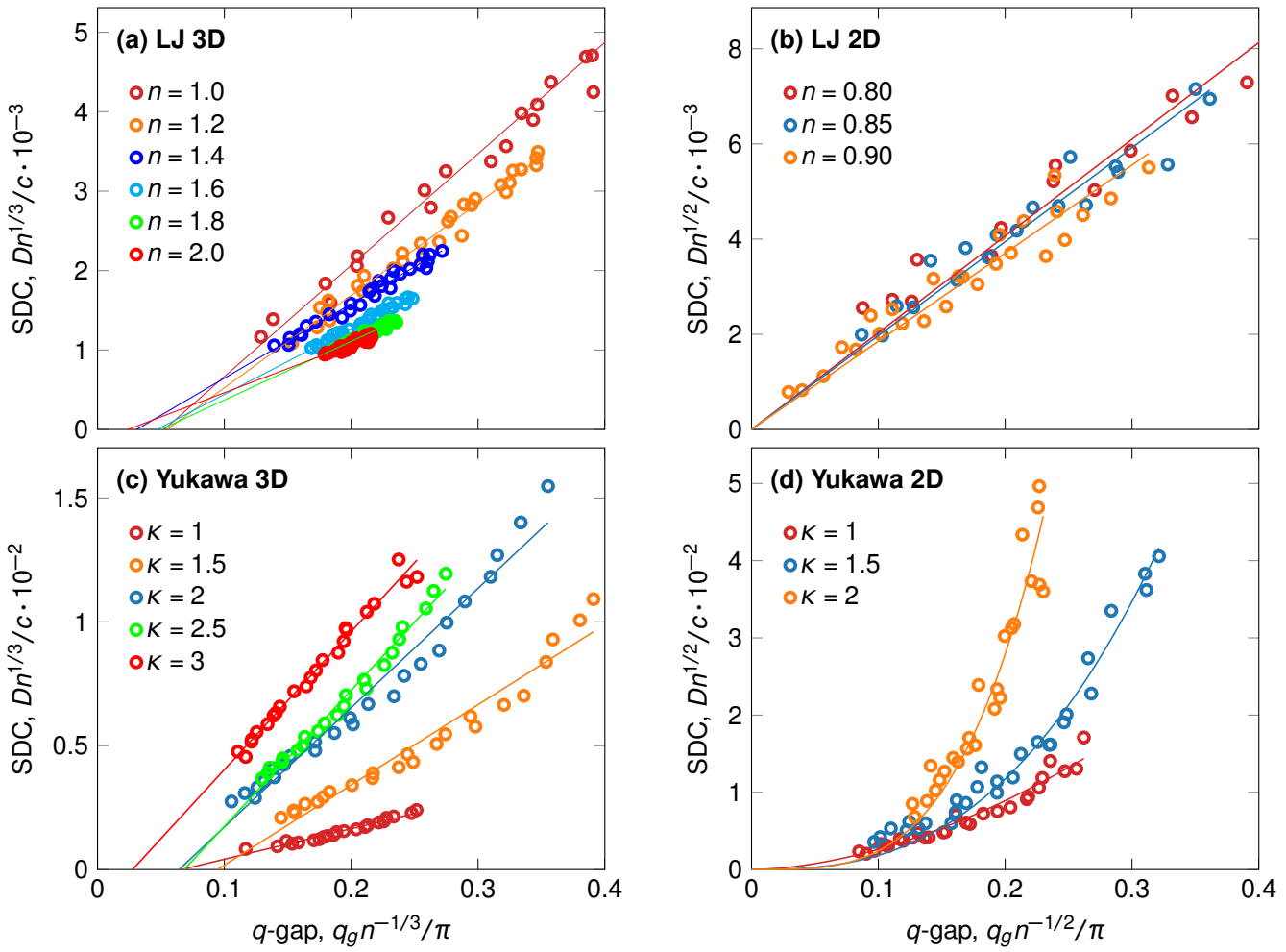

Figure 1. Dependence of the self-diffusion coefficient D on the q-gap width for (**a**),(**b**) Lennard-Jones and (**c**),(**d**) Yukawa fluids in 3D and 2D cases. For Lennard-Jones: 3D systems with densities $n = 1$–2 and 2D systems with $n = 0.8$–0.9, solid lines are linear fits. For Yukawa: 3D and 2D systems with screening parameters $\kappa = 1$—3 and $\kappa = 1$—2 respectively, solid lines indicate linear approximations in 3D case and fit by Eq.(6) in 2D.

phase transitions dominate, characterized by jumps in thermodynamic parameters and density inhomogeneities, whereas in two-dimensional systems, the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory of two-dimensional melting is applied, involving the formation of topological defects and suppression of long-range order [49]. These differences are caused by the enhanced role of thermal fluctuations at $d < 3$ and the constraints imposed by the Mermin-Wagner theorem [50], which prohibits spontaneous symmetry breaking in two-dimensional systems. However, a detailed study of this phenomenon remains a subject for future work.

The nonlinear nature of the dependence on Figure 1(b), as we suggest, may be caused by the absence of an attraction term in the Yukawa potential.

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[1] N. H. March, M. P. Tosi, and M. P. Tosi, *Introduction to liquid state physics* (World Scientific, River Edge, NJ, 2002).
[2] M. T. Dove, *Introduction to Lattice Dynamics*, 1st ed. (Cambridge University Press, 1993).
[3] J. M. Ziman, *Electrons and phonons: the theory of transport phenomena in solids*, Oxford classic texts in the physical sciences (Clarendon Press ; Oxford University Press, Oxford : New York, 2001).
[4] K. Trachenko and V. V. Brazhkin, Collective modes and thermodynamics of the liquid state, Reports on Progress in Physics **79**, 016502 (2015), publisher: IOP Publishing.
[5] N. P. Kryuchkov, L. A. Mistryukova, V. V. Brazhkin, and S. O. Yurchenko, Excitation spectra in fluids: How to analyze them properly, Scientific reports **9**, 10483 (2019), publisher: Nature Publishing Group UK London.
[6] E. V. Yakovlev, N. P. Kryuchkov, P. V. Ovcharov, A. V.

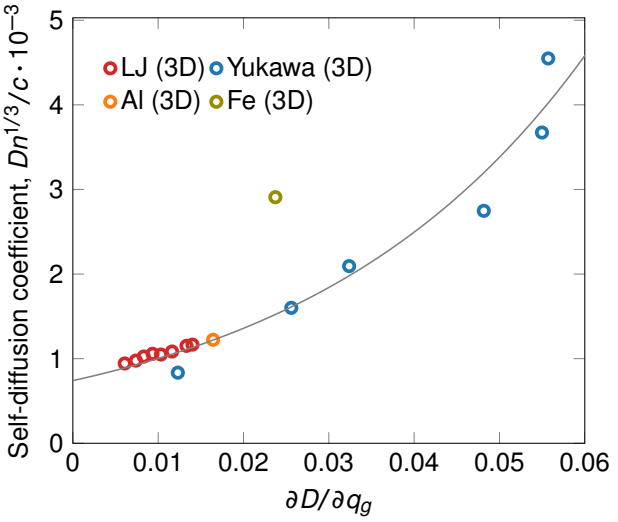

Figure 2. Dependence of the self-diffusion coefficient D on the $(\mathrm{d}D/\mathrm{d}q_g)$ slope for investigated 3D system. Gray solid line indicates theoretical fit by Eq.(7).

Sapelkin, V. V. Brazhkin, and S. O. Yurchenko, Direct experimental evidence of longitudinal and transverse mode hybridization and anticrossing in simple model fluids, The Journal of Physical Chemistry Letters **11**, 1370 (2020), publisher: ACS Publications.

[7] N. P. Kryuchkov, L. A. Mistryukova, A. V. Sapelkin, V. V. Brazhkin, and S. O. Yurchenko, Universal Effect of Excitation Dispersion on the Heat Capacity and Gapped States in Fluids, Physical Review Letters **125**, 125501 (2020).

[8] S. A. Khrapak, Vibrational model of thermal conduction for fluids with soft interactions, Physical Review E **103**, 013207 (2021), publisher: American Physical Society.

[9] N. P. Kryuchkov and S. O. Yurchenko, Collective excitations in active fluids: Microflows and breakdown in spectral equipartition of kinetic energy, The Journal of Chemical Physics **155**, 10.1063/5.0054854 (2021), publisher: AIP Publishing.

[10] C. Stamper, D. Cortie, Z. Yue, X. Wang, and D. Yu, Experimental Confirmation of the Universal Law for the Vibrational Density of States of Liquids, The Journal of Physical Chemistry Letters **13**, 3105 (2022).

[11] J. Hofmann and S. Das Sarma, Collective modes in interacting two-dimensional tomographic Fermi liquids, Physical Review B **106**, 205412 (2022), publisher: American Physical Society.

[12] A. Z. Zhao and J. E. Garay, High temperature liquid thermal conductivity: A review of measurement techniques, theoretical understanding, and energy applications, Progress in Materials Science **139**, 101180 (2023).

[13] D. Huang, M. Baggioli, S. Lu, Z. Ma, and Y. Feng, Revealing the supercritical dynamics of dusty plasmas and their liquidlike to gaslike dynamical crossover, Physical Review Research **5**, 013149 (2023).

[14] C. Cockrell and A. Dragović, Thermodynamics and collective modes in hydrogen-bonded fluids, The Journal of Chemical Physics **160**, 10.1063/5.0201689 (2024), publisher: AIP Publishing.

[15] S. A. Khrapak, Elementary vibrational model for transport properties of dense fluids, Physics Reports Elementary vibrational model for transport properties of dense fluids, **1050**, 1 (2024).

[16] N. Yu, D. Huang, S. Lu, S. Khrapak, and Y. Feng, Universal scaling of transverse sound speed and its isomorphic property in Yukawa fluids, Physical Review E **109**, 035202 (2024), publisher: APS.

[17] S. A. Khrapak, Entropy of strongly coupled Yukawa fluids, Physical Review E **110**, 034602 (2024).

[18] C. Cockrell, M. Withington, H. L. Devereux, A. M. Elena, I. T. Todorov, Z.-K. Liu, S.-L. Shang, J. S. McCloy, P. A. Bingham, and K. Trachenko, Thermodynamics and transport in molten chloride salts and their mixtures, Physical Chemistry Chemical Physics **27**, 1604 (2025), publisher: Royal Society of Chemistry.

[19] D. Huang, S. Lu, C. Liang, M. Baggioli, and Y. Feng, Fundamental Origin of Viscosity in 2D Simple Liquids, arXiv preprint arXiv:2502.12522 10.1063/5.0266423 (2025).

[20] J. Frenkel, *Kinetic Theory Of Liquids* (1946).

[21] V. Nosenko, J. Goree, and A. Piel, Cutoff wave number for shear waves in a two-dimensional Yukawa system (dusty plasma), Physical review letters **97**, 115001 (2006), publisher: APS.

[22] C. Yang, M. Dove, V. Brazhkin, and K. Trachenko, Emergence and Evolution of the k Gap in Spectra of Liquid and Supercritical States, Physical Review Letters **118**, 215502 (2017).

[23] E. Guarini, M. Neumann, A. De Francesco, F. Formisano, A. Cunsolo, W. Montfrooij, D. Colognesi, and U. Bafile, Onset of collective excitations in the transverse dynamics of simple fluids, Physical Review E **107**, 014139 (2023), publisher: APS.

[24] Y. D. Fomin, Dispersion of acoustic excitations in tetrahedral liquids, Journal of Physics: Condensed Matter **32**, 395101 (2020), publisher: IOP Publishing.

[25] J. Q. Toledo-Marín and G. G. Naumis, Viscoelasticity and dynamical gaps: rigidity in crystallization and glass-forming liquids, Journal of Non-Crystalline Solids: X **3**, 100030 (2019), publisher: Elsevier.

[26] S. A. Khrapak, N. P. Kryuchkov, L. A. Mistryukova, A. G. Khrapak, and S. O. Yurchenko, Collective modes of two-dimensional classical Coulomb fluids, The Journal of Chemical Physics **149**, 10.1063/1.5050708 (2018), publisher: AIP Publishing.

[27] T. Bryk, M. Kopcha, and I. Yidak, Propagation gap for shear waves in binary liquids: Analytical and simulation study, The Journal of Chemical Physics **161**, 10.1063/5.0236047 (2024), publisher: AIP Publishing.

[28] T. Bryk, A. Huerta, V. Hordiichuk, and A. Trokhymchuk, Non-hydrodynamic transverse collective excitations in hard-sphere fluids, The Journal of Chemical Physics **147**, 10.1063/1.4997640 (2017), publisher: AIP Publishing.

[29] S. A. Khrapak, A. G. Khrapak, N. P. Kryuchkov, and S. O. Yurchenko, Onset of transverse (shear) waves in strongly-coupled Yukawa fluids, The Journal of chemical physics **150**, 10.1063/1.5088141 (2019), publisher: AIP Publishing.

[30] Z. Ge, D. Huang, S. Lu, C. Liang, M. Baggioli, and Y. Feng, Observation of fast sound in two-dimensional dusty plasma liquids, Physical Review E **107**, 055211 (2023), publisher: APS.

[31] R. M. Khusnutdinoff, C. Cockrell, O. A. Dicks, A. C. S. Jensen, M. D. Le, L. Wang, M. T. Dove, A. V. Mokshin, V. V. Brazhkin, and K. Trachenko, Collective modes and gapped momentum states in liquid Ga: Experiment, theory, and simulation, Physical Review B **101**, 214312 (2020), publisher: American Physical Society.

[32] S. Hosokawa, M. Inui, Y. Kajihara, K. Matsuda, T. Ichitsubo, W.-C. Pilgrim, H. Sinn, L. E. González, D. J. González, S. Tsutsui, and A. Q. R. Baron, Transverse Acoustic Excitations in Liquid Ga, Physical Review Letters **102**, 105502 (2009).

[33] S. Hosokawa, S. Munejiri, M. Inui, Y. Kajihara, W.-C. Pilgrim, Y. Ohmasa, S. Tsutsui, A. Q. R. Baron, F. Shimojo, and K. Hoshino, Transverse excitations in liquid Sn, Journal of Physics: Condensed Matter **25**, 112101 (2013).

[34] S. Hosokawa, M. Inui, Y. Kajihara, S. Tsutsui, and A. Q. R. Baron, Transverse excitations in liquid Fe, Cu and Zn, Journal of Physics: Condensed Matter **27**, 194104 (2015).

[35] C. Jiang, Z. Zheng, Y. Chen, M. Baggioli, and J. Zhang, Experimental observation of gapped shear waves and liquid-like to gas-like dynamical crossover in active granular matter, Communications Physics **8**, 1 (2025), publisher: Nature Publishing Group.

[36] G. Ruocco, F. Sette, U. Bergmann, M. Krisch, C. Masciovecchlo, V. Mazzacurati, G. Signorelli, and R. Verbeni, Equivalence of the sound velocity in water and ice at mesoscopic wavelengths, Nature **379**, 521 (1996), publisher: Nature Publishing Group UK London.

[37] V. M. Giordano and G. Monaco, Fingerprints of order and disorder on the high-frequency dynamics of liquids, Proceedings of the National Academy of Sciences **107**, 21985 (2010).

[38] T. Scopigno, G. Ruocco, and F. Sette, Microscopic dynamics in liquid metals: The experimental point of view, Reviews of Modern Physics **77**, 881 (2005), publisher: APS.

[39] L. Noirez and P. Baroni, Identification of a low-frequency elastic behaviour in liquid water, Journal of Physics: Condensed Matter **24**, 372101 (2012), publisher: IOP Publishing.

[40] Y. Yu, S. Jin, X. Fan, M. Sarter, D. Yu, M. Baggioli, and L. Hong, Unveiling the solid-like dynamics of liquids at low-frequency via nano-confinement, arXiv preprint arXiv:2307.11429 10.1063/1.1637145 (2023).

[41] M. Baggioli, M. Vasin, V. Brazhkin, and K. Trachenko, Gapped momentum states, Physics Reports Gapped momentum states, **865**, 1 (2020).

[42] S. Kumar, H. Tahmasbi, K. Ramakrishna, M. Lokamani, S. Nikolov, J. Tranchida, M. A. Wood, and A. Cangi, Transferable interatomic potential for aluminum from ambient conditions to warm dense matter, Physical Review Research **5**, 033162 (2023).

[43] A. Thompson, L. Swiler, C. Trott, S. Foiles, and G. Tucker, Spectral neighbor analysis method for automated generation of quantum-accurate interatomic potentials, Journal of Computational Physics **285**, 316 (2015).

[44] The Stopping and Range of Ions in Matter, in *Treatise on Heavy-Ion Science* (Springer US, Boston, MA, 1985) pp. 93–129.

[45] S. Kumar, H. Tahmasbi, K. Ramakrishna, M. Lokamani, S. Nikolov, J. Tranchida, M. A. Wood, and A. Cangi, Training scripts and input data sets: Transferable Interatomic Potential for Aluminum from Ambient Conditions to Warm Dense Matter (2023).

[46] A. B. Belonoshko, R. Ahuja, and B. Johansson, Quasi–*Ab Initio* Molecular Dynamic Study of Fe Melting, Physical Review Letters **84**, 3638 (2000).

[47] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, Journal of Computational Physics **117**, 1 (1995).

[48] J.-P. Hansen and I. R. McDonald, *Theory of simple liquids: with applications to soft matter* (Academic press, 2013).

[49] D. E. Dudalov, Y. D. Fomin, E. N. Tsiok, and V. N. Ryzhov, How dimensionality changes the anomalous behavior and melting scenario of a core-softened potential system?, Soft Matter **10**, 4966 (2014).

[50] N. D. Mermin and H. Wagner, Absence of Ferromagnetism or Antiferromagnetism in One- or Two-Dimensional Isotropic Heisenberg Models, Physical Review Letters **17**, 1133 (1966), publisher: American Physical Society (APS).