QUANTUM THERMODYNAMICS AT THE CRITICAL POINTS
DURING MELTING AND SOLIDIFICATION PROCESSES

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ABSTRACT. Phase transitions are ubiquitous, exist in all fields of science in one form or another. The most common example in condensed matter physics is the Landau thermal phase transition, which is from a liquid to a solid phase or vice versa. Here, we systematically explore and develop unequivocal theoretical strategies, going beyond the total-energy minimization techniques to understand what constitutes the thermal phase transition. We prove the existence of finite-temperature continuous quantum phase transitions ($C_T^{QPT}$) during solidification and melting processes such that $C_T^{QPT}$ is responsible for all first-order thermal phase transitions. In fact, this $C_T^{QPT}$ is related to chemical reactions where the quantum fluctuations are caused by thermal energies, and it may occur maximally for temperatures much higher than zero-Kelvin. To extract the quantitative information related to $C_T^{QPT}$, we use the ionization energy theory to derive the electronic-excitation and atomic-disorder (or symmetry-breaking) entropies. Subsequently, we exploit the energy level spacing renormalization group method to renormalize (i) the Bose-Einstein distribution and (ii) the specific heat capacity. We also conclude that the proofs developed herein can lead us to the unification of thermodynamics and quantum mechanics such that one can evaluate the changes in specific heat due to wave function transformations (quantum mechanical effects) when one crosses over from a solid to a liquid or vice versa at a constant temperature.

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1. INTRODUCTION

Unlike any thermal fluctuation, the fluctuation at a critical point of a finite-temperature continuous quantum phase transition ($C_T^{QPT}$) is specifically called quantum fluctuation (even for finite temperatures) because it is related to the properties of electrons at a constant temperature, and therefore, it is still subject to the established Heisenberg uncertainty principle. An example in this respect is the existence of a $C_T^{QPT}$ (due to changing pressure), which is well-known for ice at a constant temperature ($0 < T < 273.16K$). The readers are referred to an elementary and straightforward discussion on these two issues (quantum fluctuation and $C_T^{QPT}$ in ice) given by Sachdev [1]. But little did we know then, that physically, and logically, not all quantum fluctuations ($\omega_{1,2,\ldots}$) will have to become “irrelevant” when $T > 0K$, i.e., not all $\omega \rightarrow$ maximum when $T \rightarrow 0K$. If the statement—all quantum fluctuations become maximum when $T \rightarrow 0K$ is true, then chemical reactions cannot exist. The above argument can be proven if we can prove the...
existence of some quantum fluctuations that become large for finite temperatures or when $T \gg 0K$.

The quantum fluctuations discussed in Refs. [2, 3] are due to temperature-independent external tuners, namely, magnetic fields, pressure and chemical composition affecting the spin carried by the electrons. Therefore, the quantum fluctuation discussed therein are entirely related to spin ordering and spin disordering, giving rise to antiferromagnetism (AFM), ferromagnetism (FM) and paramagnetism (PM). Even if the system is none of these magnetism-related, spin will still come to play its role in one way or another when $T \to 0K$. For example, a Cooper pair [4] in a superconductor consists of two electrons, one with $-\frac{1}{2} \hbar$ (spin-down) and the other with $\frac{1}{2} \hbar$ (spin-up). Anyway, it is well known that the strength of this spin ordering (AFM or FM) or Cooper pairing (pairing of electrons with spin up and down) is maximum for $T = 0K$, and the ordering or pairing gets destroyed when the electrons got excited, or when the Cooper pairs break up for some $T > 0K$.

Rightly so, Sachdev has correctly pointed out that the quantum phase transitions discussed in Refs. [1, 2] do not include the temperature effect. Furthermore, these quantum fluctuations can be examined even for $T > 0K$ provided that $\omega/T$ can be expanded for higher temperatures if $\hbar \omega > k_B T$. Therefore, we can certainly add here that the temperature effect was excluded (or included as a form of expansion on $\omega/T$) because the objective there and then was to evaluate the qualitative changes to the ground-state wave function of a particular system by varying the temperature-independent external tuners (for $T = 0K$), not because QPT has been proven not to exist for $T \gg 0K$. As a matter of fact, we prove here the existence of a QPT for $T \gg 0K$.

Now, to prove the existence of a particular QPT for $T \gg 0K$, we need to understand how the thermal energy initiates a quantum fluctuation during melting and solidification processes, and then evaluate the relationship between the thermally driven first-order TPT and $\mathcal{C}_T$QPT. Here, $\mathcal{C}_T$QPT requires quantitative changes to the properties of the electrons (due to the changes in their energy levels) that need some qualitative and/or quantitative changes to their wave functions. These changes are driven by thermal energy, not by the temperature-independent external tuners listed above. In contrast, the commonly accepted quantum phase transition for $T = 0K$ ($0K$QPT) also requires quantitative changes to the properties of the electrons (due to the changes in their energy levels) that need some qualitative and/or quantitative changes to their wave functions. However, the above changes for $T = 0K$ are driven by temperature-independent external tuners alone, not by thermal energy. Hence, we should not reserve all “quantum phase transitions” exclusively for transitions driven by temperature-independent external tuners for $T = 0K$, and not for transitions driven by thermal energy.

Such a reservation is somewhat naive because the external drivers can be anything, including thermal energy, for as long as these drivers can initiate quantum fluctuations for any $T \geq 0K$. We emphasize here that a particular quantum fluctuation that causes a phase transition is the one that should determine whether a given phase transition has a quantum origin or not, not by some ad hoc arguments. Of course, any given QPT can be driven by thermal energy, with further assistance from the temperature-independent tuners, or a QPT can be suppressed if one external tuner competes with other tuners. In this case, it is just a matter of finding which tuner is in command of which interaction and quantum fluctuation. The
quantum fluctuation we are concerned with here is the fluctuation in the energy-level spectra (energy-level spacing) at a critical point. These energy levels refer to electrons, of course. In any case, we have said enough. At the end of this section, some of you may come to realize that the quantum-fluctuation causing thermal energy holds the key to unify thermodynamics and quantum mechanics.

Having explained that, we now continue with our introduction to $\mathcal{C}_T$QPT. The quantum fluctuation associated to $\mathcal{C}_T$QPT occurring at a finite temperature quantum critical point ($T_{\text{QCP}}$) requires quantitative changes to the wave functions, such that the quantum fluctuation with an energy scale, $\hbar \omega$ can be written as,

\begin{align}
\hbar \omega(y_1) &< k_B T_\theta, \\
\hbar \omega(y_2) &= k_B T_\theta, \\
\hbar \omega(y_3) &> k_B T_\theta,
\end{align}

where $\hbar$ is the Planck constant divided by $2\pi$, $k_B$ denotes the Boltzmann constant, $\omega(y)$ and $T_\theta$ are the doping ($y$)-dependent frequency and some critical temperature ($T_{\text{QCP}}$), respectively. Later, we will come to see why the wave functions need to be changed quantitatively for $\mathcal{C}_T$QPT. For a $0K$ QCP, the relevant inequality is simply $\hbar \omega(y_1) < \hbar \omega(y_2) < \hbar \omega(y_3)$ because $T_\theta = 0K$. Here, $y_1, y_2$ and $y_3$ are related to different chemical composition, while $\theta$ represents a certain physical property under investigation.

For example, for the melting process (chemical dissociation), $T_\theta = T_{\text{point}}^{\text{melting}}$, and it satisfies the classical phase transition (due to thermal fluctuation with increasing temperature for a given chemical composition), without any microscopic understanding as to the reasons why and how the translational symmetry breaks (ice to water). This does not imply melting is a classical process not involving electrons. For instance, we have proven how the energy level spacing evolve and give rise to a changing interaction strength between a polarizable water molecule physisorbed onto the MgO surface, which then initiate the water molecule dissociation at a constant temperature [5]. Within the ionization energy theory (IET) [6, 7, 8], we can write $\hbar \omega(y) = \xi(y)$ where $\xi(y)$ is the ionization energy of a particular compound, and it is also known as the energy level spacing within the renormalization group method [9]. Hence, during chemical dissociation with changing chemical composition, $\xi(y)$ is a dynamical parameter, giving rise to quantum fluctuation.

Importantly, much below the melting point, the fluctuation in $\xi(y)$ is caused by the energy level crossings, changes in the valence states of the constituent elements, and defects due to different chemical compositions (doping) along a constant temperature line. Such fluctuations (due to defects and valence states) are responsible for the changes in the constant-temperature and composition-dependent (i) resistivity of ferromagnets [10], (ii) resistivity in the normal-state of superconductors [6, 11, 12], (iii) non-blinking effect in quantum dots [13] and (iv) reversible carrier-type transition in oxides [14]. Apart from that, experimental and theoretical developments of the popular zero temperature quantum phase transition ($0K$ QPT) in strongly interacting solids were also investigated independently, namely, in two dimensional systems [15, 16], in solids with respect to spin ordering [17, 18, 19, 20, 21, 22, 23, 24, 25, 26], in Bose-Hubbard model [27], and in antiferromagnets [28, 29].
In the subsequent section, we introduce and explain why and how the molten alkali halides give rise to the first-order thermal phase transition, and how this transition is related to the finite temperature quantum phase transition. Subsequently, we venture deeper into the details of quantum phase transitions and quantum fluctuations with respect to the ionization energy theory, which involves wave function transformations and electronic phase transitions. Along the way, the theory is discussed and crosschecked whenever necessary against the experimental observations. Finally, we will conclude that (a) the finite-temperature continuous quantum phase transition is responsible for all first-order thermal phase transitions, and (b) at a critical point of a first-order thermal phase transition, a non-divergent time-dependent specific heat can be proven to exist. Both points in (a) and (b) involves some physics beyond the traditional phase transitions and critical phenomena.

2. Further analyses

Here, we will give unambiguous logical proofs (supported by experimental results, of course) on the origin of thermal and quantum fluctuations due to temperature and doping (or $\xi(y)$) within IET. But before doing so, we need to justify the reasons why we have selected salts made up of single-valent cations and anions from group 17 of the periodic table.

2.1. Thermal and quantum fluctuations. Table 1 lists the diatomic bonding energies and melting points of these salts such that the melting points decrease systematically with decreasing bonding energies from F to I. Such a decreasing trend can be precisely overlapped with the decreasing ionization energies of the anions, namely, $\xi_{F^+}(1681 \text{ kJmol}^{-1}) > \xi_{Cl^+}(1251 \text{ kJmol}^{-1}) > \xi_{Br^+}(1140 \text{ kJmol}^{-1}) > \xi_{I^+}(1008 \text{ kJmol}^{-1})$. The values in the inequalities are given in Table 2 following the values marked with "*". Interestingly however, for a given anion, the decreasing melting points do not agree with the ionization energy values of the cations: Li, Na, K and Rb (follow their respective values listed in Table 2 marked with "†").

For example, the melting points for NaF (996°C) > KF (858°C) > LiF (848°C) > RbF (833°C) cannot be overlapped with $\xi_{Li^+}(520 \text{ kJmol}^{-1}) > \xi_{Na^+}(496 \text{ kJmol}^{-1}) > \xi_{K^+}(419 \text{ kJmol}^{-1}) > \xi_{Rb^+}(403 \text{ kJmol}^{-1})$. This is not surprising because melting is a process directly proportional to bonding strengths (see Table 1), which have been discussed earlier [14] within IET where large ionization energy values of cation-like ions ($\xi_{C^{2+}} < \xi_{O^{2+}}$) in a given molecule (C$^{2+}$O$^{2-}$ or O$^{2-}$O$^{2+}$) do not necessarily imply stronger bonds. Fortunately, we have proven that a stronger bond is predictable from IET if one considers the ionization energies of anions (say O in H$_2$O), because oxygen defines the ability to attract electrons from an atomic hydrogen [5]. In this case, smaller $\xi_O$ means weaker O–H bond, which is consistent with the above-stated ionization-energy inequalities for anions (group 17 elements) and the melting points.

In Table 2, we have deliberately selected systems consisting of single valent cations and anions from group 17 to avoid effects from different electronic interactions due to different number (and type) of constituent atoms in a given molecule. To understand this point, we again use molecular systems, in which, for a NO$_2$ molecule, N acts as a cation, while O as an anion, which means that we need to consider the valence state of 4+ since four electrons have been transferred from N$^{4+}$ to O$_2^{2-}$. This electron-transfer is due to $\xi_{N^{4+}} < \xi_{O^{4+}}$ (see Table 1). In contrast, N is an anion in NH$_3$ molecule due to $\xi_{N^{+}} > \xi_{H^{+}}$ where three electrons from three...
Table 1. Experimental values for the melting points and diatomic bonding energies of salts obtained from Refs. [30] and [31], respectively. The systematic decrease of the melting points and diatomic bonding energies with respect to anions (from F to I with increasing Z) satisfy the decreasing ionization energies for the same anions, from F to I. See the text and Table 2 (follow the values marked with “*”) for details.

| Salts | Melting points (°C) | Diatomic bonding energies (kJmol⁻¹) |
|-------|---------------------|-----------------------------------|
| LiF   | 848                 | 577                               |
| LiCl  | 610                 | 469                               |
| LiBr  | 552                 | 419                               |
| LiI   | 469                 | 345                               |
| NaF   | 996                 | 519                               |
| NaCl  | 801                 | 412                               |
| NaBr  | 747                 | 367                               |
| NaI   | 660                 | 304                               |
| KF    | 858                 | 498                               |
| KCl   | 771                 | 433                               |
| KBr   | 734                 | 380                               |
| KI    | 681                 | 325                               |
| RbF   | 833                 | 494                               |
| RbCl  | 715                 | 428                               |
| RbBr  | 682                 | 381                               |
| RbI   | 642                 | 319                               |

hydrogen atoms are transferred to nitrogen, giving N³⁻H₃⁺. Thus far, the analyses are correct. However, the polarizability of the molecule NO₂ does not solely depend on these four electrons contributed by nitrogen if we compare N⁴⁺O₂⁻ with N³⁻H₃⁺ because we cannot simplify the analysis by comparing ξN⁴⁺ with ξH⁺ (3 electrons contributed by three hydrogen ions) only. If we do so, then obviously we have ξN⁴⁺ > ξH⁺ that falsely allows us to conclude α_{dNO₂} < α_{dNH₃}⁻ because α_{d} ∝ exp(−ξ) where α_{d} is the displacement polarizability.

In other words, we cannot use the above inequality (ξ) to directly compare α_{d} between NO₂ and NH₃ molecules because N acts as a cation in a NO₂ molecule, while it is an anion for the molecule, NH₃. This implies that we need to take both the cationic- and anionic-effect into account explicitly for an accurate logical analysis, which have been correctly invoked in Ref. [5]. However, the anionic-effect can be neglected when we compare CO with O₂ because in these molecules, oxygen is the anion and therefore α_{dCO} < α_{dO₂}⁻ is valid [14]. On the other hand, the justification required to neglect the cationic-effect for doped-Pnictide superconductors is given in Ref. [12]. Finally, taking both cationic- and anionic-effect into account means that for large (many-electron) cations such as K (Z = 19) and Rb (Z = 37), there will always be some significant amount of polarization (due to large screening) from the outer core electrons, even though effectively, K⁺ and Rb⁺ are single-valent ions. This second- or third-electron polarization is negligible for few-electron atoms (due to small screening), namely, Li (Z = 3) and interestingly, also for Na (Z = 11).
Table 2. Averaged atomic ionization energies ($\xi$) for individual ions and their respective valence states ordered with increasing atomic number $Z$. All the experimental ionization energy values were obtained from Ref. [31].

| Elements | Atomic numbers | Valence states | $\xi$ (kJmol$^{-1}$) |
|----------|----------------|----------------|---------------------|
| H        | 1              | 1+             | 1312                |
| Li       | 3              | 1+             | 520 *               |
| N        | 7              | 1+             | 1402                |
| N        | 7              | 4+             | 4078                |
| O        | 8              | 1+             | 1314                |
| O        | 8              | 2+             | 2351                |
| O        | 8              | 4+             | 4368                |
| F        | 9              | 1+             | 1681 *              |
| Na       | 11             | 1+             | 496 *               |
| Cl       | 17             | 1+             | 1251 *              |
| K        | 19             | 1+             | 419 *               |
| Br       | 35             | 1+             | 1140 *              |
| Rb       | 37             | 1+             | 403 *               |
| Sr       | 38             | 2+             | 807                 |
| I        | 53             | 1+             | 1008 *              |
| La       | 57             | 3+             | 1152                |

Note here that we need smaller and larger ionization energies for cations and anions, respectively for stronger ionic bonds. Therefore, incorporating this additional amount of polarization (for cations) implies larger $\xi_{\text{cationic}}$ or equivalently, smaller $\xi_{\text{anionic}}$ that should reduce the melting point as has been observed experimentally (see Fig. 1). Importantly, this correction does not apply for anions if a given system consists of mostly ionic bonds because the anions are judged solely on their ability to attract electrons from the cations. On the contrary, for systems with mostly covalent bonds, we need to consider both cationic- and anionic-effect simultaneously as carried out in Ref. [5]. The existence of this additional polarization is consistent with the experimental results shown in Fig. 1 when one compares the slope, $dT_\theta/d\xi$ for salts containing Li and Na, for instance $(dT_\theta/d\xi)_{\text{Li}} \approx (dT_\theta/d\xi)_{\text{Na}}$, while $(dT_\theta/d\xi)_K \approx (dT_\theta/d\xi)_{\text{Rb}}$ (follow the solid lines in Fig. 1).

2.2. Finite-temperature continuous quantum phase transition in a two-atom system with asymmetric polarization. To see why and how the above quantum phase transitions (due to changing $T$ and chemical composition) come to play to give rise to two different phases (solid and liquid), a model Hamiltonian would be helpful for some readers, though it is not necessary. Unfortunately, we cannot write a quantum mechanical Hamiltonian right at the melting point because both the Hamilton operator and the wave functions are time-dependent, and they change quantitatively with time [32]. Instead, our strategy here is to first evaluate a Hamiltonian consisting of two identical atoms with interactions. After obtaining the attractive interaction energy between these two neutral polarizable atoms, we will then add the polarization induced attractive interaction term appropriately to
Figure 1. Melting points of Li(I,Br,Cl,F), Na(I,Br,Cl,F), K(I,Br,Cl,F) and Rb(I,Br,Cl,F) salts are plotted against the anionic (I,Br,Cl,F) ionization energies, which indicate a direct proportionality between them (follow the solid lines). INSET: The vertical down-arrow (solidification) denotes a first-order thermal phase transition (from liquid to solid) for LiCl when the temperature is reduced from $T > 610^\circ C$ to $T = 552^\circ C$. The horizontal arrow pointing left captures the continuous (purely electronic) quantum phase transition (from solid to liquid) at constant $T = 552^\circ C$ by changing the chemical composition systematically, LiCl$_{1-a_1}$Br$_{a_1-a_2}$I$_{a_2}$ such that LiCl $\rightarrow$ LiBr $\rightarrow$ LiI, $y_3 = 1 - a_1$, $y_2 = a_1 - a_2$ and $y_1 = a_2$.

Eq. 2.4 to obtain the total attractive interaction between two atoms with asymmetric polarizability. This total attraction is shown to exist just above the melting points of the single-valent ionic bonded salts listed in [1]. The first step is to consider two single-electron, identical and neutral atoms (A and B) depicted in Fig. 2(A). The relevant Hamiltonian (with polarizable electrons, $e_A$ and $e_B$) is given by [33]

$$H = H_O + H_I,$$

$$H_O = p_A^2 \frac{1}{2m} + k r_A^2 + p_B^2 \frac{1}{2m} + k r_B^2,$$

$$H_I = \frac{1}{4\pi \varepsilon_0} \left[ \frac{(e)(e)}{R} + \frac{(-e)(e)}{R + r_B} + \frac{(-e)(e)}{R - r_A} + \frac{(-e)(-e)}{R - r_A + r_B} \right],$$

(2.1)

which can be separated into two harmonic oscillator Hamiltonian after taking $R \gg r_{A,B}$ where $r_A$ and $r_B$ are the coordinates for electrons, $e_A$ and $e_B$, respectively [33],

$$H = \left[ \frac{1}{2m} p_A^2 + \frac{1}{2} \left( k - \frac{e^2}{2\pi \varepsilon_0 R} \right) r_A^2 \right] + \left[ \frac{1}{2m} p_B^2 + \frac{1}{2} \left( k + \frac{e^2}{2\pi \varepsilon_0 R^3} \right) r_B^2 \right].$$

(2.2)

To obtain Eq. 2.2 we have carried out the substitutions listed below [33],

$$r_+^2 = \frac{1}{\sqrt{2}} (r_A + r_B) \quad \text{and} \quad p_+^2 = \frac{1}{\sqrt{2}} (p_A + p_B).$$

(2.3)
In writing Eq. 2.1 and its solution in Eq. 2.4, we have actually assumed the two sketched atoms (A and B) to be polarizable, neutral and identical with discreet energy levels. Moreover, each atom, A and B has one equally-polarizable electron, namely, $e_A$ and $e_B$, respectively. Here, the negatively charged electrons and positively charged nuclei are arranged in this manner, $+ - + -$ along the same axis. (B): On the other hand, $V_{\text{e-ion}}$ is the renormalized screened Coulomb potential between atomic A and B, which has been added by hand into Eq. 2.5 (the first term on the right-hand side). This particular term ($V_{\text{e-ion}}$) imposes the condition that both A and B are also single electron atoms, but with a little twist such that atomic A has the least polarizable electron ($e_A$), while atomic B has the easily polarizable electron ($e_B$). In the text, we will also denote atomic A as the anions (namely, atomic Cl), whereas atomic B represents the cations, namely, atomic Li. The charge carried by each nucleus, A and B in both sketches, (A) and (B) is $+e$.

Subsequently, one obtains the ground state energy for the above Hamiltonian \[ E = \frac{1}{2} \hbar \left[ \sqrt{\frac{k - (e^2/2\pi\epsilon_0 R^3)}{m}} + \sqrt{\frac{k + (e^2/2\pi\epsilon_0 R^3)}{m}} \right]. \]

Here, $p_{A,B}$ are the electrons momenta, $m$ is the electron mass, $\hbar$ is the Planck constant divided by $2\pi$, $R$ is the distance between two neutral and identical atoms and $\epsilon_0$ is the permittivity of free space. The bounded electrons are labeled as $e_A$ and $e_B$, which are bounded within nuclei A and B, respectively. In this simple Hamiltonian, the electrons ($e_A$ and $e_B$), and the nuclei (A and B) carry the charge, $-e$ and $+e$, respectively. Furthermore, we have denoted $H_O$ as the ordinary Hamiltonian that takes the kinetic energy terms, and two semiclassical harmonic-oscillator type electron-ion potential terms into account (see Eq. 2.1). On the other hand, we also have the interaction Hamiltonian denoted by $H_I$ to capture all the Coulomb interaction between atomic A and B (see Eq. 2.1 and Fig. 2(A)). We stress here that neither $H_O$ nor $H_I$ takes the induced repulsive Coulomb forces due to polarized electrons into account. However, the attractive Coulomb interactions between the valence electrons and their respective nuclei have been correctly included in $H_O$.

In our previous work [37], we have proven the existence of a blue-shifting van der Waals (vdW) attractive interaction between two neutral atoms, after carrying out the energy-level spacing renormalization on the interaction potential constant, $k$, and after imposing an additional condition that requires atomic A to be least polarizable, while atomic B as the easily polarizable one (see Fig. 2(B)). This condition
gives the asymmetric polarization that leads to a stronger attractive interaction between atoms. Such a stronger attractive interaction can lead to chemical reactions as proven in Ref. [38]. The stronger attractive vdW interaction energy [37]

$$\tilde{V}_{\text{Waals}}(\xi) = \tilde{V}_{\text{Coulomb}} + \tilde{E} - \hbar \sqrt{\frac{k}{m}},$$

(2.5)

$$\tilde{E} - \hbar \sqrt{\frac{k}{m}} = \frac{1}{2} \hbar \tilde{\omega}_0 \left( \frac{1}{\sqrt{2}} - 1 \right) \left\{ \exp \left[ \frac{1}{2} \lambda \xi_A \right] + \exp \left[ \frac{1}{2} \lambda \xi_B \right] \right\},$$

(2.6)

and from Ref. [39]

$$\tilde{V}_{\text{Coulomb}} = \frac{(-e)(+e)}{4\pi\epsilon_0 |\mathbf{r}_A - \mathbf{r}_B|} \left\{ \exp \left[ -\mu r_A e^{-\frac{1}{2} \lambda \xi_A} \right] \right\}.$$

(2.7)

From [9]

$$\tilde{k} = k \exp [\lambda \xi],$$

(2.8)

where $\tilde{E}$ and $\tilde{k}$ are the renormalized energy (from Eq. 2.4) and interaction potential (spring) constant, respectively, $\mu$ is the screening constant of proportionality, $\lambda = (12\pi\epsilon_0/e^2)a_B$, $a_B$ is the Bohr radius of atomic hydrogen, $\mathbf{R}_A$ and $\mathbf{r}_B$ are the coordinates for the nucleus A and electron $e_B$, respectively. Here, $\hbar(\tilde{k}/m)^{1/2} = \hbar \tilde{\omega}_0$, $\hbar \tilde{\omega}_0$ is the renormalized energy when $H_I = 0$, and $\tilde{V}_{\text{Waals}}(\xi)$ is negative guaranteed by $1/\sqrt{2} - 1$ in Eq. (2.6) and $-e$ in Eq. (2.7). The term on the right-hand side of Eq. (2.6) assumes both atoms, A and B are identical, hence their electrons are equally polarizable. In Eq. (2.7), we have a unidirectional electron-ion attractive interaction between the easily polarizable $e_B$ and the nucleus A, screened by $e_A$ via $\xi_A$ (see the term in the curly bracket in Eq. (2.7)). The imposed asymmetric polarizability is captured by $\tilde{V}_{\text{Coulomb}}$, such that the respective atomic A and B represent the anions (least polarizable) and cations (easily polarizable), which is required to understand the transition from a liquid to a solid phase.

To understand the types of phase transition in the above model Hamiltonian, one needs to observe the evolution of the Hamiltonian from $H_O$ (non-interacting gas) to $H_O + H_I$ (weakly interacting liquid) to $H_O + H_I + V_{\text{Coulomb}}$ (strongly interacting liquid) to $H_{\text{solid}}$ (solid). Therefore, one can actually invoke two types of phase transitions from Eqs. (2.1) and (2.7), from a gas to a liquid phase, and then to a solid phase. For example, taking $H_I \to 0$ and $V_{\text{Coulomb}} \to 0$, one immediately obtains the non-interacting gas phase. For a liquid consisting of identical atoms, and if the atom is least polarizable, then their only interaction is the long-range vdW attraction such that Eq. (2.1) is a sufficient model Hamiltonian for this weakly interacting liquid. On the contrary, if the liquid consists of two different atoms such that one of them is highly polarizable (cation-forming (or electron-donating) atoms), while the other atom contains highly non-polarizable electrons (anion-forming (electron-accepting) atoms), then the liquid consisting of these atoms forms a strongly interacting liquid. For example, any molten solid close to the solidification point, or slightly above the melting point.

Now, you should not be carried away into thinking that a Coulombic liquid is different from the atomic molten system. For example, a system that consists of highly polarized atoms forms a strongly interacting Coulombic liquid, while the weakly interacting Coulombic liquid consists of weakly polarized atoms. Obviously,
unpolarized or uncharged system cannot form such a (Coulombic) liquid. Secondly, the model discussed above nicely corresponds to the experimental results listed in Tables 1 and 2, namely, LiF, NaF, KF and RbF have the largest melting points relative to other listed anions because the ionization energy for F is the largest (with the strongest ability to attract electrons), compared to I, Br and Cl. This implies that at the melting point, the breaking and forming of stronger bonds will lead to a strongly interacting Coulombic liquid, as it should be. Finally, based on the above model, the bond-formation and breaking mechanism is due to the quantum phase transition (giving rise to electronic phase transition), which requires a wave function transformation. The electronic phase transition stated above has got to be nonadiabatic because of electron transfer during bond-formation or -breaking (chemical reactions). However, the adiabatic approximation can still be applied, if and only if the Hamiltonian \((H(t))_{\text{chemical}}\) describing this chemical process is known explicitly [32].

It is well-known that when one cools a molten solid, then one needs a specific amount of thermal energy or simply heat \((Q_{\text{melting}})\) to initiate the quantum fluctuation right at a critical point (at the melting point) to give rise to a wave-function transformation (electronic phase transition) [32]. Any heat larger than \(Q_{\text{melting}}\) will not activate the wave function transformation required for the liquid to solid phase transition. For example, any \(Q > Q_{\text{melting}}\) implies \(Q > \langle V_{\text{Coulomb}}^{e-\text{ion}} \rangle\) and therefore, Coulomb repulsion dominates. On the other hand, if \(Q < Q_{\text{melting}}\) then one has \(Q < \langle V_{\text{Coulomb}}^{e-\text{ion}} \rangle\), which implies that the heat is insufficient to overcome the bonding energy in the solid phase, prior to melting. In the remainder of this paper, our focus is to understand how \(Q\) is related to entropy, specific heat and to the energy-level spacing \((\xi)\) of the molten system. Our strategy here is to prove that \(Q_{\text{melting}}\) drives the changes in \(\xi\), which in turn initiates the electronic phase transition. Within the Hermitian quantum mechanics, the said electronic phase transition is caused by the wave function transformation [32]. Therefore, a fluctuation in \(\xi\) corresponds to a fluctuation in the many-body wave function, and subsequently, is responsible for QPT. In other words, any external tuner, including thermal energy can cause a fluctuation in \(\xi\), which implies a quantum fluctuation that eventually could give rise to a QPT. Later, we will expose why and how the fluctuation in \(\xi\) (at a critical point) forces us to impose time-dependence into \(\xi\).

3. Renormalized entropy and Bose-Einstein distribution

Figure 1 shows the direct proportionality between melting points and ionization energies of the constituent anions (I, Br, Cl, F). The respective vertical and horizontal arrows in the inset of Fig. 1 indicate the first-order TPT and \(C_{\text{T}}\) QPT. In order to expose the existence of these phase transitions, we need to recall the first and second laws of thermodynamics. These two laws can be combined to obtain

\[
dU = dQ + dW = TdS - PdV,\tag{3.1}
\]

in which, the change in the internal energy, \(dU\) of a closed system equals the amount of heat \((Q)\) absorbed and the amount of work \((W)\) done by that system. Here, \(\delta\) is not an exact differential because the changes in \(Q\) and \(W\) depend on the thermodynamic path (or independent of a particular system and process), and therefore, \(Q\) and \(W\) are not state functions. Here, \(P\) and \(V\) denote pressure and volume, respectively and we consider only reversible processes. Unlike \(Q\) and \(W\),
the thermodynamic variable $U$, $P$ and $V$ are state functions that are unique for a
given system and process.

The second law is given by, $\delta Q = T dS$ where $S$ is the entropy, another path-

independent state function. All we need now is the relationship connecting $S$ to $\xi$
that can be obtained from the derivation of the ionization energy based Fermi-Dirac
statistics (IFDS). Denoting $N$ as the total number of particles with $n_1$ particles
have energy $(E_0 \pm \xi)_1$, $n_2$ particles with energy $(E_0 \pm \xi)_2$ and so on implies that
$N = n_1 + n_2 + \cdots + n_m$. As a consequence, the number of ways for $q_1$ unoccupied
quantum states to be arranged among $n_1$ particles is

$$\Omega(n_1, q_1) = \frac{q_1!}{n_1!(q_1 - n_1)!}, \quad (3.2)$$

satisfying the condition that one empty quantum state can accommodate only one
particle. Subsequently, the total number of ways for $q$ quantum states ($q = q_1 + \cdots + q_m$) to be arranged among $N$ particles

$$\Omega(N, q) = \prod_i \frac{q_i!}{n_i!(q_i - n_i)!}. \quad (3.3)$$

The most probable configuration for certain $T$ can be obtained by maximizing the
number of ways one can arrange $n_i$ particles in $q_i$ empty quantum states or, we
need to maximize $\Omega(N, q)$ subject to the restrictive conditions,

$$\sum_i n_i = N, \sum_i dn_i = 0, \quad (3.4)$$

$$\sum_i (E_0 \pm \xi)_i = E_0 \pm \xi = E, \sum_i (E_0 \pm \xi)_i dn_i = 0. \quad (3.5)$$

These conditions impose that the total energy, $E$ and the total number of particles, $N$
for a given system are always constant. Here, $E_0$ is the total energy for 0K. The
method of Lagrange multipliers \[33\] can be employed to maximize Eq. (3.3) by first
introducing a new function, $F_{\text{new}}(\cdots, \mu, \lambda_B, \cdots) = \cdots + \mu f_1 + \lambda_B f_2 + \cdots$, such

$$F_{\text{new}} = \ln \Omega(N, q) + \mu \sum_i n_i + \lambda_B \sum_i (E_0 \pm \xi)_i n_i, \quad (3.6)$$

where $n_1 = n_2 = n_3 = \cdots = n_i = 1$ to imply one empty quantum state ($q$) or energy
level can accommodate only one particle (either electron or hole). Subsequently
we maximize $F_{\text{new}}$,

$$\frac{\partial F_{\text{new}}}{\partial n_i} = \frac{\partial [\ln \Omega(N, q)]}{\partial n_i} + \mu \sum_i \frac{\partial n_i}{\partial n_i} + \lambda_B \sum_i (E_0 \pm \xi)_i \frac{\partial n_i}{\partial n_i} = 0. \quad (3.7)$$

Equation (3.7) can be solved subject to the conditions, $n_i \gg 1$, $q_i \gg 1$, $q_i \geq n_i$
that give us the license to use Stirling’s approximation ($\ln (n_i!) \approx n_i \ln n_i - n_i$), and
after some algebraic rearrangements, one gets

$$\frac{N}{q} = \frac{1}{\exp \left[\mu + \lambda_B(E_0 \pm \xi)\right] + 1}, \quad (3.8)$$
which is the iFDS. Taking \( \exp\left[\mu + \lambda B (E_0 \pm \xi)\right] \gg 1, \mu = -\lambda B E_0^0\) and dividing all the terms by \( T \) will lead us to the energy-level spacing entropy

\[
S_\xi = -\frac{(E_0 \pm \xi) + E_0^0}{T} = \frac{1}{(\lambda B, \lambda) T} \ln \frac{N}{q},
\]

in which,

\[
(3.10) \quad \lambda_B = \frac{1}{k_B T} \quad \text{for constant } \xi
\]

and dividing all the terms by \( T \) will lead us to the energy-level spacing entropy

\[
(3.9) \quad S_\xi = -\frac{(E_0 \pm \xi) + E_0^0}{T} = \frac{1}{(\lambda B, \lambda) T} \ln \frac{N}{q},
\]

The derivation for \( \lambda_B \) is well known in classical thermodynamics and is also given in Ref. [8] within the IET formalism, while the proof for \( \lambda \) is available in Ref. [7].

The other relevant entropy is due to atomic-disorder, \( S_D = k_B \ln D \) where

\[
(3.12) \quad D(N, q) = \prod_i \left( \frac{(n_i + q_i - 1)!}{n_i!(q_i - 1)!} \right) \approx \prod_i \left( \frac{(n_i + q_i)!}{n_i!q_i!} \right),
\]

by taking \( n_i \gg 1, q_i \gg 1 \) and defining \( N_0/q_0 \) as the ratio of the total number of identical atoms and empty lattice sites. Here, \( N_0 = \sum_i n_i, q_0 = \sum_i q_i \), and \( N_0/q_0 \) corresponds to the probability of excited identical particles from their lattice sites, which will tell us the magnitude of ionic conductivity. For example, if some large number of identical atoms can be excited, then this will lead us to large ionic conductivity, which is a telling sign that we are approaching the melting point of a particular solid. Anyway, one of the two restrictive conditions needed to maximize Eq. (3.12) remains the same (Eq. (3.4)) because the total number of particles (atoms) is also conserved. While the condition for the total energy has been renormalized (see Eq. (2.15)),

\[
(3.13) \quad \sum_i \left[ E e^{\frac{i^2}{k m}} \right] n_i = \hbar \sqrt{\frac{k}{m}} = \bar{E},
\]

to imply that the total energy (of the atoms, not electrons) is also conserved. Moreover, we have renormalized the total energy of the identical atoms (\( E \)), not of the electrons, to obtain \( \bar{E} \) so that the electronic polarizability effect is taken into account. This means that the atoms are no longer considered to be the rigid vibrating ions, independent of their surrounding electrons. Somewhat similar to iFDS derived earlier, the new function, \( F_{\text{new}}^0 \) in this case is

\[
(3.14) \quad F_{\text{new}}^0 = \ln D(N_0, q_0) + \alpha \sum_i n_i + \lambda_B \sum_i \left[ E e^{\frac{i^2}{k m}} \right] n_i,
\]

where each \( n \) can take any value such that \( n \in \mathbb{N} \) to imply one empty quantum state (\( q \)) or energy level can accommodate any number of particles. Here, \( \mathbb{N} \) is the
We solve Eq. (3.15) by invoking
\[ \frac{\partial F_{\text{new}}}{\partial n_i} = \frac{\partial \left( \ln D(N_p q_B) \right)}{\partial n_i} + \alpha \sum_i \frac{\partial n_i}{\partial n_i} + \lambda B \sum_i \left[ E_{\text{exc}}^{\lambda} \right] \frac{\partial n_i}{\partial n_i} = 0. \]

We solve Eq. (3.15) by invoking
\[ (\ln (n_i)) \approx n_i \ln(n_i - n_i). \] After some algebraic rearrangements, and taking \( \alpha = 0 \) for convenience because we are concerned with the changes to \( \xi \), we obtain the renormalized Bose-Einstein statistics (rBES)
\[ \frac{N_0}{q_B} = \frac{1}{\exp \left[ \lambda B E_{\text{exc}}^{\lambda} \right] - 1}. \]

The constant, \( \alpha \) denotes the minimum energy prior to any excitation of atoms from their equilibrium lattice sites, somewhat similar to Fermi level for electrons. It is important to note here that \( q_0 \geq N_0 \) is required so that the probability is normalized to one, even if there can be any number of \( n \) particles allowed to occupy a single empty quantum state, \( q_i \). Similar to \( S_\xi, S_0 \in \mathbb{R}^- \).

We are now ready to track the solidification of liquid LiCl from \( T_2 > 610^\circ \text{C} \) to \( T_1 = 552^\circ \text{C} \) as shown in the inset of Fig. 1. In this case, the dominant entropy change is due to the transition from the disordered (liquid) state to an ordered (solid) state in which, the liquid state is defined within \( 610^\circ \text{C} < T \leq T_2 \) and the solid state is bounded within \( T_1 \leq T < 610^\circ \text{C} \). The value \( 610^\circ \text{C} (T_2) \) is the critical point, or the melting point of LiCl and \( S_0^{\text{liquid}} > S_0^{\text{solid}} \) indicates the existence of a TPT, qualitatively that is. To claim liquid has a larger entropy than solid implies we have invoked an additional condition \( |S_0^{\text{liquid}} - S_0^{\text{solid}}| > |S_\xi^{\text{liquid}} - S_\xi^{\text{solid}}| \) because the change of entropy due to electronic excitation is always smaller compared to an atomic-disorder induced entropy (due to broken translational symmetry) within a particular system. Of course, in the absence of this temperature-induced atomic-arrangement asymmetry, electronic disorder or \( S_\xi \) is the dominant one.

 Apparently, the change in the entropy during the above-stated transition (solidification) is a first-order TPT because \( S_0^{\text{liquid}} > S_0^{\text{solid}} \) such that there exist a nonequilibrium entropy \( (S_{\text{non}}) \) that contribute to this inequality, which is classically undefined at the critical point, \( T = T_\theta = 610^\circ \text{C} \) where both solid and liquid phases coexist. However, we can define \( S_{\text{non}} \) with respect to the time-dependent energy-level spacing, \( \xi(t) \) and using Eq. (3.9) at the critical point due to time-dependent processes of breaking and forming of bonds \( q_3 q_2 \) at the solid/liquid interface (we will revisit this issue in detail shortly) for \( T = T_\theta \). In this case, \( \xi \) continuously switches between \( \xi^{\text{liquid}} \) and \( \xi^{\text{solid}} \) for \( T = T_\theta \). Consequently, one cannot write \( S_0^{\text{solid}} < S_{\text{non}} < S_0^{\text{liquid}} \), which in turn implies that solidification and melting are first-order transitions.

4. Renormalized specific heat

Traditionally, a first-order TPT is defined to exist if there is a quantitative discontinuity in the thermodynamic variable. For example, the heat capacity (a thermodynamic variable) is discontinuous at the critical point due to discontinuity in the entropy itself as stated above. Here, the constant-volume heat capacity and entropy relationship can be obtained from
\[ dS = \frac{\frac{dU + PdV}{T}}{T} = \frac{1}{T} \left[ \frac{\partial U}{\partial T} \right]_V + 0 = \frac{C_v}{T} dT, \]
using Eq. (3.1) and the definition, \( C_v = \partial U/\partial T \big|_V \), in which Eq. (4.1) tells us nothing about the changes in \( C_v \) during solidification or at the critical point, except that it diverges [40]. Anyway, on the way to understand the origin of the first order TPT (given above), we have pointed out the existence of time-dependent \( \xi(t) \), which fluctuates between \( \xi_{\text{liquid}} \) and \( \xi_{\text{solid}} \) for \( T = T_\theta \), in the presence of both solid and liquid phases. Now, the above fluctuation in \( \xi \) can be associated to the existence of \( \xi \)QPT at the critical point during the melting or solidification process in such a way that if we continue extracting heat from the LiCl system, then one has the liquid to solid transformation due to \( \xi_{\text{liquid}} \rightarrow \xi_{\text{solid}} \). This freezes LiCl completely. The formation of bonds (or releasing of heat) during solidification occurs continuously with respect to time that involves complete modification of the time-dependent many-body wave function (\( \Psi(t) \)). Within IET formalism, we do not require to know the changes in \( \Psi(t) \), instead, we have \( \xi(t) \) as the fundamental interaction-strength functional, which changes continuously and originates from the chemical constituents of a system. In other words, the chemical composition at the solid/liquid interface changes with time, giving rise to this correspondence rule, \( \Psi(t) \rightarrow \xi(t) \). For a given temperature (\( T \neq T_\theta \)), if the chemical composition is \( t \)-independent (for example, in the solid or liquid phase) but \( r \)-dependent, then \( \Psi(r) \rightarrow \xi(r) \) where \( r \) is the electron coordinate. In our earlier work [9], we have renormalized \( C_v \), that can be exploited here to rewrite Eq. (4.1) for \( T = T_\theta \)

\[
(4.2) \quad d\hat{S}_{\text{eqm}}^{\text{non}}(t) = \frac{\hat{C}_v(t)_{\text{eqm}}}{T_\theta} dt = \frac{C_v(T)}{T_\theta} \exp \left[ -\frac{3}{2} \lambda \xi(t) \right] dt,
\]

which reinforces the logic that any change to the interaction strength during solidification, even though \( T \)-independent at the critical point, never ceases to be \( t \)-dependent, giving rise to \( S_{\text{liquid}} \rightarrow S_{\text{solid}} \) and \( C_v^{\text{liquid}} \rightarrow C_v^{\text{solid}} \) transitions. These \( t \)-dependent transitions, \( \hat{S}_{\text{eqm}}^{\text{non}}(t) \) and \( \hat{C}_v(t)_{\text{eqm}} \), can be readily captured via \( \xi(t) \) without any divergence. In addition to that, we now claim that the solid \( = \) liquid transitions at \( T = T_\theta \) are associated to \( \xi \)QPT. An essential point to note here is that we did not identify \( C_v(T) \) in Eq. (4.2) as the nonequilibrium specific heat at the critical point because \( C_v(T) \) reduces to \( C_v^{\text{liquid}}(T) \) during solidification, whereas, \( C_v(T) \rightarrow C_v^{\text{solid}}(T) \) during melting. We also remind the readers to take note here that unlike \( S_\xi \) and \( S_\beta \), \( \{S_\xi, S_\beta\} \in \mathbb{R}^+ \) because \( \{N/q, N_\beta/q_\beta\} \in (0, 1] \). To those who are not comfortable with \( \{S_\xi, S_\beta\} \in \mathbb{R}^- \), we define an alternative equation

\[
(4.3) \quad S_\xi^+ = k_B \ln \left\{ \frac{q}{\exp \left[ \mu + \lambda (E_0 \pm \xi) \right] + 1} \right\} = k_B \ln N,
\]

which can be obtained from Eq. (3.8) and recall here that \( N \) is the number of excited electrons. Similarly,

\[
(4.4) \quad S_\beta^+ = k_B \ln \left\{ \frac{q_\beta}{\exp \left[ \lambda_B E_\beta^{(1/2)} \xi \right] - 1} \right\} = k_B \ln N_\beta,
\]

in this case, \( N_\beta \) is the number of ions being displaced (or excited) from their crystallographic sites. Apart from Eqs. (4.3) and (4.4), we can also enforce positivity by rewriting Eq. (3.8) such that

\[
(4.5) \quad S_\xi^+ = -k_B \frac{N}{q} \ln \frac{N}{q} \quad \text{and} \quad S_\beta^+ = -k_B \frac{N_\beta}{q_\beta} \ln \frac{N_\beta}{q_\beta},
\]
because if $N_1/q > N_2/q$ and $0 \leq N_{1,2}/q \leq 1$, then
\begin{equation}
- \frac{N_1}{q} \ln \frac{N_1}{q} > - \frac{N_2}{q} \ln \frac{N_2}{q},
\end{equation}
which will guarantee $S_1 \geq S_2$ and $S_1 > S_2$ because $N/q$ increases or decreases faster than $\ln (N/q)$. For example, taking $N = 1$, $q = x$, $f(x) = 1/x$ and $g(x) = \ln (1/x)$, one can write $h[f, g] = (1/x) \ln (1/x)$, subsequently it is straightforward to show $d^2 f/dx^2 > d^2 g/dx^2$ is always true when $x \geq 1$ and $m \geq 1$ where $x \in \mathbb{R}^+$ and $m \in \mathbb{N}^*$. In addition, $S_1 > S_2$ is consistent with increasing entropy if $N/q$ gets larger, and consequently we will always have $\{S_{\xi}(+), S_{\xi}'(+), S_0(+), S_0'\} \in \mathbb{R}^+$ where $\mathbb{R}^+$ and $\mathbb{N}^*$ are the set of real positive numbers and positive integers, including zero, respectively.

In summary, any first-order TPT has got to go through a $C_TQPT$ at constant $T$ such that
\begin{equation}
\lim_{\hbar \to 0} C_TQPT = TPT \text{ and } C_TQPT \supset TPT,
\end{equation}
which means, any first-order TPT is a limiting case in the absence of quantum fluctuations, and therefore $C_TQPT$ is a proper superset of TPT. These two claims are strong, thus we will need to provide logical proofs. The proofs consist of two parts that correspond to two claims. The first one is given above when we discussed the solidification phenomenon for LiCl, establishing the correctness of Statement 1.

**Statement 1**: All first-order TPT must go through a thermal-assisted $C_TQPT$ at constant $T$.

The second proof proves Eq. (4.7), which will be exposed shortly.

5. Finite-temperature continuous quantum phase transition

Thus far, we have exposed the existence of $C_TQPT$ during LiCl solidification at $T = T_\theta$ (see the vertical arrow in the inset of Fig. [1]), which is commonly accepted as a first-order TPT without going into the details of $C_TQPT$. Proving Eq. (4.7) requires one to track $C_TQPT$ or the changes in $\xi(t)$ during solidification for constant $T = T_\theta$.

Alternatively, one may also prove Eq. (4.7) by tracking the horizontal arrow pointing left shown in the inset of Fig. [1] by systematically changing the chemical composition via substitutional doping of Cl with Br and followed by I such that $\text{LiCl} \to \text{LiBr} \to \text{LiI}$ at constant $T = 552^\circ C$, which is the melting point of LiBr. We will first address the $C_TQPT$ occurring during solidification (for constant $T = 610^\circ C$). The above $C_TQPT$ during solidification of LiCl system can be captured by isolating the system right at the critical point $(T_\theta = 610^\circ C)$ as shown schematically in Fig. [3]. Here, the liquid phase Li and Cl are indicated with filled red circles, while the same elements in the solid phase are drawn as blue circles, but we did not bother to completely fill the solid phase with blue circles. Relevant nonequilibrium processes occur at the boundary between these two phases. These processes are due to chemical reactions between the highly-polarized Li (small $\xi_{Li}$) and the least-polarized Cl (large $\xi_{Cl}$) giving rise to the chemical association between them, forming the solid phase, which releases energy as heat ($-Q$) into the liquid phase. This energy transfer increases the kinetic energy of the liquid-phase Li and Cl that will eventually collide onto the solid-particle surfaces with increasing frequency, and thus could transfer this energy ($+Q$) back into the solid phase to initiate chemical dissociation of LiCl solid. These two thermal-assisted processes (due to $\pm Q$) are the causes for this
Both atomic Li and Cl in the liquid phase are denoted with filled red circles, while the blue circles represent the ionic Li and Cl in the solid phase. The two blue islands labeled A and B are solid particles, immersed in the liquid-phase. This system has been deliberately isolated at the critical point when $T = T_\theta = 610^\circ C$ such that the solid phase coexists indefinitely within the liquid phase. The magnified sketch beneath the main diagram shows the temperature differences between the solid phase ($T_{\text{sol}}$) and its surrounding liquid phase ($T_{\text{liq}}$) such that $T_{\text{liq}} > T_\theta > T_{\text{sol}}$ and $T_{\text{liq}} - T_{\text{sol}} \ll T_\theta$. At the boundary, the system is in extreme nonequilibrium where Li or Cl from the liquid phase may react to form a rigid ionic bond, and release heat ($-Q$) as energy. Conversely, the same amount of heat is absorbed ($+Q$) by Li or Cl in the solid phase so as to break free from the solid to liquid phase.

Figure 3. Both atomic Li and Cl in the liquid phase are denoted with filled red circles, while the blue circles represent the ionic Li and Cl in the solid phase. The two blue islands labeled A and B are solid particles, immersed in the liquid-phase. This system has been deliberately isolated at the critical point when $T = T_\theta = 610^\circ C$ such that the solid phase coexists indefinitely within the liquid phase. The magnified sketch beneath the main diagram shows the temperature differences between the solid phase ($T_{\text{sol}}$) and its surrounding liquid phase ($T_{\text{liq}}$) such that $T_{\text{liq}} > T_\theta > T_{\text{sol}}$ and $T_{\text{liq}} - T_{\text{sol}} \ll T_\theta$. At the boundary, the system is in extreme nonequilibrium where Li or Cl from the liquid phase may react to form a rigid ionic bond, and release heat ($-Q$) as energy. Conversely, the same amount of heat is absorbed ($+Q$) by Li or Cl in the solid phase so as to break free from the solid to liquid phase.

thermal-assisted (or finite-temperature) $^C$QPT. In a macroscopic point of view, this particular isolated system, containing both solid and liquid phases, is in equilibrium because the average rate of melting and solidification is the same, hence the solid-to-liquid and liquid-to-solid transitions ($^C$QPT) are in balance. But we need to go deeper to track the physico-chemical processes at the solid|liquid interface, which can be done with IET. For instance, the energy level spacings in the liquid and solid phases are $\xi_{\text{LiCl}}^{\text{liquid}}$ and $\xi_{\text{LiCl}}^{\text{solid}}$, respectively, and since the valence electrons in the liquid phase are all in the excited states (thermally polarized) then this implies $\xi_{\text{liquid}} < \xi_{\text{solid}}$. This inequality is strictly valid because the excited energy-level spacings are always narrower due to weak electron-electron ($e-e$) interaction in the presence of weak electron-nucleus ($e-nuc$) attraction. Conversely, large energy level spacings are inevitable for the energy levels close to the nucleus $[8]$. Substituting $\xi_{\text{LiCl}}^{\text{liquid}} < \xi_{\text{LiCl}}^{\text{solid}}$ into Eq. (4.5) leads to $\text{liq}S^+ > \text{sol}S^+$ and $\text{liq}S^+_D > \text{sol}S^+_D$, which then allow one to correctly conclude $S_{\text{liquid}} > S_{\text{solid}}$ where $S_{\text{liquid}} = \text{liq}S^+_\xi + \text{liq}S^+_D$ and $S_{\text{solid}} = \text{sol}S^+_\xi + \text{sol}S^+_D$. However, as we have noted earlier, $S_{\text{solid}} < S_{\text{eqm}} < S_{\text{liquid}}$ is invalid because we need to take the nonequilibrium effect (at the solid|liquid interface) into account. We now know that this effect occurs maximally at the critical point (when $T = T_\theta$), and at the solid|liquid interface where $S_{\text{non}} = S_{\text{liquid}} + S_{\text{solid}} + S_{\text{face}}$, and therefore $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{eqm}}$ that guarantees the existence of a first-order TPT, while $S_{\text{face}}$ on the other hand, ensures the existence of a $^C$QPT, as well as the coexistence of both solid and liquid phases.
(see Fig. 3). This means that if $S^\text{inter}_{\text{face}} = 0$, then $T \neq T_\theta$ and consequently we have $S^\text{non}_{\text{eqm}} \to S_{\text{liquid}}$ for $T > T_\theta$ or $S^\text{non}_{\text{eqm}} \to S_{\text{solid}}$ for $T < T_\theta$. Using Eq. (4.2), the non-divergent and renormalized

\begin{equation}
\tag{5.1}
\tilde{C}_v(T, t)^\text{non}_{\text{eqm}} = C_v(T) \exp \left\{ -\frac{3}{2} \lambda \left[ \sum_j J_j \xi_{\text{solid}} + (1 - J_j) \xi_{\text{liquid}} \right] \right\},
\end{equation}

in which, we have defined $\xi(t) = \sum_j J_j \xi_{\text{solid}} + (1 - J_j) \xi_{\text{liquid}}$ where $j = \{t_1, t_2, \cdots, t_n\}$, $J = x_{\text{LiCl}}^{\text{solid}}/x_{\text{total}}^{\text{LiCl}}$ and $J \in [0, 1]$. Here, $x_{\text{LiCl}}^{\text{solid}}$ is the number of Li and Cl atoms in the solid phase only, and $x_{\text{total}}^{\text{LiCl}}$ is the total number of Li and Cl atoms in both liquid and solid phases (or in a given system). Moreover, $J$ does not necessarily increase with time, if the heat-exchange fluctuates ($\pm Q$), and the total time between $t_1$ and $t_n$ is the time taken for a complete solidification of liquid LiCl for constant $T = T_\theta$. Equation (5.1) strictly implies that the magnitude of $C_v(t)^{\text{non}_{\text{eqm}}}$ does not change with $T$ only, but also with respect to changes in the interaction-strength parameter, $\xi(t)$. In particular, $\tilde{C}_v(t)^{\text{non}_{\text{eqm}}}$ can change due to changes in $\xi(t)$ from $\xi_{\text{liquid}}$ to $\xi_{\text{solid}}$ during solidification of LiCl liquid. In this latter case, the heat-exchange as depicted in Fig. 3 is solely used to change the interaction strength via $\xi_{\text{solid}} \neq \xi_{\text{liquid}}$.

If one employs an unrenormalized specific-heat equation, then it is always divergent for $T = T_\theta$ because it is undefined at this critical point. On the other hand, Eq. (5.1) is well-defined such that $\xi$ can be exploited at the critical points, without any divergence. For example, $\xi_{\text{liquid}}$ and $\xi_{\text{solid}}$ are constants for $T > T_\theta$ and $T < T_\theta$, respectively, and any heat exchanges that may exist between a given system and its surrounding only decrease or increase the system’s temperature. At the critical point however, the heat exchanges are used only to modify the system’s physico-chemical properties, hence, the system’s temperature remains constant. In other words, the renormalized specific-heat equation (Eq. (5.1)) reduces to

\begin{equation}
\tilde{C}_v^{\text{liquid}}(T) = C_v^{\text{liquid}}(T) \exp \left\{ -\frac{3}{2} \lambda \xi_{\text{liquid}} \right\},
\end{equation}

for liquid LiCl ($T > T_\theta$), and for solid LiCl ($T < T_\theta$), one just need to switch the label “liquid” with “solid” in the equation above. However, neither of these equations can be applied when $T = T_\theta$. We need Eq. (5.1) for $T = T_\theta$. This completes the proof for Statement 1.

If we now follow the horizontal arrow given in the inset of Fig. 3, we can show that both transitions (for vertical and horizontal arrows) are thermal-assisted $\theta$QPT, one occurring during solidification (discussed above for the vertical arrow) and the other originates due to changing chemical composition (at a constant temperature). For example, the first $\theta$QPT at the critical point during solidification (constant $T = T_\theta$) is initiated by the heat-exchange between the liquid and solid LiCl, where $dS = \delta Q/T_\theta$, and from Eq. (3.9),

\begin{equation}
\tag{5.3}
d|S_\xi| = dS = \frac{\delta Q}{T_\theta} = \left| -\frac{(E_0 \pm d\xi) + E_2^{\text{eqm}}}{T_\theta} \right|, \quad |S_\xi| \in \mathbb{R}^+.
\end{equation}

Equation (5.3) correctly implies: (a) increasing absorption of heat in a system increases the entropy of that system, or vice versa, (b) any amount of change in $Q$ ($\delta Q$) or $\xi$ ($d\xi$) corresponds accordingly to a change in entropy, as it should be, however, (c) the entropy of a given system decreases if $\xi$ increases, as strictly required by Eq. (3.9), (d) systems with large $\xi$ need large amount of heat to initiate
changes such as melting, for example, from Table 2, we know \( \xi_{\text{Br}} < \xi_{\text{Cl}} \) and \( T_{\theta}^{\text{LiBr}} < T_{\theta}^{\text{LiCl}} \), and therefore \( T^{\text{LiBr}}_{\theta} < T^{\text{LiCl}}_{\theta} \), and (e) large amount of heat is required to be removed or added to initiate large changes to \( \xi \), for example \( \xi^{\text{LiCl}}_{\text{liquid}} = \xi^{\text{LiCl}}_{\text{solid}} \). Here, \( \xi^{\text{LiCl}}_{\text{liquid}} \) is a constant, while \( Q \) is the amount of heat removed to initiate the change, \( \xi^{\text{LiCl}}_{\text{liquid}} - Q \rightarrow \xi^{\text{LiCl}}_{\text{solid}} \). Therefore, (d) refers to the entropy-change of a system prior to any phase transition, i.e., for constant \( \xi \) and \( T < T_{\theta} \) or \( T > T_{\theta} \). In contrast, (e) reveals the changes in the intrinsic physico-chemical properties of a system due to changing \( \xi \) when \( T = T_{\theta} \). This means that \( d|S_{\xi} \) is only valid at the critical point, or when \( T = T_{\theta} \) because \( \xi \) does not change with \( T \), but it changes significantly when the physico-chemical properties of a given system change.

In order to understand the existence of thermal-assisted \( T_{\theta} \) QPT due to doping (follow the horizontal arrow in the inset of Fig. 3), we increase Br content, replacing Cl for constant \( T \) to obtain a system defined by \( \text{LiCl}_{1-a} \text{Br}_a \). The inequality, \( \xi_{\text{Br}} < \xi_{\text{Cl}} \) implies \( \xi \) decreases with increasing Br content where this doping is carried out for constant \( T = 552^\circ \text{C} \). Now, the critical point can be obtained for \( a_1 = 1 \), and at this point, \( T = T_{\theta} = 552^\circ \text{C} \), which is the melting point of LiBr. As a consequence, if \( \xi^{\text{LiCl}}_{\text{solid}} \rightarrow \xi^{\text{LiBr}}_{\text{solid}} \) is achieved through doping at \( T = T^{\text{LiBr}}_{\theta} \), then \( Q \) activates the melting process, such that \( \xi^{\text{LiBr}}_{\text{solid}} + Q \rightarrow \xi^{\text{LiBr}}_{\text{liquid}} \). However, we point out that \( Q = \xi^{\text{LiBr}}_{\text{liquid}} - \xi^{\text{LiBr}}_{\text{solid}} \) is false. Note here that the above stated doping-induced \( T_{\theta} \) QPT can occur for any constant temperature, and even for \( T = 0K \). For instance, electronic phase transition (metal-to-insulator) due to doping can occur in doped-cuprates at zero Kelvin, giving rise to the usual continuous quantum phase transition (0K QPT), as explained by Sachdev [24]. Nevertheless, Eq. (4.7) remains true for both \( T_{\theta} \) QPT and 0K QPT, in accordance with the proof given for the horizontal arrow of Fig. 1.

Finally, let us now try to understand what is the implication of having \( t \)-dependent \( \xi \) on Eq. (2.7). In view of Eq. (5.1), Eq. (2.7) reads,

\[
\tilde{V}^{\text{e-ion}}_{\text{Coulomb}} (T_{\theta}, t)^{\text{eqm}} = \frac{(-e)(+e)}{4\pi\epsilon_0|\mathbf{r}_A - \mathbf{r}_B|} \times \exp \left\{ - \mu r_A \exp \left[ - \frac{1}{2} \lambda \left( \sum_j \xi^A_j \right) \right] \right\},
\]

and this is the electron-ion potential operator at the melting point. In the solid phase,

\[
\tilde{V}^{\text{e-ion}}_{\text{Coulomb}} (T_{\theta}, t)^{\text{eqm}} \rightarrow \tilde{V}^{\text{e-ion}}_{\text{Coulomb}} (\xi^A_{\text{solid}}),
\]

while in the liquid phase,

\[
\tilde{V}^{\text{e-ion}}_{\text{Coulomb}} (T_{\theta}, t)^{\text{eqm}} \rightarrow \tilde{V}^{\text{e-ion}}_{\text{Coulomb}} (\xi^A_{\text{liquid}}).
\]

As such, it is clear that there is a finite-temperature quantum phase transition from a liquid to a solid phase for a system consisting of (anion-forming) atomic A and (cation-forming) atomic B, due to \( H^{AB}_1 + H^{AB}_1 + \tilde{V}^{\text{e-ion}}_{\text{Coulomb}} (\xi^A_{\text{liquid}}) \rightarrow H^{AB}_1 + \tilde{V}^{\text{e-ion}}_{\text{Coulomb}} (\xi^A_{\text{solid}}) \) as pointed out in the introduction, and in the Further Analyses I.

In summary, the so-called activation energy in this chemical association should be equal to \( Q \), which is required to complete the liquid-to-solid transition, or \textit{vice versa}. In other words, to complete the \( \xi^{\text{LiCl}}_{\text{liquid}} \rightarrow \xi^{\text{LiCl}}_{\text{solid}} \) or \( \xi^{\text{LiBr}}_{\text{liquid}} \rightarrow \xi^{\text{LiBr}}_{\text{solid}} \) transformation, significant changes to the \( t \)-dependent many-body wave function are necessary, for example, \( \Psi(t)^{\text{LiCl}}_{\text{liquid}} \rightarrow \Psi(t)^{\text{LiCl}}_{\text{solid}} \). The existence of such a transformation in \( \Psi(t) \)
has been proven within a new quantum adiabatic theorem developed for chemical reactions [32], which can be used to understand why the wave function of unreacted species need to be combined linearly or written in a different form for the compounds formed after the chemical associations. Interestingly, Müller and Goddard [41] have also pointed out such a case must exist during chemical associations. Thus far, we have exploited the formalism developed for IET such that the only a priori information one required to know is the atomic energy-level spacings listed in Table 2.

6. Further analyses II

Here, we apply Eq. (5.1) to a water-to-ice phase transition during freezing. Figure 4 sketches the specific heat versus temperature curve for constant pressure ($C_p(T)$) for water (see the dashed line). The dashed line denotes the usual $C_p(T)$ curve with a sudden drop ($C_{\text{water}}^p(T) > C_{\text{ice}}^p(T)$) at the freezing point. Whereas, the solid line in Fig. 4 captures the whole mechanism of phase transition from water to ice, including the freezing curve occurring at the freezing point (273.16K). Obviously, the freezing curve is always hidden at the freezing point, and appears as a sudden drop in $C_p(T)$ measurements, when the temperature is lowered. Unfortunately, we do not know the explicit microscopic equation for $C_p(T) = dH/dT|_P$ where $H$ is known as the enthalpy. However, the fundamental energy-level spacing renormalization factor (the exponential term in Eq. (5.1)) for $\tilde{C}_p(T_\theta, t)_{\text{eqm}}$ should remain intact for $\tilde{C}_p(T_\theta, t)_{\text{eqm}}$ such that

$$\tilde{C}_p(T_\theta, t)_{\text{eqm}} = C_p(T) \exp \left\{ -\frac{\eta}{2} \lambda \left[ \sum_j J_j \xi_{\text{ice}} + (1 - J_j) \xi_{\text{water}} \right] \right\}. \tag{6.1}$$

The only change in the renormalizing factor is the numerical constant, 3 in $3\lambda/2$ (see the exponential term in Eq. (5.1)). The constant 3 here is unknown and therefore, we replace it with $\eta$ in Eq. (6.1). This numerical constant, $\eta$ can only be obtained by solving $C_p(T) = dH/dT|_P$, but it is irrelevant here. What we actually need are the renormalized specific heats for water and ice,

$$\tilde{C}_p^{\text{water}}(T) = C_p^{\text{water}}(T) \exp \left[ -\frac{\eta}{2} \lambda \xi_{\text{water}} \right], \tag{6.2}$$

$$\tilde{C}_p^{\text{ice}}(T) = C_p^{\text{ice}}(T) \exp \left[ -\frac{\eta}{2} \lambda \xi_{\text{ice}} \right]. \tag{6.3}$$

In Eqs. (6.2) and (6.3), only $C_p^{\text{water}}(T)$ and $C_p^{\text{ice}}(T)$ are $T$-dependent variables, and the rest are just $T$-independent variables or constants. This means that Eq. (6.2) captures the specific heat for water, whereas, Eq. (6.3) is for ice (see the dashed and solid lines for water and ice in Fig. 4). The sketched freezing curve however, follows Eq. (6.1), and is smooth here, implying there is no fluctuation in $Q$ during freezing, i.e., there is a continuous extraction of heat from the water-ice system. Recall here that the freezing curve in Fig. 4 is not observable from the $C_p$ versus $T$ measurements alone, but exists as a sudden drop in the specific heat for $T = 273.16K$ (freezing point) because $C_{\text{water}}^p(T) > C_{\text{ice}}^p(T)$ or $\xi_{\text{water}} < \xi_{\text{ice}}$. This is the reason why temperature is not a proper variable to monitor at the freezing point of any thermally-driven finite-temperature continuous quantum phase transition. To those who are not comfortable with this reason, we aggravate the situation.
by claiming— in any quantum matter, Eq. \(6.1\) proves that there is no such thing as Landau first-order transition.

In summary, we have proven that \(\xi(t)\) is the proper quantum variable to capture what is really happening at the freezing point. For example, at the freezing point, the heat that is being extracted from the water-ice system, activates the energy-level spacing transformation, \(\xi_{\text{water}} \rightarrow \xi_{\text{ice}}\) or the wave function transformation \(\Psi_{\text{water}} \rightarrow \Psi_{\text{ice}}\) due to the formation of permanent hydrogen bonds. This transformation results in \(C_{p\text{water}}(T) > C_{p\text{ice}}(T)\) that implies \(\xi_{\text{water}} < \xi_{\text{ice}}\). The latter inequality has its origin in hydrogen bonds. For example, both \(\xi_{\text{water}}\) and \(\xi_{\text{ice}}\) refer to the energy-level spacings due to hydrogen bonds, and not due to covalent bonds between \(O\) and \(H\) in a \(H_2O\) molecule. Obviously, the energy-level spacings due to hydrogen bonds are larger for ice compared to water because the hydrogen bonds in ice is permanently bonded (static) and therefore, its strength is larger in ice than in water. The hydrogen bonds in water phase is dynamic such that the bonds are broken and formed randomly. As such, indeed \(\xi_{\text{water}} < \xi_{\text{ice}}\). Now for the water vapor, all \(H_2O\) molecules are isolated, and they do not form any hydrogen bond. As a result, \(\xi_{\text{vapor}}\) refers to the energy-level spacings due to covalent bonds (between \(O\) and \(H\)) within a \(H_2O\) molecule. Since covalent bonds are much stronger than hydrogen bonds, one has \(\xi_{\text{water}} < \xi_{\text{ice}} < \xi_{\text{vapor}}\) that correctly corroborates with the experimental observations \([42, 43, 44]\), \(C_{p\text{water}} (4.187 \text{kJkg}^{-1}\text{K}^{-1}) > \overline{C_{p\text{ice}} (2.108}\)
kJkg\(^{-1}\)K\(^{-1}\) > C\(_v\)\(^{\text{apor}}\) (1.996 kJkg\(^{-1}\)K\(^{-1}\)). This concludes our analytical proofs and technical analyses on H\(_2\)O system, again supported by experimental results.

7. Conclusions

We first entered into the realm of thermodynamics and statistical mechanics to show that all thermal phase transitions occurring in any matter is a proper subset of quantum phase transition, even though at times, it is convenient to ignore the quantum effects, for example during the transition from a solid to liquid phase. We went on to renormalize the entropy and the Bose-Einstein statistics solely to prove the existence of the non-divergent specific heat capacity at the critical point via the energy level spacing renormalization method. At the critical point, the thermal energy is used to change the energy-level spacing of a system, which in turn changes the physico-chemical properties of that system. Those properties are of course different if the system is in solid phase, compared to liquid. The critical points we chose to investigate were the melting points of single-valent ionic bonded salts.

Here, we have formally shown that the finite-temperature continuous quantum phase transition (\(C\_T^{\text{QPT}}\)) is responsible for the thermal phase transition during melting and solidification processes, as well as during substitutional doping at a constant temperature. Along the way, we also have proven that the first-order transition in the constant-pressure specific heat between water and ice satisfies a \(C\_T^{\text{QPT}}\). In view of the analyses for alkali halide salts and water-ice system, we found that the \(C\_T^{\text{QPT}}\) is responsible for the liquid–solid and water–ice phase transitions, supported by experimental results. In addition, we have given sufficient proofs to claim that all first-order thermal phase transitions are equivalent to finite-temperature quantum phase transitions, which will lead us to the unification of thermodynamics and quantum mechanics.

The formal proofs developed herein allow one to obtain the precise physical mechanisms involved right at the melting point of a given solid, beyond the usual physics of a discontinuous thermal phase transition. In other words, our approach avoids the diverging thermodynamic variables (when \(T \to T_c\)) at critical points \((T_c)\), which are usually in the form of \(1/(T - T_c)^a\) where \(a\) is some constant. For example, we have been able to formally prove the existence of a finite-temperature quantum phase transition due to some wave function transformations (giving rise to changing ionization energies) during the melting of alkali halides, and also when water freezes over. This means that one can gain a far more detailed understanding of the physical phenomena occurring at a critical point as a result of quantum effects (namely, wave function transformations that give rise to a quantum phase transition).

In particular, we have shown that the discontinuous thermal phase transition is actually a continuous quantum phase transition, which is observable as an electronic phase transition. This electronic phase transition is the cause for the solid-to-liquid (or liquid-to-solid) and liquid-to-gas (or gas-to-liquid) transformations with well defined (non-divergent) thermodynamical properties at the critical points. Moreover, we found that the theoretical predictions extracted from the proofs are very well supported by the experimental results obtained from the alkali halides, namely, the atomic ionization energies, melting points and diatomic bonding energies. For
water and ice, we had the constant-pressure specific heats and atomic ionization
energies in complete agreement with the time-dependent specific heat formula.

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8. Appendix

8.1. Renormalization of Eq. (2.4). The renormalization of Eq. (2.4) is straight-
forward where we substitute all \( k \) (interaction potential constant (also known as
the spring constant)) with Eq. (2.8) to obtain

\[
\tilde{E} = \frac{1}{2} \hbar \left[ \sqrt{\frac{k - (e^2/2\pi\epsilon_0 R^3)}{m}} + \sqrt{\frac{k + (e^2/2\pi\epsilon_0 R^3)}{m}} \right].
\]  
(8.1)

Any variable found to wear a tilde, here or in the text, is a renormalized parameter.

8.2. Derivation of Eq. (2.6). We start from Eq. (8.1) and expand it in series in
the form of \( \sqrt{1 + x} = 1 + x/2 - x^2/8 + x^3/16 - \cdots \),

\[
\tilde{E} = \frac{1}{2} \hbar \left[ \frac{\sqrt{k - (e^2/2\pi\epsilon_0 R^3)}}{m} + \frac{\sqrt{k + (e^2/2\pi\epsilon_0 R^3)}}{m} \right]
\]  
(8.2)

Substituting \( \tilde{\omega}_0 = \sqrt{k/m} \) into Eq. (8.2) and noting that \( x = \mp (e^2/2\pi\epsilon_0 R^3 k) \),

\[
\tilde{E} = \frac{1}{2} \hbar \tilde{\omega}_0 \left\{ \left[ 1 + \frac{1}{2} \left( -\frac{e^2}{2\pi\epsilon_0 R^3 k} \right) \right] - \frac{1}{8} \left( -\frac{e^2}{2\pi\epsilon_0 R^3 k} \right)^2 + \frac{1}{16} \left( -\frac{e^2}{2\pi\epsilon_0 R^3 k} \right)^3 - \cdots \right\}
\]  
(8.3)

It is clear from Eq. (8.3) that all the terms with odd powers \( (x^{1,3,5,\cdots}) \) cancel out,
and the terms with only even powers, \( x^{2,4,6,\cdots} \) survive. Consequently, we just need to
impose the condition, \( k \exp[\lambda \xi] \gg (e^2/2\pi\epsilon_0 R^3) \), which means \( (e^2/2\pi\epsilon_0 R^3)^n k^{n-3} \approx 0 \)
for all \( n \geq 4 \) where \( n \in \mathbb{N}_{\text{even}} \). Here, \( \mathbb{N}_{\text{even}} \) is the set of even natural numbers. After
To see if there is any (repulsive or attractive) interaction between the two identical and neutral atoms (see Fig. 2(A)) as a result of $H_1$, we need to subtract $\hbar \tilde{\omega}_0$ (the solution for $H_O$) from $\tilde{E}$ (the solution for $H_O + H_1$) such that

$$\tilde{E}(\xi) - \hbar \tilde{\omega}_0 = \hbar \tilde{\omega}_0 \left\{ \frac{1}{2} \left[ 2 - \frac{1}{4k^2} \left( \frac{e^2}{2\pi\epsilon_0 R^3} \right)^2 \right] - 1 \right\}$$

(8.5)

We now substitute $\tilde{k}^2 = \tilde{\omega}_0^2 m^2$ and then followed by the substitution [9], $\tilde{\omega}_0 = \omega_0 \exp \left\{ \frac{1}{2} \lambda \xi \right\}$ into Eq. (8.5) to arrive at

$$\tilde{E}(\xi) - \hbar \tilde{\omega}_0 = \tilde{V}_{\text{Waals}}^{\text{std}}(\xi) = \left\{ - \frac{\hbar}{8m^2 \omega_0^3} \left( \frac{e^2}{2\pi\epsilon_0 R^3} \right)^2 \frac{1}{R^6} \right\} \exp \left\{ - \frac{3}{2} \frac{\lambda \xi}{2} \right\}.$$ 

(8.6)

The negative sign in Eq. (8.6) implies there is an attractive interaction, and this is the van der Waals attraction in its renormalized form. But Eq. (8.6) is only valid for small polarization, made sure by the condition [37], $k \exp[\lambda \xi] \gg (e^2/2\pi\epsilon_0 R^3)$. For large polarization, which is necessary at melting points, we take $k \exp[\lambda \xi] \approx (e^2/2\pi\epsilon_0 R^3)$ and this leads us to rewrite [37] Eq. (8.1),

$$\tilde{E}(\xi)' - \hbar \tilde{\omega}_0 = \frac{1}{2} \hbar \sqrt{2k/m}.$$ 

(8.7)

Hence, the van der Waals attraction in the presence of large polarization [37],

$$\tilde{E}(\xi)' - \hbar \tilde{\omega}_0 = \tilde{V}_{\text{Waals}}^{\text{std}}(\xi) = \frac{1}{2} \hbar \sqrt{\frac{2k}{m}} - \hbar \tilde{\omega}_0.$$ 

(8.8)

Again, noting that $\tilde{k} = k \exp[\lambda \xi]$ and $\tilde{\omega}_0 = \omega_0 \exp[\frac{1}{2} \lambda \xi]$, we can simplify Eq. (8.8),

$$\tilde{E}(\xi)' - \hbar \tilde{\omega}_0 = \hbar \omega_0 \left( \frac{1}{\sqrt{2}} - 1 \right) \exp \left\{ \frac{1}{2} \lambda \xi \right\}.$$ 

(8.9)

Since the attractive interaction is mutual between two identical and neutral atoms, we can then average their contributions by rewriting Eq. (8.9),

$$\tilde{E}(\xi)' - \hbar \tilde{\omega}_0 = \frac{1}{2} \hbar \omega_0 \left( \frac{1}{\sqrt{2}} - 1 \right) \left\{ \exp \left\{ \frac{1}{2} \lambda \xi_A \right\} + \exp \left\{ \frac{1}{2} \lambda \xi_B \right\} \right\},$$

(8.10)

and this is Eq. (2.6).
8.3. Derivation of Eq. (2.5). The attractive interaction captured in Eq. (8.10) is due to large polarization in the absence of Coulomb repulsion between the polarized electrons \(^{[37]}\). If we include the Coulomb repulsion, then we strictly require \(\tilde{V}_{\text{Coulomb}} < |\tilde{V}_{\text{Waals}}(\xi)|\) (see Eqs. (8.11) and (8.10)) where,

\[
\tilde{V}_{\text{Coulomb}} = \frac{1}{2} \frac{(-e)(-e)}{4\pi\varepsilon_0 |\mathbf{r}_A - \mathbf{r}_B|} \left[ \exp \left( -\mu (r_A + r_B)e^{-\frac{1}{2}\lambda \xi A} \right) \right. \\
+ \left. \exp \left( -\mu (r_A + r_B)e^{-\frac{1}{2}\lambda \xi B} \right) \right].
\]

(8.11)

Now to guarantee an attractive interaction without the additional condition, \(\tilde{V}_{\text{Coulomb}} < |\tilde{V}_{\text{Waals}}(\xi)|\), we need to eliminate the Coulomb repulsion given in Eq. (8.11) by imposing an asymmetric polarization as depicted in Fig. 2(B). This asymmetric polarization is obtainable between a cation and an anion where the attraction is between the anion (ion A, charge +) and the outer electron (e, charge \(-e\)) of a cation (ion B) \(^{[37]}\) such that

\[
\tilde{V}_{\text{e-ion}}_{\text{Coulomb}} = \frac{1}{2} \frac{(-e)(+e)}{4\pi\varepsilon_0 |\mathbf{R}_A - \mathbf{r}_B|} \left[ \frac{1}{|\mathbf{R}_A - \mathbf{r}_B|} \exp \left( -\mu r_A e^{-\frac{1}{2}\lambda \xi A} \right) \right. \\
+ \left. \frac{1}{|\mathbf{R}_B - \mathbf{r}_A|} \exp \left( -\mu r_B e^{-\frac{1}{2}\lambda \xi B} \right) \right].
\]

(8.12)

Obviously, the second term in the curly bracket on the right-hand side of Eq. (8.12) is zero and the factor, 1/2 disappears because the attraction now is unidirectional. This means that the outer electron of the easily polarizable cation (B) is attracted to an anion (A), which has the least polarizable electron, i.e., the Coulomb repulsion has been eliminated. Putting Eqs. (8.10) and (8.12) together gives Eq. (2.5).

8.4. Derivation of Eq. (3.8). Technically, it is easier to work with sums (\(\sum_i\)) compared to products (\(\prod_i\)), and therefore, we convert

\[
\Omega(N,q) = \prod_i \frac{q_i!}{n_i!(q_i - n_i)!} \rightarrow \ln \Omega(N,q) = \sum_i \ln \frac{q_i!}{n_i!(q_i - n_i)!}.
\]

(8.13)

As a consequence,

\[
\ln \Omega(N,q) = \sum_i \ln q_i! - \ln n_i! - \ln(q_i - n_i)!.
\]

(8.14)

Note here that this conversion does not disturb the “exactness” of the derivation in any way because we are interested in the maximum of \(\Omega(N,q)\), not in its absolute value such that

\[
\frac{\partial}{\partial n_i} \left[ \ln \Omega(N,q) \right] = 0 = \frac{\partial \Omega(N,q)}{\partial n_i}.
\]

(8.15)

Using Stirling’s approximation, we can write \(\sum_i \ln n_i! = \sum_i n_i \ln n_i - n_i, \sum_i \ln q_i! = \sum_i q_i \ln q_i - q_i\) and \(\sum_i \ln(q_i - n_i)! = \sum_i (q_i - n_i) \ln(q_i - n_i) - (q_i - n_i)\), substituting
We now recall Eq. (3.15) will lead us to
\[
\ln \Omega(N, q) = \sum_i \left\{ q_i \ln q_i - q_i - (n_i \ln n_i - n_i) - [(q_i - n_i) \ln(q_i - n_i) - (q_i - n_i)] \right\}
\]
(8.16)
\[
= \sum_i \left\{ q_i \ln q_i - n_i \ln n_i - q_i \ln(q_i - n_i) + n_i \ln(q_i - n_i) \right\},
\]
The next step is
\[
\frac{\partial [\ln \Omega(N, q) \ln]}{\partial n_i} = \sum_i \left\{ 0 - \left[ n_i \frac{1}{n_i} + \ln n_i \right] - \left[ q_i \frac{1}{q_i - n_i} + 0 \right] + \left[ n_i \frac{1}{q_i - n_i} + \ln(q_i - n_i) \right] \right\}
\]
(8.17)
\[
= \sum_i \left\{ -1 - \ln n_i + \ln(q_i - n_i) + \left[ \frac{q_i}{q_i - n_i} - \frac{n_i}{q_i - n_i} \right] \right\}
\]
We now substitute Eq. (8.17) into Eq. (3.7)
\[
\frac{\partial F_{\text{new}}}{\partial n_i} = \sum_i \ln \frac{q_i - n_i}{n_i} + \mu \sum_i \frac{\partial n_i}{\partial n_i} + \lambda_B \sum_i (E_0 \pm \xi) \frac{\partial n_i}{\partial n_i}
\]
(8.18)
\[
= \sum_i \left\{ \ln \frac{q_i - n_i}{n_i} + \lambda_B (E_0 \pm \xi) \right\} + \mu = 0.
\]
After summing over all the particles \(n_i\) and quantum states \(q_i\), one gets
\[
\ln \frac{q - N}{N} = -\mu - \lambda_B (E_0 \pm \xi), \quad \frac{N}{q - N} = \exp[\mu + \lambda_B (E_0 \pm \xi)],
\]
(8.19)
\[
\frac{N}{N(q/N - 1)} = \exp[\mu + \lambda_B (E_0 \pm \xi)].
\]
Equation (8.19) leads straight to Eq. (3.8) after replacing \(\mu = -\mu\) and \(\lambda_B = -\lambda_B\).
These replacements are necessary to make sure \(\lim_{\mu \to \infty} \lim_{\lambda_B \to -\infty} N/q = 0\).

8.5. **Derivation of Eq. (3.16).** The derivation here is similar to Eq. (3.8), hence we can skip the conversion (\(\prod_i \to \sum_i \ln\)) and the Stirling’s approximation, and start from
\[
\frac{\partial [\ln \mathcal{D}(N_b, q_b)]}{\partial n_i} = \sum_i \frac{\partial}{\partial n_i} \left\{ n_i \ln(n_i + q_i) + q_i \ln(n_i + q_i) - n_i \ln n_i - q_i \ln q_i \right\}
\]
\[
= \sum_i \left\{ \left[ \frac{n_i}{n_i + q_i} + \ln(n_i + q_i) \right] + \left[ \frac{q_i}{n_i + q_i} + 0 \right] - \left[ n_i \frac{1}{n_i} + \ln n_i \right] - 0 \right\}
\]
\[
= \sum_i \left\{ \ln(n_i + q_i) - \ln n_i + \frac{n_i}{n_i + q_i} + \frac{q_i}{n_i + q_i} - 1 \right\}
\]
(8.20)
\[
= \sum_i \ln \frac{n_i + q_i}{n_i}.
\]
We now recall Eq. (3.15)
\[
\frac{\partial F_{\text{new}}}{\partial n_i} = \sum_i \left\{ \ln \frac{n_i + q_i}{n_i} + \alpha \frac{\partial n_i}{\partial n_i} + \lambda_B [E e^{\frac{\lambda{\xi}}{2}}] \frac{\partial n_i}{\partial n_i} \right\} = 0.
\]
After summing over,

\[
\ln \frac{N_0 + \phi_0}{N_0} + \alpha + \lambda_B \left[ Ee^{\frac{1}{2} \lambda \xi} \right] = 0.
\]  

(8.22)

Subsequently, we get

\[
\frac{N_0}{N_0(1 + \phi_0/N_0)} = \exp \left[ \alpha + \lambda_B Ee^{\frac{1}{2} \lambda \xi} \right].
\]  

(8.23)

Equation (8.23) is nothing but Eq. (3.16), after replacing \( \alpha = -\alpha \) and \( \lambda_B = -\lambda_B \).

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