Generalised Ramachandran pairing interaction in helium-4 and helium-3 superfluids

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Abstract. We make use of the ionisation energy theory, Ramachandran interaction theory and the energy-level spacing renormalisation group technique to extend the Drude Hamiltonian to derive the Ramachandran pairing mechanism. This particular mechanism is exploited to explain the notorious discontinuous jumps in the specific heat data at critical points in both He-4 and He-3 superfluids. The well-known spin states (due to Balian–Werthamer and Anderson–Brinkman–Morel theories) and the Leggett's spontaneously broken spin-orbit symmetry are shown to enhance Ramachandran attraction between two He-3 atoms without the need to invoke the spin-induced pairing or the phonon-mediated Cooper pairing mechanism in superconductors. In addition, we shall show physically that the spin-exchange mechanism can neither cause pairing between electrons nor between He-3 atoms.

1. Introduction

The correct spin-related and Bose–Einstein physics needed to explain the superfluid phases in both helium-3 (He-3) and helium-4 (He-4) were reported by many researchers [1,2]. But the problem remains as to the identification of the proper and correct interaction term that causes (or responsible for the formation of) superfluidity in both He-4 and He-3. We shall derive the physical mechanism for superfluidity in He-4 and He-3, and explain why the mechanism stays the same for both due to the contribution made by the outer electrons in each He-4 and He-3 atoms. This mechanism is shown to be valid in the presence of these known contributions from Bose–Einstein condensation in He-4 superfluid [1–7], as well as the contributions made by the composite integer neutron spin states and the Leggett's spontaneously broken spin-orbit symmetry in He-3 superfluid.

Our proposition here reads as the interaction between two spin-$\frac{1}{2}$ neutrons in each nucleus (of a He-3 atom) and the Leggett's spontaneously broken spin-orbit symmetry do not cause superfluidity. Instead, they remove the obstacles that have prevented the formation of superfluid phase(s) in He-3. For example, integer nuclear spin

and the Leggett's broken symmetry have removed the obstacle originating from the spin-$\frac{1}{2}$ interaction between two neutrons where each of this neutron is from each He-3 atom. In other words, superfluidity is actually activated by some outer electron-induced interaction between He-3 atoms, but this interaction cannot be properly activated due to the two quantum phenomena, namely, the half-integral spin and the spin-orbit symmetry. For He-3 to pair with another He-3, we require an integral spin for the pair, and for certain temperatures and pressures, we also need the spin-orbit symmetry to be broken as an additional condition, as discovered by Leggett.

The said phenomena are known as obstacles (not the causes for superfluidity) that have been correctly captured by the Anderson–Brinkman–Morel (ABM) and the Balian–Werthamer (BW) spin states that demand the composite (or total) nuclear spin in the superfluid phases of He-3 to be an integer (ferromagnetic), including zero (antiferromagnetic), as well as the spin-orbit symmetry to be spontaneously broken for certain temperatures and pressures. These obstacles do not exist in He-4 liquid because the total spin within the nucleus of a He-4 atom and the total spin for the outer electrons in each He-4 atom is always an integer. Hence,

He-4 can Bose condense to form bosons due to Bose–Einstein condensation (BEC), but then BEC does not and cannot automatically activate or imply superfluidity [2,8,9]. This means that, the interaction between outer electrons between two He-4 atoms has to play the pivotal role in the transition from normal liquid to superfluid. In particular, when the maximum interaction between two He atoms is activated, then this pair has to interact minimally or not at all with other He atoms or with other similar pairs. Hence, we shall deal essentially with a two-body problem here. It is worth noting that the first proposition of He-4 atoms pairing can be traced back to Bogoliubov [10] even before the invention of Cooper pairs in BCS theory.

In fact, the pairing of two or more He-4 atoms [11], and even the popular two-fluid model assumes the existence of superfluidity to formulate the excitation properties of the superfluid [12]. Therefore, the microscopic origin of the discontinuous jump at the critical point observed in the specific heat data still remains as an unsolved problem. Here, we provide the proper pairing mechanism between two He-4 atoms by taking the polarisation effect of the outer or valence electrons for each atomic He-4 to solve this problem such that BEC is indeed physically permitted so that three or more-body interaction is automatically ruled out.

To understand the importance of the said interacting outer electrons, we need to realise that unlike photons or any other elementary particle bosons, He-4 atoms are not elementary particle-like neutral bosons due to electronic polarisability of He-4 atoms leading to a repulsive interaction between He-4 atoms, and they are not yet bosons, until BEC is activated because each He-4 atom has two polarisable outer electrons that need to interact in such a way that can allow BEC at a certain critical temperature (usually at a very low temperature). Similarly, He-3 is a neutral fermion, but again the outer electrons in He-3 atoms are polarised, giving rise to a repulsive interaction between He-3 atoms. At low enough temperatures, He-3 atom's spin-$\frac{1}{2}$ effect becomes significant when the repulsive outer electrons between He-3 atoms is negligible, thus BEC is not possible, until He-3 atoms can overcome the spin-$\frac{1}{2}$ effect.

Compared to He-3, He-4 atoms can Bose condense without any significant obstacle to the formation of He-4 superfluid where the only primary obstacle originates from the repulsive outer electron interaction between two or more He-4 atoms. These polarised outer electrons also determine the precise mechanism that is responsible for generating superfluid phase(s) in He-3 and He-4 atoms. Here and elsewhere, note that the term, 'polarised outer electrons' means that the atoms are polarised due to the electronic polarisation of each atom's outer electrons. Consequently, both He-4 and He-3 atoms are repulsive due to the polarised outer electrons, which needs to be converted into an attractive interaction to activate pairing of some sort between He-4 atoms and between He-3 atoms. The pairing of He-4 atoms is straightforward, whereas the pairing of He-3 atoms needs to satisfy additional requirements such as integer spin and the Leggett's spontaneously broken spin-orbit symmetry (for some temperatures and pressures). These requirements actually act as the obstacles that have prevented the formation of superfluid phases in He-3 atoms at a temperature closer to He-4.

There are two superfluid phases for He-3 atoms, one of them is known as the BW spin state (or the B-phase of superfluid He-3), which refers to the *p*-wave triplet pairing states, namely, $\uparrow\uparrow$, $\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$ and $\downarrow\downarrow$. Hence, the *p*-wave pairing wave functions read as

$$\Psi_{\text{pair}}^{\text{BW}} = \psi_+(\mathbf{r})\,\uparrow\uparrow, \quad \Psi_{\text{pair}}^{\text{BW}} = \psi_0(\mathbf{r})\left[\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)\right]$$

and

$$\Psi_{\text{pair}}^{\text{BW}} = \psi_-(\mathbf{r})\,\downarrow\downarrow .$$

These wave functions treat each He-3 atom as a proper fermion without taking into account the effect of outer electrons between the paired He-3 atoms. Here, $\mathbf{r}$ is the standard relative coordinate, while the said interaction (due to outer electrons between two He-3 atoms) is supposed to be captured by the following wave functions, $\psi_+(\mathbf{r})$, $\psi_0(\mathbf{r})$ and $\psi_-(\mathbf{r})$ and/or the relevant interaction term.

The interaction term that is needed to evaluate the electron–electron interaction between two He-3 atoms are yet to be found because $\psi_+(\mathbf{r})$, $\psi_0(\mathbf{r})$, $\psi_-(\mathbf{r})$ and the interaction term (between He-3 atoms) themselves were treated as guessed functions with no direct relation to electrons. Guessed functions here mean constructed mathematical functions, including wave functions or any formulas that contain one or more adjustable parameters. The other spin state, which is known as the ABM spin state, refers to the A-phase of superfluid He-3. In this second phase, the pairing states are composed of $\uparrow\uparrow$ and $\downarrow\downarrow$ spin states where $\Psi_{\text{pair}}^{\text{ABM}} = \psi_+(\mathbf{r})\uparrow\uparrow + \psi_-(\mathbf{r})\downarrow\downarrow$. Here, the electron–electron interaction between He-3 atoms in the A-phase has remained unknown and undefined with respect to the formation of superfluid. Keep in mind that these spins ($\uparrow$ and $\downarrow$) belong to the neutrons from two He-3 nuclei, not to their outer electrons. In the presence of applied magnetic field, the symbolic wave function, $\Psi_{\text{pair}}^{\text{ABM}} = \psi_+(\mathbf{r})\uparrow\uparrow + \psi_-(\mathbf{r})\downarrow\downarrow$, automatically reduces to $\Psi_{\text{pair}}^{\text{ABM}} = \psi_+(\mathbf{r})\uparrow\uparrow$, leading us to the A$_1$ superfluid phase.

Before we begin our analysis on the superfluid phases of He-3, we shall first justify our proposed electron–electron interaction between He atoms (caused by the outer electrons) and how it is responsible for the superfluidity by first applying it to He-4 liquid. In other words, He-4 is our reference system that shall be exploited to study the influence of electron–electron interaction such that the said interaction shall be proved to be the cause for superfluidity in both He-4 and He-3 liquids separately. In our subsequent analysis, we shall apply the derived interaction to both He-4 and He-3 to evaluate the specific heat capacity jump at their respective critical temperatures.

The superfluid critical temperature for He-4 is called the lambda temperature, T_λ, which is about 2.2 K [13]. The superfluid critical temperature for He-3 is approximately 0.0026 K (2.6 mK) [13]. The generalised mechanism presented here also invalidates the claim made in ref. [13], that 'any other mechanism leading to attraction between electrons at the Fermi surface (of a solid) is equally well suited for producing superconductivity'. For example, even at the outset, this claim falsely assumes that the electrons at the Fermi surface are absolutely free. Absolutely free electrons have no repulsive interaction between Fermi-surface electrons and also, the scattering of Fermi-surface electrons by phonons is ignored.

In particular, we have no other choice but to invoke the BCS Cooper pairs in its original form, to overcome the Coulomb repulsion between electrons and the scattering caused by the phonons to eventually produce superconductivity [14]. It is worth mentioning that in ref. [14], the solutions to the strange metallic phase (based on the ionisation energy theory (IET) formalism) and the transition to superconductivity (based on the Bardeen–Cooper–Schrieffer (BCS) theory extended within IET formalism) were derived contrary to the suggestions (to solve superconductivity problem) made in ref. [15]. Apart from that, one can also evaluate the Raman effect [16] and the structural phase transition [17] in cuprates for various doping unambiguously with IET.

As a matter of fact, methods similar to refs [15,18,19] that need adjustable and guessed wave functions shall not be considered here because these approaches that make use of the said wave functions cannot automatically imply first-principles approach because the wave function is always a guessed function with adjustable parameters, except for atomic hydrogen. In addition, no other attraction proposed thus far has been theoretically justified or proven to overcome these two ultimate phenomena, Coulomb repulsion and electron–phonon scattering, in any solids.

Now, both He-4 and He-3 superfluids are unique compared to other interacting liquids [20–22] due to the special contribution made by the outer electrons when the temperature is very low to produce superfluidity. Unfortunately, this contribution has been ignored or sidestepped. For example, the only attraction (between He atoms) considered to occur is the van der Waals (vdW) type that can be obtained from the repulsive interaction between He-4 atoms [23]. And then, we also have the so-called Aziz potential [24] and its improved version [24] that can handle the interatomic interaction between two or more He-4 atoms in the normal phase. However, refs [23,24] neither studied nor provided the essential physics of superfluidity, namely, as to why and how this vdW attraction [23] or the Aziz potential [24] can cause or can be responsible for superfluidity. For example, their discussion was to prove the existence of vdW attraction between two repulsive helium atoms [23], as well as to study the changes to the interaction energy between helium atoms [24], both in the normal phase of liquid helium. In contrast, in this work, the said outer-electron contribution shall be properly taken into account to expose the complete mechanism of superfluidity in both He-4 and He-3 liquids.

It is worth noting here that apart from the London brothers [25,26] and Landau's [27] contributions to the understanding of He-4 superfluid based on plausibility arguments, Feynman and Cohen's [15] contributions are quantum mechanical, but their arguments relied on this assumption from the start – He-4 atoms are quantum mechanical Bose liquid below T_λ due to BEC, which is not entirely incorrect (see the following paragraph). Feynman and Cohen further assumed that for $T > T_\lambda$, He-4 atoms collectively represent an ideal Bose gas (or free Bose particles) in accordance with the proposal originally made by the London brothers [25].

The above Feynman–London assumptions, which are related to the BEC-induced transition from ideal Bose to quantum-mechanical Bose liquid, has one fundamental problem as correctly realised by Feynman and Cohen in ref. [15] – the said transition cannot explain the discontinuous jump in the specific heat data at $T = T_\lambda$. This means that, as correctly pointed out earlier in the first paragraph, the origin of phase transition from the normal He-4 liquid to superfluid remains unknown because BEC of He-4 atoms on its own cannot produce the discontinuous jump in the specific heat for $T = T_\lambda$.

The missing physics associated with the origin of the above-stated discontinuity should be obvious even from the outset because the London brothers, Landau and Feynman neither identified nor derived the proper interatomic interaction energy between He-4 atoms, and consequently, they could not deduce the

required physical mechanism responsible for the phase transition to produce He-4 superfluid. In the absence of this microscopic interaction energy, it is not surprising that Feynman had no other choice but to surmise that He-3 requires physics [15] different from that of He-4 Bose liquid with BEC, to the extent that Feynman also believed He-3 liquid cannot form superfluid [15].

Fortunately, Feynman correctly believed in the claim made by one of the London brothers [26], which is related to the application of zero-point energy to explain why He-4 superfluid cannot form solid when $T \rightarrow 0$ K. The said claim shall be proved to be correct here. In particular, for $T = 0$ K, the zero-point energy contribution made by He-4 atoms cannot be negligible even in the presence of the correct interatomic interaction between He-4 atoms, for otherwise, He-4 atoms should condense to form non-bonded solid when $T \rightarrow 0$ K. In other words, finite zero-point energy is a necessary condition to prevent He-4 superfluid from condensing into a non-bonded solid (a solid without chemical bonds).

In this work, we shall also explain the required physical condition(s) for He-4 atoms to form non-bonded solid, as well as the condition(s) that permit He-4 atoms to remain superfluid when the temperature approaches 0 K. As for the origin of superfluidity in He-4 liquid, it remains unsolved with respect to finding the microscopic mechanism for the interaction between He-4 atoms [11,15,28–31]. The same situation exists for He-3 liquid, and we shall begin our exposition for the superfluidity of He-4 first, and then we shall move on to tackle the superfluid phases in He-3, which is somewhat more complicated as expected.

2. Results and discussion

2.1 *Ramachandran attraction and energy-level spacing in He-4 liquid*

The interparticle interaction that will be considered here is a proper quantum mechanical version, which is the renormalised Ramachandran attraction of the first type ($V_{\text{Type:I}}^{\text{R}}(\xi)$) [32],

$$V_{\text{Type:I}}^{\text{R}}(\xi) = \hbar\omega \left(\frac{1}{\sqrt{2}} - 1 \right) \exp \left[\frac{1}{2} \lambda \xi \right]. \tag{1}$$

Here, $V_{\text{Type:I}}^{\text{R}}(\xi)$ given in eq. (1) is stronger than that of the van der Waals attraction, and this equation is valid for a given atomic separation, R, such that the atoms are strongly interacting (see ref. [32]). In eq. (1), the temperature effect can be taken into account by noting that $\lambda = 1/k_{\text{B}}T$, but this equality

does not and cannot always represent the temperature dependence of a process accurately because the process is not restricted solely to a particular variable such that there can be other temperature-dependent parameters in a given physical process, and this additional contribution is not always known *a priori* or captured solely by the exponential factor that appears in the renormalised equations used here. This means that, $\lambda = 1/k_{\text{B}}T$, which is a classical (or the thermodynamic) version, should be interpreted with caution with respect to the experimental data.

For a detailed discussion on the complication of evaluating the temperature effect, namely, in calculating the temperature-dependent resistivity properly in solids, the reader may refer to ref. [14]. On the other hand, the following temperature-independent formula, $\lambda = (12\pi\epsilon_0/e^2)a_{\text{B}}$, is valid for all cases, which is based on quantum mechanical formalism where ϵ_0 is the permittivity of free space, e is the electron charge and a_{B} is the Bohr radius. The parameters, $\hbar\omega$ is the ground-state energy and ξ is nothing but the energy-level spacing for each He-4 atom (in this case). Note here that the exponential factor is also known as the renormalisation factor, while T and k_{B} denote the usual temperature and Boltzmann constant, respectively.

In eq. (1), $V_{\text{Type:I}}^{\text{R}}(\xi)$ captures the proper attraction between two polarised He-4 atoms due to electronic polarisation and the strength of screened positively-charged nucleus. At higher temperatures, the spherically polarised He-4 atoms due to polarisable electrons gives rise to a repulsive Coulomb interaction between He-4 atoms. Spherical polarisation of atoms is due to temperature such that the average temperature-induced polarisation is equal in all directions (or the said polarisation is directionless). Only at a much lower temperature, $V_{\text{Type:I}}^{\text{R}}(\xi)$ is activated where the electron polarisation is no longer spherical, but directed between two He-4 atoms because the positively charged nucleus from atom-1 polarises the outer electron from atom-2, and vice versa. This implies that $V_{\text{Type:I}}^{\text{R}}(\xi)$ activates the transition from the repulsive normal He-4 liquid to He-4 superfluid at the λ-point (T_λ). In the transition from He-4 liquid to He-4 superfluid, spin-related physics does not play any significant role due to integral spin, and moreover, the spin-orbit coupling symmetry of one He-4 atom also does not oppose the pairing of two He-4 atoms.

Obviously, the pairing of two He-4 atoms is due to (Type-I) Ramachandran attraction, and it has got nothing to do with the BCS Cooper-pair mechanism [33–38] in conventional and unconventional superconductors.

Hence, He-4 pairs will be rightfully called the Ramachandran pairs where the pairing of He-4 atoms is due to a critical value acquired by $V_{\text{Type:I}}^{\text{R}}(\xi)$ that has overcome the competing repulsive interaction due to temperature-induced spherically polarised He-4 atoms, which in turn gives rise to another interesting effect – the said pairing deactivates the Ramachandran attraction or any other significant interaction between any two Ramachandran pairs.

The above deactivation of interaction between Ramachandran pairs automatically explains why the formation of the so-called 'frictionless flow' in the superfluid phase below T_λ is a proper possibility, as it should be, and also why He-4 solid is not yet a possibility, unless the pressure is high enough that can deactivate the Ramachandran pairs, and activates the Ramachandran attraction among all the nearest-neighbour He-4 atoms. Note that, the so-called Ramachandran attraction (needed to form He-4 solid) does not lead to any chemical bonds via chemical reaction between any two or more He-4 atoms. For He-4 to react chemically with another He-4 atom, we need Type-II Ramachandran attraction [32], which may require extremely high pressure to even activate it.

To verify how (Type-I) Ramachandran pairs could be responsible for the above mechanism (the formation of Ramachandran pairs and the deactivation of interaction between Ramachandran pairs), we shall exploit the fact that when the number of Ramachandran pairs is increased at the λ-point (when T is decreased from T_λ), then ξ of the system is decreased because the energy-level spacing contributed by the He-4 atoms ($\xi_{\text{Atom}}^{\text{He}}$) is decreased because we need to replace the unpaired atomic He's energy-level spacing with the energy-level spacing of paired atomic He ($\xi_{\text{Pair}}^{\text{Ramachandran}}$). This process is reversed when the temperature T is greater than T_λ ($T > T_\lambda$). Here, obviously, $\xi_{\text{Pair}}^{\text{Ramachandran}} < \xi_{\text{Atom}}^{\text{He}}$. In particular, $\xi_{\text{Pair}}^{\text{Ramachandran}}$ is the energy-level spacing for the polarised outer electron in each He-4 atom of a Ramachandran pair, which is relatively smaller compared to each unpolarised He-4 atom, which is without the Ramachandran attraction.

The stated energy-level spacing inequality can be used to predict the specific heat capacity jump at the critical point for both He-4 and He-3 liquid. The specific heat [39] jumps up at T_λ when the temperature is decreased from T_λ, whereas the same specific heat jumps down at T_λ when the temperature is greater than T_λ. Similar observation [40,41] is also observed when He-3 liquid becomes superfluid at a much lower critical temperature ($T_C \approx T_\lambda/1000$). We shall evaluate He-3 liquid and its superfluid phases after completing the necessary analysis on He-4 liquid.

2.2 *Ramachandran pairing mechanism and specific heat capacity*

Above T_λ, He-4 liquid is composed of He-4 atoms with repulsive interaction, and these atoms are not an ideal Bose gas. The repulsive interaction is due to Coulomb. After taking into account the screening effect, the renormalised Coulomb repulsive interaction between electrons from two He-4 atoms is given by [42]

$$V_{\text{Coulomb}}^{\text{e}-\text{e}} = \frac{1}{2} \cdot \frac{(-e)(-e)}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}$$
$$\times \left\{ \exp\left[-\mu(r_1 + r_2) \exp\left(-\frac{1}{2}\lambda\xi_1 \right) \right] \right.$$
$$\left. + \exp\left[-\mu(r_1 + r_2) \exp\left(-\frac{1}{2}\lambda\xi_2 \right) \right] \right\}, \quad (2)$$

where r_1 and r_2 are the coordinates for the He-4 outer-most electrons, namely, the outer-most electron-1 and electron-2 from He-4 atom-1 and He-4 atom-2, respectively, while $|\mathbf{r}_1 - \mathbf{r}_2|$ is the separation between the two outer-most electrons. Furthermore, ξ_1 and ξ_2 denote the energy-level spacings for the outer electrons from He-4 atom-1 and He-4 atom-2 respectively.

The renormalisation factor in eq. (2) is nothing but the exponential term, $\exp\left[-\frac{1}{2}\lambda\xi_2\right]$, which exists due to energy-level spacing renormalisation that takes different interaction strength into account between He-4 atom-1 and He-4 atom-2. For example, electron-2 from atom-2 is screened by the outer electrons from atom-1, and vice versa. The other exponential term, $\exp\left[-\mu(r_1 + r_2)\right]$, takes the mutual screening effect into account, and this implies that the renormalised interaction strength (with ξ_1 and ξ_2) refers to the screening strength [42].

The above Coulomb repulsion (see eq. (2)) is between any two nearest-neighbour He-4 atoms where these atoms are spherically (isotropically) polarised for $T > T_\lambda$ due to temperature. Temperature cannot give rise to directional (or anisotropic) polarisation of an atom and for more details on the Ramachandran attraction and the different types of polarisation, see ref. [32], including the physics of eq. (1) such that the Ramachandran attraction can never represent a repulsive hardcore interaction. When the temperature is lowered, spherical (or isotropic) polarisation of He-4 atoms is also systematically reduced, which in turn decreases the Coulomb repulsion between atoms, which eventually increases the directional Ramachandran attraction (see eq. (1)) between two He-4 atoms due to directional polarisation. The said Ramachandran attraction has to be directional theoretically and is directed between two He-4 atoms such that when $V_{\text{Coulomb}}^{\text{e}-\text{e}} + V_{\text{Type:I}}^{\text{R}}(\xi) = 0$ one obtains the onset of the λ-point. Note that, for

$T > T_\lambda$, $V_{\text{Coulomb}}^{\text{e-e}} + V_{\text{Type:I}}^{\text{R}}(\xi) > 0$ that destroys the formation of Ramachandran pairs due to temperature-induced isotropic polarisation.

Consequently, it should be straightforward to deduce that the superfluid phase can be formed when sufficient number of Ramachandran pairs are produced that activates the following inequality:

$$V_{\text{Coulomb}}^{\text{e-e}} < \left| V_{\text{Type:I}}^{\text{R}}(\xi) \right|, \tag{3}$$

where this inequality can only become strongly asymmetric by further decreasing the temperature, for example, when $T_\lambda > T \rightarrow 0$ K. When the temperature approaches 0 K, the Ramachandran attraction, $|V_{\text{Type:I}}^{\text{R}}(\xi)| \rightarrow$ maximum, while $V_{\text{Coulomb}}^{\text{e-e}} \rightarrow$ minimum when the separation between two Ramachandran pairs does not reactivate the Coulomb repulsion such that $V_{\text{Coulomb}}^{\text{e-e}}$ is large.

Another effect is in play here when $|V_{\text{Type:I}}^{\text{R}}(\xi)|$ is activated. Each Ramachandran pair does not interact with another pair due to $|V_{\text{Type:I}}^{\text{R}}(\xi)|$ because the already polarised outer electrons (to form Ramachandran pairs) can no longer be further polarised in another direction so as to interact with another He-4 atom and/or with another Ramachandran pair at another position and angle. Therefore, these Ramachandran pairs (not the unpaired He-4 atoms) are the ones that should be represented as the quantum mechanical Bose liquid below T_λ as proposed by Feynman. Consequently, London's zero-point energy had to be the proper reason why He-4 superfluid stays superfluid when $T \rightarrow 0$ K.

In view of eqs (1)–(3), it is straightforward to deduce that the formation of Ramachandran pairs is not induced by temperature, but due to the Ramachandran attractive interaction that is much stronger than the van der Waals attraction. Therefore, the claim made by Leggett in his Nobel lecture – 'The atomic electrons in liquid He form inert closed shells, with excitation energies of the order of 50 eV, so any contribution from them at temperatures in the mK range should be utterly negligible', is spectacularly flawed. For example, the excitation energies of the order of 50 eV is due to Coulomb force (a type of electrostatic interaction), and this force between two charges is not, and cannot be induced by temperature because it is independent of temperature. As a matter of fact, we have actually removed the temperature effect to activate the Ramachandran attraction between two He-4 atoms, which is also a type of electrostatic interaction.

In particular, we have justified that the temperature of the order of T_λ or lower gives rise to anisotropic (directional) polarisation with increasing strength between two He-4 atoms. In contrast, for $T > T_\lambda$, the He-4 atoms are polarised spherically or isotropically with no preferred direction of polarisation due to significant temperature effect. For example, for higher temperatures, the electrons tend to be polarised spherically giving rise to increasing Coulomb repulsion between He-4 atoms.

As a consequence, the outer electrons with ionisation energies of about 54 (for the inner electron) and 24 eV (for the outer electron and its energy is lower due to screening) in an atomic He-4 start to play the leading role in eqs (1)–(3) for $T \leq T_\lambda$. As a result of these large ionisation energies, the Ramachandran attraction (given in eq. (1)) is activated such that the electron polarisation is directed between two He-4 nuclei, and it can only become stronger when the temperature is further reduced below T_λ to 0 K.

In addition, Leggett [2] assumed that an ideal Bose gas (normal phase liquid helium) with the critical exponent $\alpha = -1$ (with continuous specific heat) is unstable and changes to another universality class with $\alpha \sim 0$ (with discontinuous specific heat) due to BEC in the presence of infinitesimal repulsive interaction. In other words, superfluidity arises from its dynamical stability with the repulsive interaction where the change to the critical exponent is due to this spontaneous symmetry breaking (or sometimes, spontaneous gauge-symmetry breaking) to produce the shift in the global phase. Hence, it is clear from ref. [2] that Leggett assumed the said symmetry breaking as the origin of the discontinuous specific heat and superfluidity in helium-4, which is based on guessed functions and adjustable science, and therefore, Leggett was not able to provide any microscopic physical mechanism (with respect to changing interatomic interaction strength).

In particular, the Leggett's adjustable critical exponent, α, is adjusted without relating it to any proper microscopic interatomic interaction term, despite the fact that only by knowing the interatomic interaction term and its changing strength, can we then go on to justify and elaborate specifically whether the specific heat has to jump up or down discontinuously, or not at all. In addition, the phrase, 'by knowing the interatomic interaction term' means that the said interaction should be derived from the first principles, which is not the case from ref. [24], and this particular interaction term should not be made adjustable by means of some guessed wave function, which is not the case from ref. [23].

Here, α also appears as a fitting parameter in the adjustable Kosterlitz–Thouless physics, which can be adjusted to produce BEC in any cold atoms [8]. Even though the said adjustable physics [8] was, and has been the first line of attack to evaluate critical-point phenomena, such approach does not and cannot provide relevant microscopic physics with respect to changing specific interaction strength between specific atoms at

the critical point. In particular, it is essential to identify the specific interaction between atoms to justify superfluidity in some atoms. In other words, the interaction strength between similar or different types of atoms should be specific enough so as to expose and justify the microscopic physics responsible for the existence of superfluidity for certain atoms, and its absence in others.

Further studies based on scaling-parameter approach have been carried out to computationally evaluate the superfluid transition, including the specific heat jump at the critical point in He-4 [43,44]. In these reports, the hyperscaling relation, $\alpha = 2 - d\nu$, is calculated and compared with experimentally extracted scaling parameter such as ν. Here, α and ν are the specific heat and the correlation length exponents, respectively, while d denotes the dimensionality parameter. The experimental value for ν is determined [45] by fitting the appropriate guessed function (up to six adjustable parameters) with experimental data [44]. Apparently, even though this type of evaluation is useful to study the universality class in liquid He-4 by means of fitting-parameter approach, the said evaluation surely lacks the ability to expose any microscopic physics associated with the interacting He-4 atoms that are responsible for the superfluid transition.

Let us now evaluate whether the formation of Ramachandran pairs can explain the discontinuous specific heat capacity jump for $T = T_\lambda$. Earlier in ref. [14], we have found a way to associate ξ to the Cooper pairs, which can be readily exploited here for the Ramachandran pairs. To do this properly, we shall invoke the finite-temperature phase transition theory developed in ref. [46] to address the finite-temperature phase transition (FPT$^{T_\lambda}$) in He-4 liquid at the λ-point. We need to explain why and how ξ determines the discontinuous jump for C_v at T_λ, which should include why C_v has to jump up (not down) such that $C_v^{\text{R:pairs}}(T < T_\lambda) > C_v^{\text{unpaired:He}}(T > T_\lambda)$.

Apparently, for $T > T_\lambda$, the specific heat capacity for the unpaired He-4 atoms is denoted by $C_v^{\text{unpaired:He}}(T > T_\lambda)$, whereas $C_v^{\text{R:pairs}}(T < T_\lambda)$ is activated below T_λ. This means that, both $C_v^{\text{unpaired:He}}(T > T_\lambda)$ and $C_v^{\text{R:pairs}}(T < T_\lambda)$ are invalid for $T = T_\lambda$ because they are only valid for $T > T_\lambda$ and $T < T_\lambda$, respectively [46], not at the critical point. Therefore, for $T = T_\lambda$, the formation of Ramachandran pairs gives rise to FPT$^{T_\lambda}$ where $V_{\text{Type:I}}^{\text{R}}(\xi)$ becomes significant such that $V_{\text{Coulomb}}^{\text{e}-\text{e}} > |V_{\text{Type:I}}^{\text{R}}(\xi)| \rightarrow V_{\text{Coulomb}}^{\text{e}-\text{e}} < |V_{\text{Type:I}}^{\text{R}}(\xi)|$. The above transformation is possible if and only if we allow ξ to change significantly at T_λ.

Unlike the changes to ξ at the critical point discussed for Cooper pair formation in cuprates in ref. [14], the change in ξ at the λ-point ($T = T_\lambda$) does refer to

changing ionisation energy (or the energy-level spacing) and changing number of Ramachandran pairs. For example, at the critical point, the transition is from $\frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}] \sum_i I_i \rightarrow [\xi_{\text{Pair}}^{\text{Ramachandran}}] \sum_j J_j$ where I and J denote the appropriate fractions (see eqs (6) and (7)), $\xi_{\text{Atom}}^{\text{He}} > \xi_{\text{Pair}}^{\text{Ramachandran}}$ (as pointed out earlier) and the subscript j counts the number of Ramachandran pairs. The sum, $[\xi_{\text{Pair}}^{\text{Ramachandran}}] \sum_j J_j$ counts the number of paired He-4 atoms due to pairing mechanism induced by $V_{\text{Type:I}}^{\text{R}}(\xi)$, while the other sum, $\frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}] \sum_i I_i$ counts the unpaired He-4 atoms that remain unpaired due to $V_{\text{Coulomb}}^{\text{e}-\text{e}}$ (between two He-4 atoms) when the temperature is decreased from T_λ.

Here, we do not have the option to either count the unpaired or the paired He-4 atoms because we need to count them both. For example, both the pairs and the unpaired He-4 atoms contribute to ξ in their own way at the critical point. In contrast, BCS Cooper pairs are not subjected to ξ because these pairs flow without resistance and produce supercurrent and therefore, ξ cannot exist for BCS Cooper pairs in solids [14]. In other words, BCS Cooper pairs switch-off the effect of ξ. Anyway, the relation between ξ and $C_v^{\text{R:pairs}}(T < T_\lambda) = C_v(T < T_\lambda)$ and between ξ and $C_v^{\text{unpaired:He}}(T > T_\lambda) = C_v(T > T_\lambda)$ can be constructed from refs [14,42,46]. In particular, for $T > T_\lambda$

$$\tilde{C}_v(T > T_\lambda) = C_v(T > T_\lambda)$$
$$\times \exp\left[-\frac{3}{4}\lambda[\xi_{\text{Atom}}^{\text{He}}]\sum_i I_i\right], \qquad (4)$$

where the fraction $\sum_i I_i$ equals one ($\sum_j J_j = 0$), whereas for $T < T_\lambda$

$$\tilde{C}_v(T < T_\lambda) = C_v(T < T_\lambda)$$
$$\times \exp\left[-\frac{3}{2}\lambda[\xi_{\text{Pair}}^{\text{Ramachandran}}]\sum_j J_j\right]. \quad (5)$$

The tilde worn by the specific heat capacity here means that it has been renormalised to capture the changes to the specific heat capacity at the critical point. The full energy-level spacing renormalisation technique and its physical implications are presented in ref. [42].

In eqs (4) and (5), the fraction $\sum_j J_j = 1$ and $\sum_i I_i = 0$ such that $\sum_j J_j \geq 0$, $\sum_i I_i \geq 0$ and $\sum_j J_j + \sum_i I_i = 1$. In particular,

$$\sum_i I_i = \frac{\sum_i [n_{\text{He}}^{\text{unpaired}}]_i}{N_{\text{total}}^{\text{unpaired}}} \qquad (6)$$

and

$$\sum_j J_j = \frac{\sum_j [n_{\text{R:pairs}}]_j}{N_{\text{total}}^{\text{R:pairs}}}. \qquad (7)$$

Here, $n_{\text{He}}^{\text{unpaired}}$ and $N_{\text{total}}^{\text{unpaired}}$ denote the number of unpaired He-4 atoms and its total number, respectively, and similarly, $n_{\text{R:pairs}}$ and $N_{\text{total}}^{\text{R:pairs}}$ refer to the Ramachandran pairs.

Subsequently, at the critical point, we need to construct the time-dependent non-equilibrium specific heat capacity formula (following refs [42,46]), which reads as

$$C_{\text{v}}(T_\lambda, t)_{\text{eqm}}^{\text{non}} = C_{\text{v}}(T_\lambda)$$
$$\times \exp\left[-\frac{3}{2}\lambda\left(\frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}]\sum_i I_i \right.\right.$$
$$\left.\left. +[\xi_{\text{Pair}}^{\text{Ramachandran}}]\sum_j J_j\right)\right]. \quad (8)$$

When the temperature is lowered from T_λ, the contribution from $\frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}]\sum_i I_i$ decreases due to the decreasing number of unpaired He-4 atoms, and these unpaired He-4 atoms are substituted with increasing number of Ramachandran pairs that gives rise to increasing $[\xi_{\text{Pair}}^{\text{Ramachandran}}]\sum_j J_j$.

Therefore, one can readily deduce that $C_{\text{v}}(T_\lambda, t)_{\text{eqm}}^{\text{non}}$ has to jump up at T_λ when the temperature is lowered from above T_λ due to these two facts: (a) $\xi_{\text{Atom}}^{\text{He}} > \xi_{\text{Pair}}^{\text{Ramachandran}}$ and (b) increasing number of Ramachandran pairs or J. Alternatively, if the temperature is increased from T to T_λ, then obviously, $C_{\text{v}}(T_\lambda, t)_{\text{eqm}}^{\text{non}}$ has to jump down because in this alternative case, $\frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}]\sum_i I_i$ increases drastically at the critical point due to the increasing number of unpaired He-4 atoms, while the contribution from $[\xi_{\text{Pair}}^{\text{Ramachandran}}]\sum_j J_j$ decreases suddenly due to the decreasing number of Ramachandran pairs.

If the temperature is increased from below T_λ, then the term $C_{\text{v}}(T_\lambda)$ in eq. (8) equals to $\tilde{C}_{\text{v}}(T < T_\lambda)$ that transforms into $\tilde{C}_{\text{v}}(T > T_\lambda)$,

$$C_{\text{v}}(T_\lambda) \to \tilde{C}_{\text{v}}(T > T_\lambda). \quad (9)$$

On the other hand, if the temperature is lowered from above T_λ, then obviously we should have $C_{\text{v}}(T_\lambda) = \tilde{C}_{\text{v}}(T > T_\lambda)$, which follows the following transformation:

$$C_{\text{v}}(T_\lambda) \to \tilde{C}_{\text{v}}(T < T_\lambda). \quad (10)$$

Hence, solely on the basis of Drude Hamiltonian extended within IET formalism, we have derived the stronger Ramachandran attraction to prove that $\tilde{C}_{\text{v}}(T > T_\lambda)$ jumps up for $T = T_\lambda$ if we start lowering the temperature from above T_λ.

In contrast, by increasing the temperature from below T_λ, $C_{\text{v}}(T < T_\lambda)$ jumps down at the critical point. These
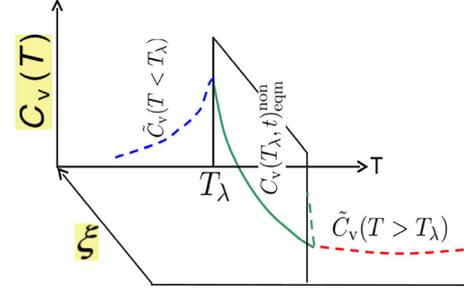

Figure 1. Temperature(T)- and time(t)-dependent specific heat capacity for all temperature range, $T > T_\lambda$, $T = T_\lambda$ and $T < T_\lambda$ denoted respectively by $C_{\text{v}}(T > T_\lambda)$, $C_{\text{v}}(T_\lambda, t)_{\text{eqm}}^{\text{non}}$ and $C_{\text{v}}(T < T_\lambda)$. The specific heat capacity $(C_{\text{v}}(T))$ with its discontinuous jump is sketched by the exponential solid (blue) line connecting the two temperature axes at the critical point (T_λ). In this sketch, the axis ξ refers to $\frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}]\sum_i I_i + [\xi_{\text{Pair}}^{\text{Ramachandran}}]\sum_j J_j$ where J increases if the temperature is lowered (from above T_λ) or I increases if the temperature is increased (from below T_λ). The exponential solid line is obtained from the quantum thermodynamical approach formulated in ref. [46].

jumps refer to the same measured specific heat discontinuity for $T = T_\lambda$ and the said discontinuity is captured in a sketch depicted in figure 1. The discontinuous jump that is indicated in figure 1 is actually due to a time-dependent specific heat capacity at the critical point (see the term, $\frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}]\sum_i I_i + [\xi_{\text{Pair}}^{\text{Ramachandran}}]\sum_j J_j$ in eq. (8)). We have derived our theory, its implications and the physical mechanism on Ramachandran pairs entirely from the first principles, without having to invoke any adjustable parameter, which is also in agreement with the experimentally measured discontinuous jump in the specific heat data reported by Donnelly and Barenghi [39] and Hill and Lounasmaa [47].

2.3 *Some background information on He-3 liquid and its superfluid phases*

As already discussed, which is well-known, He-3 atoms are fermions because each of their nuclei contains an unpaired spin-$\frac{1}{2}$ neutron. The spin-$\frac{1}{2}$ proton in the nucleus is paired with another proton. However, we should not forget that the outer electrons in each He-3 atom are also polarisable, producing properties similar to Fermi liquid in Fermi solids such as the T-linear specific heat capacity above the He-3 superfluid transition temperature (T_{C}). The physics of electronic polarisation for atomic He-3 is similar to He-4 atoms that we have dealt with above, and that is why both He-4 and He-3 liquids (above their respective superfluid transition temperatures, T_λ and T_{C}, respectively), are repulsive

(temperature-induced). We shall return to electronic polarisation for atomic He-3 shortly.

The pairing mechanism based on spin fluctuation in He-3 liquid reads along this line (somewhat identical to BCS Cooper-pair mechanism) – He-3 liquid is treated as Fermi liquid, thus, a passing He-3 atomic quasiparticle in this liquid may polarise the spins of neighbouring quasiparticles such that these neighbouring spins become parallel to the spin of the passing quasiparticle. Another nearby quasiparticle with parallel spin is attracted to this spin-polarised cloud, forming the He-3 Cooper pair. This particular pairing requires non-zero spin and orbital angular momentum [1]. We still do not know what is the physical mechanism that is responsible for this spin-induced pairing, except that the attraction originates from spin exchange mechanism [18,19,48]. We shall elaborate on this spin-induced interaction in the subsequent subsection. In addition, we are also left stranded as to why the electrostatic forces from the two polarised He-3 atoms are conveniently ignored without any proper physics [2,18,19]. But never mind, we do acknowledge here that the spin of the pair ($S = 1$) and the pair's orbital angular momentum, $l = 1$ are the internal degrees of freedom [2] that actually give rise to some complicated effects for the pairing of He-3 atoms to produce superfluidity.

There are two superfluid phases in liquid He-3 (in the absence of applied magnetic field: they are known as the A (or ABM)- and B (or BW)-phases (for different temperatures and pressures). The Larmor frequency in the B-phase stays the same while its magnetic susceptibility decreases with lowering temperature. In the A-phase on the other hand, the Larmor frequency increases with lowering temperature with no change to the nuclear magnetic resonance (NMR) absorption amplitude, but its magnetic susceptibility remains the same when the temperature is lowered [1]. Leggett [2] made use of the concept known as the spontaneously broken spin-orbit symmetry (SBSOS) to formulate and explain the Larmor frequency shift with lowering temperature. Leggett's theory demands all the paired spin and the paired orbital angular momentum to be aligned in the A-phase, and the interaction behind this pairing comes from the nuclear dipole–dipole interaction, which is a type of spin non-conserving energy. The B-phase on the other hand, requires the angle between spin and orbital angular momentum for each He-3 atom (or quasiparticle) to be fixed.

Before we can apply the Ramachandran pairing mechanism in He-3 superfluidity, we should first uncover additional facts about atomic He-3 compared to He-4. In particular, the energy-level spacing or the magnitude of ξ in an atomic He-3 is slightly smaller than that of He-4 atom [49]. The first ionisation energy for atomic He-4 is 5945,204,290 $\pm$ 33 MHz, while for an atomic He-3, its first ionisation energy is slightly smaller, which is estimated to be 5944,890,770 $\pm$ 33 MHz [49], and the difference is 313,520 MHz. The first thing that we should be noting here is the fact that $\xi_{\text{He:3}} < \xi_{\text{He:4}}$. Assuming the spin configuration (singlet or triplet) for the two outer electrons in a He-3 atom is identical to an atomic He-4, then the lower first ionisation energy (for He-3 atom) has got to be due to neutron's spin-$\frac{1}{2}$ effect (the so-called magnetic perturbation [49]) affecting the outer electron's energy levels, which in turn is responsible for the increase in the ground-state energy for the atomic He-3, compared to the atomic He-4.

In other words, the additional magnetic interaction in a He-3 atom decreases the strength of the electron–nucleus Coulomb attraction, which in turn lowers the first ionisation energy (or increases the ground-state energy). For example, the electron–nucleus Coulomb attraction in a He-3 atom has to overcome an effective additional obstacle due to magnetic perturbation coming from the nucleus of He-3 atom, which eventually decreased the strength of electron–nucleus Coulomb attraction. Therefore, the outer-most electron in an atomic He-3 is slightly less strongly bound to its nucleus because of smaller electron–nucleus Coulomb attraction, which is due to the said magnetic interaction-induced obstacle. Apparently, this additional obstacle cannot exist in He-4 atoms for they are bosons.

The second point one can deduce here is that the said ionisation-energy inequality, $\xi_{\text{He:3}} < \xi_{\text{He:4}}$ implies the outer electrons in He-3 atoms are more polarisable than the outer electrons from He-4 atoms, for a given temperature and external disturbance. The relative higher electronic polarisability for He-3 atoms compared to He-4 atoms has to be correct because the nuclear charge for both He-3 and He-4 atoms is the same, which is 2+. Hence, He-3 atoms should be more repulsive (due to larger temperature-induced electronic polarisation) than He-4 atoms for a given temperature, pressure and concentration above 4.2 K. We now have enough background physics to go on and physically justify why and how the Ramachandran pairing mechanism can be activated in He-3 liquid, and what are the implications of this particular pairing with respect to the above stated additional internal degrees of freedom.

2.4 *Discontinuous jump in specific heat capacity due to Ramachandran pairs*

From our Ramachandran interaction theory employed to validate the transition to superfluidity in He-4 liquid, the

Ramachandran pairing mechanism shall be proven here to be responsible for the superfluidity in He-3. However, this mechanism can only be properly activated if the above internal degrees of freedom, namely, the paired spin and orbital angular momentum with a particular configuration are separately and differently satisfied for A and B superfluid phases (in the absence of applied magnetic field).

Our task now is to properly argue whether the spin-polarised nuclear dipole–dipole interaction between two spin-$\frac{1}{2}$ He-3 nuclei does provide the attraction between the nuclei, in addition to the Ramachandran attraction, or alternatively, the said dipole interaction is not an attraction or a repulsion, but the said dipole–dipole energy actually lowers the magnetic perturbation between two He-3 nuclei such that the Ramachandran attraction is activated for the He-3 pairing, somewhat similar to He-4 pairing. We shall argue unambiguously that the latter option is the correct physical mechanism from the physics that we have accumulated thus far. From ref. [49], we have established the following physics: the magnetic perturbation reduces the strength of the electron–nucleus Coulomb attraction. Consequently, the perturbation due to spin-$\frac{1}{2}$ and the orbital angular momentum between two spin-$\frac{1}{2}$ He-3 nuclei further reduces (apart from the temperature-induced isotropic electronic polarisation) the Ramachandran attraction due to smaller ionisation energy.

For example, the magnetic perturbation lowers the first ionisation energy of an atomic He-3 [49], which increases the temperature-induced electronic polarisation, and reduces the strength of Ramachandran attraction in He-3 liquid compared to He-4 liquid. Hence, we can readily anticipate that the transition to any superfluid phase for He-3 liquid has to occur at a lower temperature ($T_C < T_\lambda$). Secondly, the special configurations for the paired spin and paired orbital angular momentum in A and B superfluid phases lower the spin and the orbital angular momentum perturbation affecting the energy levels, which in turn increases the first ionisation energy and subsequently, activating the effective Ramachandran attraction between two He-3 atoms.

The effective Ramachandran attraction in the A-phase is activated after the obstacle originating from the collective perturbation of the spin and orbital angular momentum is lowered when all the paired spins and all the paired orbital angular momenta are aligned. In the B-phase, the same obstacle is overcome when the angle between the spin and orbital angular momentum for each He-3 atom is fixed. However, these special alignments (in the A and B phases) themselves are needed to overcome the obstacles in the first place

that have prevented He-3 liquid to become a superfluid at a higher temperature, higher than T_C (2.6 mK). Overcoming these obstacles (by means of these special alignments) have provided the setting needed to activate the Ramachandran attraction.

Let us first evaluate the discontinuous specific heat data reported in ref. [41], which is straightforward. These data confirm that the specific heat capacity jumps up at $T_C^{\text{A:phase}}$ when He-3 liquid is cooled from the temperature above $T_C^{\text{A:phase}}$. In particular,

$$C_v(T_C^{\text{A:phase}}, t)_{\text{eqm}}^{\text{non}} = C_v(T_C^{\text{A:phase}})$$
$$\times \exp\left[-\frac{3}{2}\lambda\left(\frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}]\sum_i I_i + [\xi_{\text{A:phase}}^{\text{R:pair}}]\sum_j J_j\right)\right],$$
$$\tag{11}$$

where $\xi_{\text{A:phase}}^{\text{R:pair}}$ denotes the energy-level spacing for the Ramachandran pairs in the A-phase. Obviously, $\xi_{\text{A:phase}}^{\text{R:pair}} < \frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}]$ and the electronic anisotropic polarisation between two He-3 atoms leads to the formation of Ramachandran pairs for $T = T_C^{\text{A:phase}}$ when $|V_{\text{Type:I}}^{\text{R}}(\xi)| > V_{\text{Coulomb}}^{\text{e}-\text{e}}$. The said discontinuous jump automatically (see the discussion on He-4) proves that eq. (8) and its related equations and physics are responsible for the phase transition from He-3 liquid to the A-phase superfluid due to the formation of Ramachandran pairs where each pair now is composed of two He-3 atoms. The new physics in He-3 (compared to He-4) however, comes from the obstacle explained above. Of course, we can remove all the obstacles to Ramachandran pairing (by adding another neutron into the nucleus of He-3 atom), but this would simply imply that He-3 atom has been transformed into a He-4 atom, as it should be.

If the phase transition to B-phase superfluid is directly from the normal He-3 liquid without passing through the A-phase, then the specific heat capacity at the normal to B-phase critical point ($T_C^{\text{NB:phase}}$) has to follow the following equation, which is identical to eq. (11). In particular,

$$C_v(T_C^{\text{NB:phase}}, t)_{\text{eqm}}^{\text{non}} = C_v(T_C^{\text{NB:phase}})$$
$$\times \exp\left[-\frac{3}{2}\lambda\left(\frac{1}{2}[\xi_{\text{Atom}}^{\text{He}}]\sum_i I_i + [\xi_{\text{NB:phase}}^{\text{R:pair}}]\sum_j J_j\right)\right],$$
$$\tag{12}$$

where $T_C^{\text{A:phase}}$ in eq. (11) has been replaced with $T_C^{\text{NB:phase}}$ accordingly in eq. (12). Therefore, the direct phase transition to B-phase from He-3 liquid ought to produce an upward discontinuous jump in the specific

heat capacity data for $T = T_C^{\text{NB:phase}}$ due to the formation of Ramachandran pairs. We stress here that the formation of Ramachandran pairs due to Ramachandran attraction is a prerequisite for superfluidity in both He-4 and He-3 liquids (for both A- and B-phases).

Unfortunately, we cannot by deduction alone determine the origin of the phase transition between the phases, A to B or vice versa, whether the obstacle in the A-phase is higher or lower than the obstacle in the B-phase. Both are possible that shall be evaluated below. Recall that the effective Ramachandran attraction is blocked by these obstacles, and the sizes of these obstacles (whether larger or smaller) determine the strength of the attraction in each phase. For example, smaller obstacle gives stronger Ramachandran attraction, which then leads to strongly bound Ramachandran pairs. Strangely, not a single experimental specific heat data is reported for the transition from A- to B-phase (or vice versa) so as to pin point which obstacle (from the A- or B-phase) is larger or of higher magnitude.

The above-stated undecidability can be broken down to four possible cases (see figure 2): (i) the formation of Ramachandran pairs with weaker attraction in the B-phase (compared to A-phase) requires the specific heat to jump up discontinuously for $T = T_C^{\text{B:phase}}$, when the temperature is lowered from $T_C^{\text{A:phase}}$ where $T_C^{\text{B:phase}} < T_C^{\text{A:phase}}$, (ii) the formation of Ramachandran pairs with stronger attraction in the B-phase (compared to A-phase) demands the specific heat capacity to jump down discontinuously for $T = T_C^{\text{B:phase}}$, again when the temperature is lowered from $T_C^{\text{A:phase}}$, (iii) the specific heat data are discontinuous for $T = T_C^{\text{B:phase}}$ but without any drastic jump, and finally, (iv) no change to the specific heat data for $T = T_C^{\text{B:phase}}$, there is no discontinuity of any type at the critical point. Before discussing the implications of these points, (i) to (iv), we should keep the following physical effects in mind. Larger obstacle gives smaller effective Ramachandran attraction. The obstacle in the A-phase, O_{phase}^A, exists because all the paired spin and the paired orbital angular momentum are aligned in the A-phase. In contrast, the obstacle in the B-phase, O_{phase}^B, exists due to the fixed angle between spin and orbital angular momentum for each He-3 atom where $O_{\text{phase}}^A \neq O_{\text{phase}}^B$.

The first possibility (i) implies that the obstacle in the B-phase (O_{phase}^B) is larger than the obstacle in the A-phase, or $O_{\text{phase}}^B > O_{\text{phase}}^A$. Consequently, the strength of the activated effective Ramachandran attraction in the A-phase is smaller than the effective attraction in the B-phase, which means the phase transition between A and B phases is induced by the transformation from O_{phase}^A
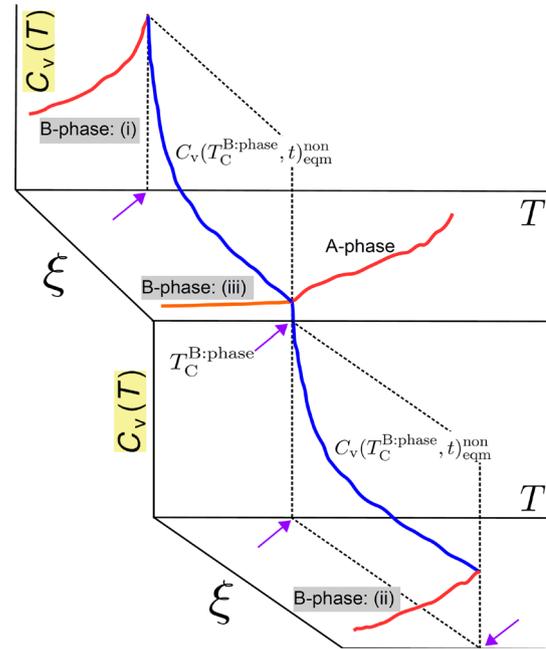

Figure 2. Three different types of changes to the specific heat capacity to capture the transition from A- to B-phase where the B-phase transition point is denoted by $T_C^{\text{B:phase}}$. Three cases considered here, (i), (ii) and (iii) are listed in the text. The first case (i) shows the transition to B-phase: (i) with a discontinuous jump where the temperature (T)- and time (t)-dependent specific heat capacity ($C_v(T_\lambda, t)_{\text{eqm}}^{\text{non}}$) jumps up for $T = T_C^{\text{B:phase}}$. In the second case, (ii), the specific heat jumps down to the B-phase: (ii) controlled by $C_v(T_\lambda, t)_{\text{eqm}}^{\text{non}}$ at the critical point. In the third case, (iii), there is no discontinuous jump to the B-phase: (iii), in other words, the specific heat curve is discontinuous at the critical point without any drastic change or jump.

(that is larger) to O_{phase}^B, which is smaller. Subsequently, we can deduce $|V_{\text{Type:I}}^R(\xi_{\text{B:phase}})| < |V_{\text{Type:I}}^R(\xi_{\text{A:phase}})|$ from $O_{\text{phase}}^B > O_{\text{phase}}^A$.

Given these relations, we can easily construct the specific heat capacity formula at the critical point ($T = T_C^{\text{B:phase}}$) to read (following eq. (8)) as

$$C_v(T_C^{\text{B:phase}}, t)_{\text{eqm}}^{\text{non}}$$
$$= C_v(T_C^{\text{B:phase}}) \exp\left[-\frac{3}{2}\lambda\left([\xi_{\text{A:phase}}^{\text{R:pair}}] \sum_i I_i + [\xi_{\text{B:phase}}^{\text{R:pair}}] \sum_j J_j \right)\right]. \quad (13)$$

Here, $\xi_{\text{A:phase}}^{\text{R:pair}}$ and $\xi_{\text{B:phase}}^{\text{R:pair}}$ denote the energy-level spacing for the Ramachandran pairs in the A- and B-phases, respectively. From eq. (13), one can conclude that the specific heat has to jump up for $T = T_C^{\text{B:phase}}$ because

at this critical point, $[\xi_{\text{A:phase}}^{\text{R:pair}}] \sum_i I_i$ decreases, while $[\xi_{\text{B:phase}}^{\text{R:pair}}] \sum_j J_j$ increases and $\xi_{\text{B:phase}}^{\text{R:pair}} < \xi_{\text{A:phase}}^{\text{R:pair}}$ as a result of $|V_{\text{Type:I}}^{\text{R}}(\xi_{\text{B:phase}})| < |V_{\text{Type:I}}^{\text{R}}(\xi_{\text{A:phase}})|$. As a consequence, the specific heat capacity has to jump up at the A to B transition critical point when the temperature is reduced from above $T_{\text{C}}^{\text{B:phase}}$. In this case, the Ramachandran pairs are weakly bounded in the B-phase compared to the pairs in the A-phase.

The second possibility is equally probable. In this case, $O_{\text{phase}}^{\text{B}} < O_{\text{phase}}^{\text{A}}$ and therefore, $|V_{\text{Type:I}}^{\text{R}}(\xi_{\text{B:phase}})| > |V_{\text{Type:I}}^{\text{R}}(\xi_{\text{A:phase}})|$. The specific heat for these inequalities follow eq. (13) exactly, including the following changes: $[\xi_{\text{A:phase}}^{\text{R:pair}}] \sum_i I_i$ decreases, while $[\xi_{\text{B:phase}}^{\text{R:pair}}] \sum_j J_j$ increases. However, the inequality, $\xi_{\text{B:phase}}^{\text{R:pair}} > \xi_{\text{A:phase}}^{\text{R:pair}}$ differs from the first case, and this inequality originated from $|V_{\text{Type:I}}^{\text{R}}(\xi_{\text{B:phase}})| > |V_{\text{Type:I}}^{\text{R}}(\xi_{\text{A:phase}})|$. After making use of these inequalities, one can deduce from eq. (13) that the specific heat capacity has to jump down for $T = T_{\text{C}}^{\text{B:phase}}$ due to the strongly bounded Ramachandran pairs in the B-phase (compared to the pairs in the A-phase).

The third and fourth cases are straightforward to evaluate. For example, if the specific heat is discontinuous without any drastic jump (case (iii)), then the stated discontinuity is due to the changes in the interaction between the Ramachandran pairs (not between the paired He-3 atoms) at the critical point. In particular, as the interaction between Ramachandran pairs cannot be repulsive or attractive so as to avoid destroying the superfluid phase, then we are left with only one option, the already negligible interaction between Ramachandran pairs is further deactivated, which in turn activates a closely-packed Ramachandran pairs for $T = T_{\text{C}}^{\text{B:phase}}$ (case (iii)) due to the spin-state transformation, ABM $\rightarrow$ BW between two paired He-3 atoms. Here, the equality, $\xi_{\text{A:phase}}^{\text{R:pair}} = \xi_{\text{B:phase}}^{\text{R:pair}}$ implies that the attractive strength between the paired He-3 atoms is not modified, which denies the existence of any discontinuous jump in the specific heat data for $T = T_{\text{C}}^{\text{B:phase}}$.

On the other hand, if there is no discontinuity or any change in the specific heat data at the critical point (case (iv)), then the strength of the Ramachandran attraction ($|V_{\text{Type:I}}^{\text{R}}(\xi)|$), the interaction between the Ramachandran pairs (if any) and the sizes of the obstacles ($O_{\text{phase}}^{\text{B}}$ and $O_{\text{phase}}^{\text{A}}$) remain the same for both A- and B-phases. In this last case, the A to B transition is entirely due to the so-called wave function transformation, from the ABM to BW spin-state ($\Psi_{\text{pair}}^{\text{ABM}} \rightarrow \Psi_{\text{pair}}^{\text{BW}}$) with no change to

the packing of Ramachandran pairs and to the ground-state energy between A- and B-phases where $\xi_{\text{A:phase}}^{\text{R:pair}} = \xi_{\text{B:phase}}^{\text{R:pair}}$. Unfortunately, we are unable to choose the most physically acceptable case deductively, which can only be confirmed by measuring the specific heat capacity at the transition from A- to B-phase, as well as the direct transition from the normal He-3 liquid to B-phase He-3 superfluid. However, we can rule out case (iv) by realising that the Larmor frequency shift [1] becomes zero suddenly for $T = T_{\text{C}}^{\text{B:phase}}$ when the temperature is lowered from the A-phase.

The existence of obstacles explained thus far may seem unnecessary to some researchers based on Leggett's theory on Larmor's frequency shift [2] and the spin-induced pairing of He-3 atoms [18,19] because these theories do not require such things. Though the proposals made in refs [2,18,19] are correct to some extent with respect to ABM and BW spin states and Leggett's spontaneously broken spin-orbit symmetry (SBSOS), these physical mechanisms are only partially relevant for superfluidity in He-3 due to Ramachandran pairing mechanism. In addition, refs [2,18,19] also do not give out the details on the spin-induced pair interaction potential operator ($V_{\mathbf{k},\mathbf{k}'}$) that is claimed to be responsible for the pairing of two spin-$\frac{1}{2}$ He-3 quasiparticles.

Apart from that, the pairing potential $V_{\mathbf{k},\mathbf{k}'}$ is always treated as an adjustable parameter such that the attraction is assumed to be activated by Pauli's exchange interaction [2,18,19]. For example, in solids, the Pauli's exchange term between two electrons is given by (from the Hartree–Fock (HF) formalism) [14],

$$\frac{1}{2} \sum_{i \neq j} \int \psi_j^{\text{HF}}(\mathbf{r}_j)^* \psi_i^{\text{HF}}(\mathbf{r}_i)^* \frac{e^2}{4\pi \epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$$
$$\times \left[-\psi_i^{\text{HF}}(\mathbf{r}_j) \psi_j^{\text{HF}}(\mathbf{r}_i) \right] \mathrm{d}\mathbf{r}_i \mathrm{d}\mathbf{r}_j, \tag{14}$$

where ψ_i^{HF} and ψ_j^{HF} are the HF wave functions, $e^2/4\pi \epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|$ denotes the electron–electron potential operator without the screening effect (and it is not an attractive interaction term), $|\mathbf{r}_i - \mathbf{r}_j|$ is the separation between two electrons, while $\mathbf{r}_i$ and $\mathbf{r}_j$ are the coordinates for the first and second electrons.

First, note that this exchange interaction is neither related to the electron–electron repulsion nor related to the attraction. Secondly, the negative sign in eq. (14) is due to the Pauli's exclusion principle,

$$\Psi^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) = -\Psi^{\text{HF}}(\mathbf{r}_2, \mathbf{r}_1), \tag{15}$$

which lowers the HF ground-state energy due to spin-exchange interaction. Therefore, eq. (14) does not

represent the attractive interaction between two electrons due to spin exchange. In other words, the spin exchange interaction captured by eq. (14) reduces the obstacle due to spin such that the electron–nucleus attraction (for both electrons) is relatively larger (with lower ground-state energy) in the presence of spin exchange interaction as compared to the same system with no spin exchange interaction. Earlier, we have also justified how the spin-$\frac{1}{2}$ induced magnetic interaction adjusts the first ionisation energy (using the data from ref. [49]) for atomic He-3 compared to He-4 atom by acting as an additional obstacle to the electron–nucleus Coulomb attraction.

In summary, in the absence of properly defined spin-induced pair interaction potential operator ($V_{\mathbf{k},\mathbf{k}'}$), we are not able to justify the existence of spin-induced pairing or derive any proper physical mechanism for superfluidity in He-3 liquid. Furthermore, without explicitly-defined function for $V_{\mathbf{k},\mathbf{k}'}$, we are not able to explain or predict any discontinuity in the specific heat data at the critical points, namely, for both $T = T_{\mathrm{C}}^{\mathrm{A:phase}}$ and $T = T_{\mathrm{C}}^{\mathrm{B:phase}}$. Here in this work, we have made use of the Ramachandran interaction theory [32] and the energy-level spacing renormalisation group technique [42] to study and evaluate the specific heat capacity right at the critical points where this particular technique can handle such points without any divergence or diverging physical parameters [46]. Another method that has been useful to study specific heat phase transition is presented by Murthy *et al* [50]. However, this approach does not invoke any interatomic interaction potential to evaluate the microscopic mechanism of superfluidity.

3. Conclusion

In conclusion, the Ramachandran interaction theory corrects some past mistakes on the origin of superfluidity in both He-4 and He-3 liquids. For example, the superfluid phase in He-4 is not entirely due to BEC of an ideal Bose gas as assumed by Feynman, or the BEC of a van der Waals (vdW) gas as formulated by Leggett because neither vdW attraction nor BEC by itself cannot cause superfluidity. The missing microscopic physics exposed here is due to the Ramachandran attraction that is activated at the critical point to form atomic He-4 pairs, leading to a discontinuous specific heat jump. On the other hand, in He-3 liquid, there is this thing called the broken spin-orbit symmetry due to Leggett and magnetic interaction both of which are due to spin-$\frac{1}{2}$ effect that actually give rise to some obstacles.

These obstacles prevent the formation of He-3 pairs, until the Ramachandran attraction is strong enough to

eventually overcome the said obstacles, which is only possible at a much lower temperature. We also have provided the consistent microscopic physics to explain the discontinuous specific heat capacity between A- and B-phases, and between normal phase and B-phase. In the absence of Ramachandran attraction (derived from the first principles without any guessed functions and adjustable parameters), it is impossible to capture the variety of discontinuous specific heat at the critical points in He-4 and He-3 consistently. Finally, our qualitative predictions on discontinuous specific heat (with or without jumps at the critical points) can be readily and unequivocally verified with suitable experiments. In addition, it is worth noting that one of the implications of Ramachandran pairing mechanism is that pure BEC observed in ^{87}Rb, ^{23}Na and ^{7}Li cold atoms [51] can only produce discontinuous 'cusp' or 'cusp-like' feature in the specific heat data at the critical point. In particular, pure BEC in the absence of changing Ramachandran attraction cannot induce any discontinuous 'jump' (however small) at the critical point.

Acknowledgements

Appendix

Derivation of the Ramachandran attraction: Eq. (1)

In order to derive eq. (1), we need to first derive some relevant equations which are needed to understand the existence of the so-called Ramachandran attraction. We start from the one-dimensional Drude model Hamiltonian for a two-atom system (isolated), which is given by [52,53]

$$H = H_{\mathrm{O}} + H_{\mathrm{I}}, \tag{16}$$

$$H_{\mathrm{O}} = \frac{p_1^2}{2m} + \frac{1}{2}Qr_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}Qr_2^2, \tag{17}$$

$$H_{\mathrm{I}} = \frac{1}{4\pi\epsilon_0}\left[\frac{(e)(e)}{R} + \frac{(-e)(e)}{R + r_2}\right.$$
$$\left. + \frac{(-e)(e)}{R - r_1} + \frac{(-e)(-e)}{R - r_1 + r_2}\right], \tag{18}$$

where $p_{1,2}$ and $Q_1 = Q_2 = Q$ are the electrons momenta and spring's (interaction potential) constant,

respectively, and R is the distance between two neutral atoms (interatomic distance). The subscripts 1 and 2 are used to identify electrons 1 and 2, both bounded to nuclei 1 and 2, respectively. The ordinary Hamiltonian without interaction, H_O, consists of two kinetic energy terms and two semiclassical harmonic-oscillator type el–ion potential terms. These potential terms refer to the el–ion interactions within their respective atoms (see figure 1 in ref. [32]). In contrast, the interaction Hamiltonian, H_I, captures all the Coulomb interactions that may exist between the two interacting atoms.

Assuming that the polarisation of electrons obey harmonic oscillation with very weak interaction, we can impose these conditions, namely, $|r_1| \ll R$ and $|r_2| \ll R$, which means $|Rr_1 - Rr_2| \approx |R^2 r_1 - R^2 r_2| \approx 0$ and $R^3 \gg |Rr_1 r_2|$, and therefore, we can readily rearrange H_I to read,

$$H_I \cong \frac{e^2 r_1 r_2}{2\pi \epsilon_0 R^3}. \tag{19}$$

Subsequently, we can further rearrange eqs (17) and (19) by using the following variables [52]:

$$r_\pm = \frac{1}{\sqrt{2}}(r_1 \pm r_2) \tag{20}$$

and

$$p_\pm = \frac{1}{\sqrt{2}}(p_1 \pm p_2) \tag{21}$$

to arrive at

$$H = \left[\frac{1}{2m} p_+^2 + \frac{1}{2}\left(Q - \frac{e^2}{2\pi \epsilon_0 R^3} \right) r_+^2 \right]$$
$$+ \left[\frac{1}{2m} p_-^2 + \frac{1}{2}\left(Q + \frac{e^2}{2\pi \epsilon_0 R^3} \right) r_-^2 \right]. \tag{22}$$

Equation (22) is in a suitable form to be compared with eq. (23),

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} m\omega^2 x^2 \psi = \hat{H}\psi = E\psi, \tag{23}$$

(see the kinetic and potential energy operators on the left-hand side of eq. (23)). In doing so, we should be able to infer the ground-state energy from the Drude Hamiltonian given in eq. (22), which is

$$E = \frac{1}{2}\hbar(\omega_+ + \omega_-), \tag{24}$$

$$= \frac{1}{2}\hbar \left[\sqrt{\frac{Q - (e^2/2\pi \epsilon_0 R^3)}{m}} + \sqrt{\frac{Q + (e^2/2\pi \epsilon_0 R^3)}{m}} \right]. \tag{25}$$

We shall not work out the algebraic rearrangements here because the complete solution is already available in ref. [52], and the rearrangements are straightforward. Anyway, it should be clear that m is the electron mass, while the interaction constant Q is different for different atoms. Before we move on to derive the Ramachandran interaction potential operator, let us prove the following theorem:

Theorem 1. *The coordinates, $\mathbf{r}_1$ and $\mathbf{r}_2$ are vectors such that we have aligned them to obtain maximum electronic polarisation along the x-axis where $\mathbf{r}_1 \to r_1$ and $\mathbf{r}_2 \to r_2$. Therefore, eq. (22) also applies to real (three-dimensional) atoms such that the polarisation has been confined to a particular direction (one-dimensional).*

Proof. First, imagine that there are two polarisable spherical atoms. Subsequently, suppose the electron coordinate, $\mathbf{r}_1$ (from sphere 1) has been aligned along the x-axis, so that $|\mathbf{r}_1| = r_1$. The induced polarisation caused by sphere 1 due to $\mathbf{r}_1$ shall affect $\mathbf{r}_2$ giving rise to

$$|\mathbf{r}_2| = r_2(\theta, \phi), \tag{26}$$

where

$$\theta < \pi/4, \ \phi < \pi/4, \tag{27}$$

θ is the angle in the xy-plane and ϕ denotes the angle in the xz-plane. It is easily verified that if $\theta \geq \pi/4$ and $\phi \geq \pi/4$, then there is an additional induced polarisation affecting $|\mathbf{r}_2| = r_2(\theta, \phi)$. If such an additional polarisation does exist, then we can take it into account by realigning the coordinate, $\mathbf{r}_2$ (from sphere 2) with respect to this new $\mathbf{r}_1'$. In this 'additional-polarisation' case, $|\mathbf{r}_1'| = r_1'$, which then leads to

$$|\mathbf{r}_2'| = r_2'(\theta, \phi), \tag{28}$$

where the angles remain the same, for example, $\theta < \pi/4$ and $\phi < \pi/4$. This means that,

$$\theta \in (0, \pi/4], \ \phi \in (0, \pi/4]. \tag{29}$$

For one-dimensional polarisation cases, we always have $\theta = 0 = \phi$, which is the case for eq. (22), while for two-dimensional polarisation cases, one has $\theta \in (0, \pi/4]$ and $\phi = 0$. $\square$

Renormalised Van der Waals interaction

Before one can derive the Ramachandran interaction potential operator, we need to first derive the standard vdW interaction operator, which can be obtained from the ground-state energy E (see eq. (25)) and from the ground-state energy E' when $H_I = 0$. This is important to observe and acknowledge the fundamental difference

between vdW and Ramachandran attraction. It is trivial to derive E' because $H_I = 0$. Hence, eq. (22) reduces to

$$H' = \left[\frac{1}{2m}p_+^2 + \frac{1}{2}Qr_+^2\right] + \left[\frac{1}{2m}p_-^2 + \frac{1}{2}Qr_-^2\right]. \quad (30)$$

Subsequently, eq. (30) directly leads us to

$$E' = \hbar\omega' = \hbar\sqrt{\frac{Q}{m}}. \quad (31)$$

After imposing the condition,

$$Q \gg \frac{e^2}{2\pi\epsilon_0 R^3} \quad (32)$$

in eq. (25), we can find the standard vdW interaction potential,

$$V_{\text{vdW}} = E - E' \cong -\frac{\hbar}{8m^2\omega'^3}\left(\frac{e^2}{2\pi\epsilon_0}\right)^2\frac{1}{R^6}. \quad (33)$$

The negative sign in eq. (33) implies that V_{vdW} is an attractive interaction, and also, it is weak due to $1/R^6$ dependence. From eq. (34),

$$Q^{\text{dressed}} = Q\exp[\lambda(\xi - E_F^0)], \quad (34)$$

the renormalised Q,

$$\tilde{Q} = Q\exp[\lambda\xi], \quad (35)$$

where we prefer to denote any renormalised parameter with a tilde. Recall here that $\tilde{Q}$ (from eq. (35)) replaces the standard Q given in H_O to evaluate the changes to Q when we replace one atom with another. Moreover, we (as required by the Drude Hamiltonian) do not allow any electronic wave function overlapping, in which, the said overlapping shall lead to quantum phase transition.

Subsequently, we need to renormalise eq. (33), which can be done by first substituting all Q in eq. (25) with eq. (35), which leaves us with

$$\tilde{E} = \frac{1}{2}\hbar\left[\sqrt{\frac{\tilde{Q} - (e^2/2\pi\epsilon_0 R^3)}{m}}\right.$$
$$\left. +\sqrt{\frac{\tilde{Q} + (e^2/2\pi\epsilon_0 R^3)}{m}}\right]. \quad (36)$$

Here, any variable found to wear a tilde is a renormalised parameter. We now expand eq. (36) using the series,

$$\sqrt{1 + (\pm x)} = 1 \pm \frac{x}{2} - \frac{x^2}{8} \pm \frac{x^3}{16} - \cdots \quad (37)$$

to arrive at

$$\tilde{E} = \frac{1}{2}\hbar\left[\sqrt{\frac{\tilde{Q}}{m} - \frac{e^2/2\pi\epsilon_0 R^3}{m}} + \sqrt{\frac{\tilde{Q}}{m} + \frac{e^2/2\pi\epsilon_0 R^3}{m}}\right], \quad (38)$$

$$= \frac{1}{2}\hbar\sqrt{\frac{\tilde{Q}}{m}}\left[\sqrt{1 + \left(-\frac{e^2/2\pi\epsilon_0 R^3}{\tilde{Q}}\right)}\right.$$
$$\left. +\sqrt{1 + \left(\frac{e^2/2\pi\epsilon_0 R^3}{\tilde{Q}}\right)}\right]. \quad (39)$$

Substituting

$$\tilde{\omega}' = \sqrt{\frac{\tilde{Q}}{m}}, \quad (40)$$

into eq. (39) and noting that,

$$x = \mp\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}, \quad (41)$$

we can get

$$\tilde{E} = \frac{1}{2}\hbar\tilde{\omega}'\left\{\left[1 + \frac{1}{2}\left(-\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}\right)\right.\right.$$
$$-\frac{1}{8}\left(-\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}\right)^2$$
$$\left. +\frac{1}{16}\left(-\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}\right)^3 - \cdots\right]$$
$$+\left[1 + \frac{1}{2}\left(\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}\right) - \frac{1}{8}\left(\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}\right)^2\right.$$
$$\left.\left. +\frac{1}{16}\left(\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}\right)^3 - \cdots\right]\right\}. \quad (42)$$

It is clear from eq. (42) 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. Moreover, we should also observe that

$$\left|\pm\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}\right| \le 1. \quad (43)$$

Consequently, we just need to impose the condition,

$$Q\exp[\lambda\xi] \gg \frac{e^2}{2\pi\epsilon_0 R^3}, \quad (44)$$

which means,

$$\left(\frac{e^2}{2\pi\epsilon_0 R^3}\right)^{\text{n}}\tilde{Q}^{-\text{n}} \approx 0, \quad (45)$$

for all $\text{n} \ge 4$ where $\text{n} \in \mathbb{N}_{\text{even}}$. Here, $\mathbb{N}_{\text{even}}$ is the set of even natural numbers. After imposing the said condition,

$$\tilde{E} = \frac{1}{2}\hbar\tilde{\omega}'\left\{\left[1 - \frac{1}{8}\left(-\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}\right)^2\right]\right.$$
$$\left. +\left[1 - \frac{1}{8}\left(\frac{e^2}{2\pi\epsilon_0 R^3 \tilde{Q}}\right)^2\right]\right\}, \quad (46)$$

$$= \frac{1}{2}\hbar\tilde{\omega}'\left[2 - \frac{1}{4\tilde{Q}^2}\left(\frac{e^2}{2\pi\epsilon_0 R^3}\right)^2\right]. \tag{47}$$

To see if there is any (repulsive or attractive) interaction between the two identical and neutral atoms as a result of H_{I}, we need to subtract $\hbar\tilde{\omega}'$ (see eq. (31)) from eq. (47) to obtain

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

$$= \hbar\tilde{\omega}'\left[-\frac{1}{8\tilde{Q}^2}\left(\frac{e^2}{2\pi\epsilon_0 R^3}\right)^2\right]. \tag{48}$$

We now substitute $\tilde{Q}^2 = (\tilde{\omega}')^4 m^2$ and then followed by the substitution, $\tilde{\omega}' = \omega' \exp\left[\frac{1}{2}\lambda\xi\right]$ into eq. (48) to arrive at,

$$\tilde{V}_{\mathrm{vdW}}(\xi) = \tilde{E}(\xi) - \hbar\tilde{\omega}'$$

$$= \left\{-\frac{\hbar}{8m^2(\omega')^3}\left(\frac{e^2}{2\pi\epsilon_0}\right)^2\frac{1}{R^6}\right\}$$

$$\times \exp\left[-\frac{3}{2}\lambda\xi\right], \tag{49}$$

$$= V_{\mathrm{vdW}}\exp\left[-\frac{3}{2}\lambda\xi\right]. \tag{50}$$

The negative sign in eq. (49) implies that there is an attractive interaction, and this is the van der Waals attraction in its renormalised form. The standard (or unrenormalised) vdW formula is given in the curly bracket. Regardless of whether V_{vdW} is renormalised or not, eq. (49) is only valid for weakly interacting systems due to the condition given in eq. (44). Apparently, $\hbar\tilde{\omega}'$ is the renormalised ground-state energy $\tilde{E}'(\xi)$ when $H_{\mathrm{I}} = 0$. The compatibility of eq. (49) with eq. (33) is obvious, while the additional physics that can be extracted from eq. (49) is as follows: for a given interatomic distance, R, we should have

$$\tilde{V}_{\mathrm{vdW}}(\xi) \to 0, \text{ when } \xi \to \infty, \tag{51}$$

where eq. (51) implies that the valence electrons are literally not polarisable, which is as it should be. In contrast, $\tilde{V}_{\mathrm{vdW}}(\xi)$ gets a maximum value if ξ is permitted to reach a physically allowable minimum value. Here, we did not take the minimum value to read, $\xi \to 0$ because this is physically not acceptable for atomic systems where all electrons in such systems are bound to their respective nucleus. Thus $\xi \neq 0$ is always valid. In solids however, $\xi = 0$ is permitted entirely for a different reason. In particular, we should note that there is such a thing as many-body potential giving rise to metallic bond that keeps all the electrons bounded within a given solid. Even though these electrons are collectively kept bounded within the solid, they can be effectively free

(not bounded to any particular ion or group of ions) to form Fermi metals, for which $\xi = 0$ or ξ is an irrelevant constant.

Ramachandran interaction theory and analysis

The essence of the Ramachandran interaction is the existence of a stronger attraction between two atoms, stronger than the vdW attraction. As pointed out above, even the renormalised version of the standard vdW attraction (see eq. (49)) is too weak due to this $1/R^6$ dependence. In this weak interaction case, the induced electronic polarisation in each atom is either too small or, if the polarisation is relatively large, then the polarisation is still approximately isotropic (see figure 2 in ref. [32]). The condition that assures this weak interaction and isotropic polarisation is given in eq. (44). Basically, there are three types of polarisation between interacting atoms. The first is the weakly interacting atom, before or after the atom is exposed to an external disturbance, namely, intense laser or high temperatures. Such exposure leads to an isotropically polarised atom, hence weakly interacting. On the other hand, strongly interacting atoms can give rise to anisotropic polarisation and asymmetric polarisation. However, an additional interaction is activated due to anisotropic polarisation. The said additional interaction is nothing but the stronger el–el Coulomb repulsion between the anisotropically polarised atoms.

On the contrary, if two atoms are of different types (atom-1 $\neq$ atom-2) such that one of the atoms is easily-polarisable, while the other is a less polarisable atom, then the atoms are asymmetrically polarised. In this case, the el–el Coulomb repulsion is weaker than anisotropically polarised atoms, for a given R. If the two atoms are identical, then, we definitely need external assistances (high temperature, pressure and concentration that can lead to violent atomic collisions) to form the transition state. But to complete the chemical reaction from the transition state to the product, one still needs strong attraction that can only be made available by a Coulomb-type attraction, which leads to wave function transformation that induces chemical reaction. Therefore, identical atoms eventually require stronger attraction, in addition to other external help, to proceed further from the transition state to the final product. In contrast, the asymmetrically polarised atoms do not explicitly need any external 'help', and the reaction between dissimilar atoms can be spontaneous.

Theorem 2. *For the Ramachandran attraction of the first type, asymmetric and anisotropic polarisation can be induced with a stronger vdW attraction between dissimilar and identical atoms, respectively, regardless of*

whether $R \gg r_1 + r_2$ or $R > r_1 + r_2$ where r_1 and r_2 denote the radii of atom-1 and atom-2, respectively. Here, strong attraction can be imposed manually by requiring,

$$Q \exp[\lambda \xi] = \tilde{Q} = \frac{e^2}{2\pi \epsilon_0 R^3}, \tag{52}$$

instead of eq. (44). Equation (44) is the condition for weak attraction, used earlier to derive the vdW attraction. Here, eq. (52) is valid even if $R \gg r_1 + r_2$ where $R \gg r_1 + r_2$ is a necessary condition so as to make sure eq. (19) is also valid. This condition (eq. (52)) gives us the interatomic Ramachandran attraction of the first type,

$$\tilde{V}_{\text{Ramachandran}}^{\text{I}}(\xi) = \hbar \omega' \left(\frac{1}{\sqrt{2}} - 1 \right) \exp \left[\frac{1}{2} \lambda \xi \right]. \tag{53}$$

Equation (53) imposes a large anisotropic polarisation, much larger than what is allowed by the standard vdW attraction. The new condition allows a large interatomic interaction energy even if ξ is small (see eq. (53)). Here, eq. (53) is the analytic relation that permits ξ to have the smallest value – in other words, $\xi = 0$ is forbidden as demanded by all the physical atoms found in the Periodic Table of Chemical Elements.

Proof. The interatomic Ramachandran attraction of the first type gives rise to the transformation

$$\exp \left[-\frac{3}{2} \lambda \xi \right] \rightarrow \exp \left[\frac{1}{2} \lambda \xi \right], \tag{54}$$

which can be confirmed by comparing eq. (49) with eq. (53), whereas the interatomic Ramachandran attraction of the second type gets rid of the el–el Coulomb repulsion by activating $\tilde{V}_{\text{Coulomb}}^{\text{el–ion}}(\xi)$. From now on, we shall drop the term 'interatomic' for convenience because of course we are exclusively dealing with interatomic interaction in the atomic systems. The physics of the standard renormalised vdW attraction (eq. (49)) relies on the fact that polarisation is small due to weak interaction such that ξ is not even allowed to reach zero where $\xi \neq 0$ because atomic systems cannot permit $\xi = 0$, and therefore, $0 \ll \xi < \infty$ (see eq. (44)), which is indeed a condition for small polarisation.

For large polarisation however, we need $0 < \xi \ll \infty$, and rightly so, the transformation (eq. (54)) is automatically activated in our derivation of the Ramachandran attraction of the first type. Note that, the large polarisation here refers to the polarisation of electron-1 due to atom-2 and vice versa, and that is why we need larger ξ to enhance the Ramachandran attraction. In other words, the Ramachandran attraction is activated when the atomic polarisation is large in the presence of

large ionisation energy, which can only be true for atoms that interact strongly such that this strong interaction is not due to temperature.

The said large polarisation can be imposed by invoking eq. (52) that is in agreement with $0 < \xi \ll \infty$. Consequently, we can readily make use of eq. (52), which enforces eq. (36) to reduce to a mathematically simpler form (for strongly interacting atoms),

$$\tilde{E}(\xi)' = \frac{1}{2} \hbar \left[0 + \sqrt{\frac{2\tilde{k}}{m}} \right], \tag{55}$$

but physically, it is difficult to understand eq. (55) within the standard vdW formulation due to eq. (54). But never mind, the Ramachandran attraction (type I) in the presence of large polarisation (and large ionisation energy) is as follows:

$$\tilde{V}_{\text{Ramachandran}}^{\text{I}}(\xi) = \tilde{E}(\xi)' - \hbar \tilde{\omega}'$$
$$= \frac{1}{2} \hbar \sqrt{\frac{2\tilde{Q}}{m}} - \hbar \tilde{\omega}'. \tag{56}$$

Again, noting that $\tilde{Q} = Q \exp[\lambda \xi]$ and $\tilde{\omega}' = \omega' \exp[\frac{1}{2} \lambda \xi]$, we can simplify eq. (56) as

$$\tilde{V}_{\text{Ramachandran}}^{\text{I}}(\xi) = \hbar \omega' \left(\frac{1}{\sqrt{2}} - 1 \right) \exp \left[\frac{1}{2} \lambda \xi \right], \tag{57}$$

which is eq. (53). □

Quantitative comparison in support of Ramachandran attraction

We have achieved our original objectives by first proving that the Ramachandran attraction between He atoms is responsible for the specific heat capacity to jump up discontinuously at the critical point during cooling. This is only possible with the formation of Ramachandran pairs between two He atoms, be they He-4 or He-3, which automatically proves why BEC does not imply superfluidity. In particular, only a cusp-like feature is observed if the transition is induced by pure BEC. Apart from that, we also have proved that there are four possibilities for the A-phase to B-phase transition in the specific heat capacity during cooling for the He-3 superfluid. To choose the correct microscopic physics for this particular transition, we have to rely on the specific heat experimental data, whether there is a cusp or a discontinuous jump and whether the jump is upward or downward during cooling.

Despite the above facts, it is always worthwhile to provide some numerical comparison in support of our theory presented thus far, especially in support of the Ramachandran attraction, at least indirectly. From the experimental data reported by Morton *et al* [49],

we know that $\xi_{\text{He:4}} > \xi_{\text{He:3}}$ when $\xi_{\text{He:4}} - \xi_{\text{He:3}} = 313{,}520$ MHz. As a consequence, from the Ramachandran attraction formula (see eq. (1)) between neutral atoms, we can readily deduce that Ramachandran attraction is stronger for He-4 pairs than for He-3 pairs, which means that the superfluid critical temperature for liquid He-4 should be higher to form superfluidity. This is indeed the case from the specific heat data reported in ref. [47] for He-4 (at saturated He vapour) and in ref. [41] for He-3 (at 33.4 bar), even though both measurements were carried out at different pressures. Note that no estimate is available for the ground-state energies for He-4 or He-3 pairs and that there are two unknowns (ω_{pair} and ξ_{pair}) and only one equation, eq. (1), for each system.

When we say that the Ramachandran attraction is stronger than that of the vdW force, it means for strongly interacting atoms, the strongest Ramachandran attraction for atomic He or for any particular system does not imply that the attraction of one system should be of the same order or magnitude in other systems. Hence, such numerical comparison (between different systems), even by means of inequalities, would be misleading.

What we can say here is that when we consider the attraction between any strongly correlated atoms, the Ramachandran attraction is always stronger than that of the vdW force, which is indeed the case from the above derivation. For example, it is worth noting that we can substitute eq. (52) into eq. (53) so as to derive the Ramachandran attraction as a function of R, i.e., $V_{\text{Ramachandran}}^{\text{I}}(R)$, which is given by

$$V_{\text{Ramachandran}}^{\text{I}}(R) = \frac{e\hbar}{\sqrt{2m\pi\epsilon_0}}\left(\frac{1}{\sqrt{2}} - 1\right)\frac{1}{R^{3/2}}, \quad (58)$$

where the effect of ξ is replaced by R, the distance between two atoms. We can estimate the value for $V_{\text{Ramachandran}}^{\text{I}}(R)$ between two atomic helium from the above formula, which is about 1 eV or between 1.3×10^{-19} J (0.8 eV) and 1.9×10^{-19} J (1.2 eV) when R is between 300 pm and 240 pm, respectively. Here, the van der Waals separation between two helium atoms is 280 pm. We stress that the stated range for $V_{\text{Ramachandran}}^{\text{I}}(R)$ between two atomic helium differs for different interacting chemical element pairs as pointed out in the above paragraph.

Our estimate makes physical sense (as anticipated) because it is larger than that of the van der Waals highest value, which is about 0.04 eV. However, our estimate is still rather crude and sensitive to R where the choice of R should be large due to electron–electron repulsion (between helium atoms), which will reduce the magnitude of the above estimate. Nevertheless,

$V_{\text{Ramachandran}}^{\text{I}}$ by definition, can be larger than all other weak intermolecular interactions such as van der Waals, hydrogen bonds, ionic interaction and hydrophobic interaction because the next step after $V_{\text{Ramachandran}}^{\text{I}}$ is the type-II Ramachandran attraction that can induce chemical reaction.

In addition, we also have discussed the proper numerical comparison in ref. [54] to evaluate the stronger Ramachandran attraction in physical chemistry to study the microscopic physics of hydration energy for different cations. Hence, only for weakly interacting atoms, the Ramachandran attraction is not activated (that can be deduced from the above derivation where eq. (52) is not activated, instead, eq. (32) is activated), and in this case, the usual vdW attraction plays its part, which is indeed true for weakly interacting gases. If we take $V_{\text{Type:I}}^{\text{R}}(\xi) \propto k_B T_{\text{C},\lambda}$, which is reasonable, then there are two factors that have led to $T_{\text{C}} < T_{\lambda}$, namely, $\xi_{\text{He:3}} < \xi_{\text{He:4}}$ and the obstacle due to spin-half effect.

Of course, one can argue that the said lower critical temperature for He-3 is entirely due to the effect of spin-$\frac{1}{2}$ nuclei as discussed in the earlier sections. If this is the case, then we do not know what is the interaction responsible for superfluidity in He-4. Moreover, we have to assume that the spin interaction is responsible for He-3 pairing despite the fact that this is not possible physically as discussed using eq. (14). It is unfortunate that we only have two superfluids, namely, He-4 and He-3, and therefore unambiguous numerical or quantitative analysis in support of Ramachandran attraction can only come from novel measurements, which can be used to verify whether He-4 pairing does occur in He-4 superfluids. It is worth noting that the Ramachandran attraction is not responsible or is not activated for water at different temperatures (between 600 and 250 K) and pressures (between 0.1 and 100 MPa) [55].

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