

# The quantum potential: the missing interaction in the density maximum of $\text{He}^4$ at the lambda point?

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**Abstract:** The lambda point in liquid  $\text{He}^4$  is a well established phenomenon acknowledged as an example of Bose-Einstein condensation. This is generally accepted, but there are serious discrepancies between the theory and experimental results, namely the lower value of the transition temperature  $T_\lambda$  and the negative value of  $dT_\lambda/dP$ . These discrepancies can be explained in term of the quantum stochastic hydrodynamic analogy (SQHA). The SQHA shows that at the  $\text{He}^4_{\text{I}} \rightarrow \text{He}^4_{\text{II}}$  superfluid transition the quantum coherence length  $\lambda_c$  becomes of order of the distance up to which the wave function of a couple of  $\text{He}^4$  atoms extends itself. In this case, the  $\text{He}^4_2$  state is quantum and the quantum pseudo-potential brings a repulsive interaction that leads to the negative  $dT_\lambda/dP$  behavior. This fact overcomes the difficulty to explain the phenomenon by introducing a Hamiltonian inter-atomic repulsive potential that would obstacle the gas-liquid transition.

**Keywords:** Lambda Point, Liquid  $\text{He}^4$ , Maximum Density, Low Temperature Critical Dynamics, Ballistic to Diffusive Transition, Anomalous Transport

## 1. Introduction

To explain the  $\text{He}^4_{\text{I}} \rightarrow \text{He}^4_{\text{II}}$  superfluid transition London [1] in 1938 made the hypothesis that  $\text{He}^4$  lambda point might be an example of Bose-Einstein (BE) condensation (BEC). This hypothesis was based upon the similarity between the shape of the heat capacity of an ideal boson gas at the BEC transition and the data for the  $\text{He}^4_{\text{I}} \rightarrow \text{He}^4_{\text{II}}$  transition. This convincement was reinforced by the observation that there is no similar phase transition in the Fermi liquid  $\text{He}^3$ . However, even if the basic BEC hypothesis is acknowledged, looking in details some discrepancies exist [2]. Among those, two are the majors: (1) the calculated BE transition temperature  $T_B$  for an ideal gas is 3.14 K while the measured one for the  $\text{He}^4$  is of 2.17K. (2) The variation of the transition temperature  $T_\lambda$  with pressure is negative and is opposite in sign to that expected from the BEC. The standard way out is to address the differences to the fact that the BEC theory is applied to an ideal gas while the  $\text{He}^4$  is clearly not, since it shows a van der waals-like

liquid gas phase transition. Therefore, the inter-molecular potential must be taken into account when we calculate the transition temperature  $T_B$  and its variation with temperature.

The BEC theory [3] affirms that below the BE temperature  $T_B$  the number of particles,  $N_e$ , in the excited state reads

$$N_e = h^{-3} \int \frac{1}{\exp[\epsilon/kT] - 1} d^3q d^3p \quad (1)$$

and hence

$$N_e(T) = 2,612 V \frac{2\pi(2m)^{3/2}}{h^3} T^{3/2} \quad (2)$$

At the BE temperature  $T_B$ , it is assumed that all the particles go in the excited state so that

$$T_B = \frac{h^2}{2\pi mk} \left( \frac{N}{2,612V} \right)^{2/3} \quad (3)$$

As equation (3) shows, the increase of pressure, leading to the volume  $V$  decrease, will bring to the increase of  $T_B$ . This contradicts what is experimentally observed at lambda point where  $dT_\lambda/dP$  is negative.

By considering the van der Waals state equation

$$P = \{n k T / (V - n b)\} - a n^2 / V^2, \quad (5)$$

(where  $n$  is the number of molecules,  $b$  is the fourfold atomic volume and  $a$  is the mean inter-molecular potential energy derived by using the rigid sphere approximation given by (21-22)) that for punctual particles (i.e.,  $b = 0$ ) with an attractive potential (i.e.,  $a > 0$ ) reads

$$P = n k T / V - a n^2 / V^2 \quad (6)$$

we can see that the pressure decrease  $-a n^2 / V^2$  is a consequence of the attractive intermolecular potential. This is equivalent to a compression of the ideal gas and, since the integration in (1) is carried out on the system volume, we can say that a cohesive intermolecular potential reduces the system volume and by (3) that  $T_B$  increases.

Therefore, given the ideal gas pressure  $P_{IG} \equiv n k T / V$ , the variation of BEC critical temperature in a real gas  $\Delta T_c = T_c - T_B$  has the same sign of the pressure variation  $\Delta P$  (with respect to the real gas) according to the expression

$$\Delta T_B \propto \Delta P = P_{IG} - P \equiv a n^2 / V^2 > 0 \quad (7)$$

Moreover, given  $dT_c/dP \sim d\Delta T_c/dP$  it follows that

$$dT_c/dP \propto a n^2 d(V^{-2})/dP > 0 \quad (8)$$

since  $V$  decreases with the pressure.

Feynman [4] in 1953 and later Butler and Friedman [5,6] calculated in detail the contribution of the inter-molecular potential for a bosonic system showing that it would need a repulsive potential, causing an expansion of the gas, in order to lower  $T_B$  as one might expect from (7) (i.e.,  $\Delta T_c < 0$ ).

Shortly afterwards, ter Haar [7], pointed out that the repulsive potential was unphysical and would hinder the gas-liquid transition from taking place.

Recently, Deeney et al. [8] showed that a quantum source of energy leading to the expansion of the condensate may explain the negative  $dT_\lambda/dP$  behavior. The SQHA model supports this hypothesis showing that the quantum pseudo potential (QPP) (that acts only in the quantum condensed state) generate a repulsive force leading to the anomalous behavior at lambda point.

The QPP is a well-defined potential energy in the Madelung's quantum hydrodynamic analogy (QHA). It is responsible for the realization of the eigenstates and the consequent quantum dynamics. As shown by Weiner [9], this energy is a real energy of the system and consists in the difference between the quantum energy and the classical

one.

If fluctuations are present, the stochastic quantum hydrodynamic analogy (SQHA) shows that the quantum potential may have a finite range of interaction  $\lambda_q$  [10] so that dynamics on a much larger scale acquire the classical behavior. On the opposite side, on a scale shorter than the quantum coherence length  $\lambda_c$  the quantum behavior is restored [10].

Following this approach, when the couples of  $\text{He}^4$  molecules lie at a distance smaller or equal to the quantum coherence length  $\lambda_c$ , the atomic dynamics becomes quantum (the related quantum pseudo potential interaction appears) and the systems makes the  $\text{He}^4_{\text{I}} \rightarrow \text{He}^4_{\text{II}}$  transition (see section A.3. in appendix [A]).

In the following the effects of the quantum pseudo potential energy onto the BEC temperature as well as on the sign of  $dT_\lambda/dP$  are derived.

## 2. The SQHA Equation of Motion

The QHA-equations are based on the fact that the Schrödinger equation, applied to a wave function  $\psi(q,t) = A(q,t) \exp[i \frac{S(q,t)}{\hbar}]$ , is equivalent to the motion of a fluid with particle density  $n(q,t) = A^2(q,t) = |\psi|^2$  and a velocity  $\dot{q} = \frac{\nabla_q S(q,t)}{m}$ , governed by the equations [11]

$$\partial_t n(q,t) + \nabla_q \cdot (n(q,t) \nabla_q \dot{q}) = 0, \quad (9.a)$$

$$\dot{q} = \nabla_p H, \quad (9.b)$$

$$\dot{p} = -\nabla_q (H + V_{qu}) \quad (9.c)$$

$$H = \frac{p \cdot p}{2m} + V(q). \quad (9.d)$$

Where  $m$  is the mass of the structureless particles of the system and  $V_{qu}$  is the quantum pseudo-potential that originates the quantum non-local dynamics and reads

$$V_{qu} = -\left(\frac{\hbar^2}{2m}\right) n^{-1/2} \nabla_q \cdot \nabla_q n^{1/2}. \quad (10)$$

When fluctuations are considered into the hydrodynamic quantum equation of motion, the resulting stochastic QHA dynamics preserve the quantum behavior on a scale shorter than the theory defined quantum coherence length  $\lambda_c$  [10]. Moreover, in the case of non-linear systems, on very large scale the local classical behavior can be achieved when the quantum pseudo potential has a finite range of interaction

given by the non-locality length  $\lambda_L$  [10] (with  $\lambda_L > \lambda_c$ ).

Following the procedure given in reference [10], with  $n_{(q,t)} = \iiint \rho_{(q,p,t)} d^3p$ , where  $\rho_{(q,p,t)}$  is the probability density function (PDF) of the system (whose spatial density  $n_{(q,t)}$  represents the squared wave function modulus), the SQHA equation of motion can be established to read

$$\partial_t n_{(q,t)} = -\nabla_q \cdot (n_{(q,t)} \nabla_q \dot{q}) + \eta_{(q_\alpha,t,\Theta)}, \quad (11)$$

$$\begin{aligned} &< \eta_{(q_\alpha,t)}, \eta_{(q_\alpha+\lambda,t+\tau)} > = \\ &= \mu \frac{4m(k\Theta)^2}{\pi^3 \hbar^2} \exp[-(\frac{\lambda}{\lambda_c})^2] \delta(\tau) \delta_{\alpha\beta} \end{aligned} \quad (12)$$

$$\lambda_c = (\frac{\pi}{2})^{3/2} \frac{\hbar}{(2mk\Theta)^{1/2}} \quad (13)$$

where  $\Theta$  is a measure of the noise amplitude.

Moreover, given that (for the mono-dimensional case) the quantum potential range of interaction  $\lambda_q$  reads [10]

$$\lambda_q = \lambda_c \frac{\int_0^\infty |q^{-1} \frac{dV_{qu}}{dq}| dq}{|\frac{dV_{qu}}{dq}| (q=\lambda_c)}, \quad (14)$$

Where the origin (0, 0) is the point of minimum Hamiltonian potential energy that is the rest mean position of the particle, for  $\lambda_c \cup \lambda_q \ll \Delta\Omega$  (where is the phase space discrete minimal resolution cell) equations (11-13) acquire the classical stochastic form

$$\partial_t n_{(q,t)} = -\nabla_q \cdot (n_{(q,t)} \nabla_q \dot{q}) + \eta_{(q_\alpha,t,\Theta)} \quad (15)$$

$$< \eta_{(q_\alpha,t)}, \eta_{(q_\alpha+\lambda,t+\tau)} > = \mu \delta_{\alpha\beta} \frac{k\Theta}{\lambda_c} \delta(\lambda) \delta(\tau) \quad (16)$$

$$\begin{aligned} \dot{q} &= \frac{p}{m} = \nabla_q \lim_{\Delta\Omega/\lambda_q \rightarrow \infty} \frac{S}{m} \\ &= -\nabla_q \{ \lim_{\Delta\Omega/\lambda_q \rightarrow \infty} \frac{1}{m} \int_{t_0}^t dt (V_{(q)} + V_{qu}(n_0) + I^*) \} \\ &= -\frac{1}{m} \nabla_q \{ \int_{t_0}^t dt (V_{(q)} + I^*) \} = \frac{p_{cl}}{m} + \frac{\Delta p_{st}}{m} \end{aligned} \quad (17)$$

The reader who is interested in more detail about the SQHA picture of a gas phase can refer to the Appendix A.

### 3. Determination of the Quantum Potential at the He<sup>4</sup><sub>I</sub>→He<sup>4</sup><sub>II</sub> Transition

In order to calculate the experimental outputs of the He<sup>4</sup><sub>I</sub>→He<sup>4</sup><sub>II</sub> superfluid transition we make use of the well-established statistical method of the Virial expansion that fits very fine for van der Waals fluids. This is possible in the stochastic hydrodynamic analogy since the presence of the quantum pseudo potential brings in the Virial expansion the quantum contribution to the system energy. A central point to derive the thermodynamic quantity by means of the Virial approach is the knowledge of the interaction in the pair of molecules (quantum potential included). Therefore, we firstly calculate the features of the He<sup>4</sup> - He<sup>4</sup> couple interaction.

As shown in ref. [19], the He<sup>4</sup> -He<sup>4</sup> interaction can be approximated by means of a square well potential of depth U\* and width 2Δ such as

$$V_{(x)} = \infty \quad x < \sigma \quad (18)$$

$$V_{(x)} = -U^* \quad \sigma < x < \sigma + 2\Delta \quad (19)$$

$$V_{(x)} = 0 \quad x > \sigma + 2\Delta \quad (20)$$

(where  $\sigma + \Delta$  is about the mean molecular (half) distance) and by introducing the self states wave functions

$$\psi = B \sin[K_n (x - \sigma)] \quad (21)$$

for  $\sigma < x < \sigma + 2\Delta$   $E_n > -U^*$  and

$$\psi = B \sin[K_n (2\Delta)] \exp[-\Gamma_n (x - (\sigma + 2\Delta))] \quad (22)$$

for  $x > \sigma + 2\Delta$   $E_n < 0$  where  $\Gamma_n = (-2mE_n/\hbar^2)^{1/2}$ ,  $K_n = (2m(U^* + E_n)/\hbar^2)^{1/2}$ , into relation (10), the quantum potential reads

$$V_{qu} = -(\hbar^2/2m) \Gamma_n^2 = E_n \quad (23)$$

for  $x > \sigma + 2\Delta$ , and

$$V_{qu} = (\hbar^2/2m) K_n^2 = (U^* + E_n) \quad (24)$$

for  $\sigma < x < \sigma + 2\Delta$ , where the values  $E_n$  are given by the trigonometric equation

$$\tan[K_n (2\Delta)] = -K_n / \Gamma_n = -(- (U^* + E_n) / E_n)^{1/2} E_n < 0 \quad (25)$$

and hence

$$\begin{aligned} \Delta &= (\hbar^2/8km)^{1/2} \arctan[-(- (U^* + E_0) / E_0)^{1/2}] / (U^*/k + E_0/k)^{1/2} \\ &= 1.231 \times 10^{-10} \{ \arctan[-(- (U^* + E_0) / E_0)^{1/2}] \} / (U^*/k + E_0/k)^{1/2} \end{aligned} \quad (26)$$

Moreover, by evaluating that the value of the energy  $E_0$  of

the fundamental state at the transition is about

$$-E_0/k \sim T_{cr} = 5.19 \text{ }^\circ\text{K} \quad (27)$$

and by choosing  $U^*$  to obtain the value for “a” given by (B.5) (see appendix B) it follows that

$$U^*/k \equiv [V_{cr}/N_A((\sigma+2\Delta)^3 - (\sigma)^3)] U/k = 0.82 U/k = 8.9 \text{ }^\circ\text{K}, \quad (28)$$

where  $U$  is the L-J potential deepness measured to be  $U/k \equiv 10.9 \text{ }^\circ\text{K}$  [16,17], it follows that

$$\Delta \sim 1.54 \times 10^{-10} \text{ m} = 2.9 \text{ Bohr} \quad (29)$$

and that the mean  $\text{He}_2^4$  atomic distance

$$\sigma + \Delta \equiv 3.82 \times 10^{-10} \text{ m} = 7.2 \text{ Bohr} \quad (30)$$

that well agrees with the values 7.1 Bohr given in ref. [16].

Reaching the lambda point (let's suppose by  $\text{He}^4$  -  $\text{He}^4$  cooling), the mean half atomic distance decreases to the value  $\sigma + \Delta$  of the fundamental state and the wave function variance decreases to  $2\Delta$  (the  $\text{He}^4$  atoms lie almost inside the potential well). Therefore, assuming that at the lambda-point the quantum coherence length  $\lambda_c$  becomes of order of the dimension of space domain where the wave function of the couple of  $\text{He}^4$  -  $\text{He}^4$  atoms is physically different from zero (i.e., a little bit larger than the  $\text{He}^4$  -  $\text{He}^4$  atoms distance  $\sigma + 2\Delta$ ) and it reads

$$\lambda_c = \pi \frac{\hbar}{(2mk\Theta)^{1/2}} \equiv \sigma + 2\Delta \quad (31)$$

for the couple of  $\text{He}^4$  -  $\text{He}^4$  atoms, at lambda point by (28) it follows that

$$\Theta_\lambda \equiv 2.07 \text{ }^\circ\text{K} \quad (34)$$

Even if  $\Theta$  is not exactly the thermodynamic temperature  $T$ , the result (34) is satisfying since it correctly agrees with the transition temperature of the lambda point. The fact that  $\Theta$  is close to  $T$  can be intuitively understood with the fact that going toward the absolute null temperature, correspondingly,  $\Theta$  must decrease since the systems fluctuations must vanish in both cases.

As shown in [10] a relation between  $\Theta$  and  $T$  can be established for an ideal gas at equilibrium. In this case, the thermodynamic temperature  $T$  converges to the vacuum fluctuation amplitude  $\Theta$  in going toward the to absolute zero. In the case of a real gas and its fluid phase, a bit of difference between  $\Theta$  and  $T$  may exists for  $\Theta \neq 0$ .

The result (34) definitely says that below a temperature of about 6,3°K degrees Kelvin the quantum potential enters more and more in the  $\text{He}_I^4$ - $\text{He}_I^4$  pair interaction. As it is shown in the following section, this well agrees with the features of the He lambda point that show how the increase

of  $\text{He}^4$  density (consequence of the quantum potential interaction) starts before the transition  $\text{He}_I^4 \rightarrow \text{He}_{II}^4$  takes place.

### 3.2. The Sign of $(T_\lambda - T_B)$ and that one of $dT_\lambda/dP$ at $\text{He}^4$ Lambda Point

The above equation (22) holds for normal fluid phases at a temperature above the superfluid transition one. Below the superfluid transition temperature, as shown by (31, 47) the quantum coherence length  $\lambda_c$  becomes larger than the inter-atomic  $\text{He}^4$  -  $\text{He}^4$  distance and hence the quantum potential contributes to the molecular energy and it must be taken into account in the calculation of the mean inter-molecular potential energy “a” that reads

$$\begin{aligned} a &\equiv -2\pi \int_{r_0}^{\infty} (V_{(r)} + V_{qu}) r^2 dr \\ &= -2\pi \left\{ \int_{r_0}^{\infty} V_{(r)} r^2 dr + \int_{r_0}^{\infty} V_{qu} r^2 dr \right\} \\ &= a^{cl} + a^{qu} \end{aligned} \quad (35)$$

where

$$\begin{aligned} a^{qu} &= -2\pi \int_{r_0}^{\infty} V_{qu} r^2 dr = -2\pi (U^* + E_0) \int_{\sigma}^{\sigma+\Delta} r^2 dr \\ &= -\frac{2}{3}\pi (U^* + E_0) [(\sigma + \Delta)^3 - 2^{1/2}(\sigma)^3] < 0. \end{aligned} \quad (36)$$

From (36) we can observe that  $a^{qu}$  is negative since from (24)  $V_{qu} = (U^* + E_0)$  is positive. Therefore, below the superfluid transition temperature, the state equation (B.3) (see appendix B) reads:

$$\begin{aligned} \{P + a^{cl} n^2/V^2 + a^{qu} n^2/V^2\} (V - nb) \\ = \{P + a^{cl} n^2/V^2 + \Delta P^{qu}\} (V - nb) \\ = n k T \end{aligned} \quad (37)$$

where  $\Delta P^{qu} = a^{qu} n^2/V^2$ , so that the pressure for  $\text{He}_I^4$  and  $\text{He}_{II}^4$  respectively reads

$$P_I(\text{He}_I^4) \equiv \{n k T / (V - nb)\} - a^{cl} n^2/V^2 \quad (38)$$

$$P_{II}(\text{He}_{II}^4) = \{n k T / (V - nb)\} - a^{cl} n^2/V^2 - \Delta P^{qu} \quad (39)$$

Where it is posed  $V \equiv V_I \equiv V_{II}$  since the fluid phase is poorly compressible. By using the same criterion of (7) we can end with the result that the variation  $\Delta T_\lambda = T_\lambda - T_B$  due to

the presence of quantum potential has the same sign of the pressure difference to read

$$\Delta P = (P_I - P_{II}) = \Delta P^{qu} = a^{qu} n^2 / V^2 < 0 \quad (40)$$

and the sign of  $dT_\lambda/dP$  is the same of the derivative

$$d\Delta P^{qu}/dP = a^{qu} n^2 d(V^{-2})/dP < 0. \quad (41)$$

given that  $d(V^{-2})/dP$  is positive.

Therefore, the quantum potential of the SQHA leads to both  $\Delta T_\lambda$  and  $dT_\lambda/dP$  negative.

Finally, in order to show that the result obtained above is a direct consequence of the convex (repulsive) harmonic quantum potential, we use the more precise expression given in appendix C, where the interaction of a couple of He<sup>4</sup> - He<sup>4</sup> atoms is approximated by a harmonic well (as given by the atomic Lennard-Jones potential) and coherently found to be

$$\begin{aligned} V_{qu} &= -(\hbar^2/2m)|\psi|^{-1}\partial^2|\psi|/\partial q\partial q \\ &= -(2\hbar^2/2m)K_0^4(q-q)^2 + (\hbar^2/m)K_0^2, \end{aligned} \quad (42)$$

where  $K_0 = (2m(U + E_0)/\hbar^2)^{1/2}$  and  $q = \sigma + \Delta$  is the mean He<sup>4</sup> - He<sup>4</sup> inter-atomic (half) distance.

## 4. Discussion

The negative sign of both  $\Delta T_\lambda = T_\lambda - T_B$  and of  $dT_\lambda/dP$  are the direct consequence of the convex harmonic quantum potential that leads to a repulsive inter-atomic force so that the pressure of the superfluid He<sup>4</sup><sub>II</sub> is higher of that one it would assume the He<sup>4</sup><sub>I</sub> at the same temperature. Due to the repellent quantum potential energy, the passage from the He<sup>4</sup><sub>II</sub> state to the equivalent He<sup>4</sup><sub>I</sub> one (submitted to a lower pressure) needs less kinetic energy to happen and hence  $T_\lambda$  is smaller than the condensation temperature  $T_B$  (He<sup>4</sup><sub>I</sub>).

Moreover, since a higher pressure in He<sup>4</sup><sub>II</sub> than in He<sup>4</sup><sub>I</sub> is needed to maintain the same atomic distance, when the temperature is lowered at constant pressure near the lambda point (crossing  $T_\lambda$ ) a decrease in density is produced.

Therefore, during the cooling process the He<sup>4</sup> shows a maximum in its density just above the He<sup>4</sup><sub>I</sub>→He<sup>4</sup><sub>II</sub> transition as confirmed by the experimental outputs.

It must be noted that for the realization of the maximum density, the crossover between the rate of He<sup>4</sup><sub>I</sub> thermal shrinking and that one of the He<sup>4</sup><sub>II</sub> quantum dilatation is needed.

Moreover, since the density maximum is at 2.2 °K while

$T_\lambda = 2.17$  °K, we can infer that the quantum interaction starts before the transition temperature as (37) signals (a larger and large fraction of He<sup>4</sup> atoms fall in the quantum interaction closer and closer we get to  $T_\lambda$ ).

Moreover, it is worth mentioning that the SQHA model does not exclude the possibility of similar maximum density phenomena close to liquid-solid transitions since, in this case, the quantum interaction between the atoms in a crystal is also set by the quantum potential whose interaction range  $\lambda_q$  becomes larger than the typical inter-atomic distances (see appendix [C]). This fact well agrees with the similarity between the He<sup>4</sup><sub>I</sub>→He<sup>4</sup><sub>II</sub> and the water-ice transitions widely accepted by the scientific community. Nevertheless, in order to have the maximum density at the liquid solid transition, the quantum dilation must overcome the thermal shrinking velocity. The van der Waals approach describing the He<sup>4</sup><sub>I</sub>→He<sup>4</sup><sub>II</sub> transition has also proposed by in a recent paper [23].

## 5. Conclusion

The finite range the quantum interaction in the SQHA is able to explain the controversial aspect of negative  $dT_\lambda/dP$  at

the He<sup>4</sup> lambda point without the introduction of a non-physical repulsive atomic potential that would hinder the gas-liquid phase transition [20,21]. The quantum pseudo-potential of the SQHA model is exactly the required potential: it is repulsive as widely requested by the scientific community to explain the maximum density of He<sup>4</sup> lambda point, but it also has the property to disappear in the classical phase and to not hinder the liquid-gas phase transition as any Hamiltonian potential would do.

The pseudo-potential of the SQHA approach also explains both why the lambda transition temperature  $T_\lambda$  is smaller than the BE one  $T_B$  and why the liquid He<sup>4</sup> has a maximum in its density just above the lambda point in agreement with the experimental measurements. The model puts in evidence that the perfect BE condensation is a phenomenon that happens between an ideal gas and its condensed quantum phase while the He<sup>4</sup><sub>I</sub>→He<sup>4</sup><sub>II</sub> transition happens between a real gas (in the fluid phase) and its quantum condensed phase (so that the transition temperature  $T_\lambda$  is smaller). The SQHA approach show the theoretical connection between the He<sup>4</sup><sub>I</sub>→He<sup>4</sup><sub>II</sub> maximum density and that one at the water-ice transition.

## Appendix A

### The SQHA Model for Gas and Condensed Phases

#### A.1. Analysis of the Quantum Potential of Localized Free Particles

In order to elucidate the particle PDF evolution, in a classical phase (i.e., the mean inter-particle distance bigger than  $\lambda_q$ ) we inspect the interplay between the Hamiltonian potential and the quantum potential that define the quantum non-locality length.

Fixed the PDF at the initial time, then the Hamiltonian potential and the quantum one determine the evolution of the PDF that on its turn modifies the quantum potential.

A Gaussian PDF has a parabolic repulsive quantum potential, if the Hamiltonian potential is parabolic too (the free case is included), when the PDF wideness adjusts itself to produce a quantum potential that exactly compensate the force of the Hamiltonian one, the Gaussian states becomes stationary (eigenstates). In the free case, the stationary state is the flat Gaussian (with an infinite variance) so that any Gaussian PDF expands itself following the ballistic dynamics of quantum mechanics [12, 24].

From the general point of view, we can say that if the Hamiltonian potential grows faster than a harmonic one, the wave equation of a self-state is more localized than a Gaussian one, and by (10) leads to a stronger-than-linear quantum potential (also at large distance).

On the contrary, a Hamiltonian potential that grows slower than a harmonic one will produce a less localized (stationary) PDF that decreases slower than the Gaussian one [see Appendix D], so that the quantum potential grows less-than-linearly and may lead to a finite quantum non-locality length by (15).

As shown in ref. [10], the large distances exponential-decay of the PDF such  $\lim_{|q| \rightarrow \infty} |n^{1/2}| \approx \exp[-P^h(q)]$  with  $h < 3/2$  is a sufficient condition to have a finite quantum non-locality length.

Thence, we can enucleate three typologies of quantum potential interactions:

- (1)  $h > 2$  strong quantum potential that leads to quantum force  $\partial V^{qu}(q)/\partial q$  that grows faster than linearly and  $\lambda_q$  is infinite (*super-ballistic* free particle PDF expansion)

$$\lim_{q \rightarrow \infty} \partial V^{qu}/\partial q \sim q^{1+\epsilon}. \quad (\epsilon > 0) \quad (A.1)$$

- (1)  $h = 2$  strong quantum potential that leads to quantum force  $\partial V^{qu}/\partial q$  that grows linearly and  $\lambda_q$  is infinite (*ballistic* free PDF enlargement)

$$\lim_{q \rightarrow \infty} |\partial V^{qu}/\partial q| \propto q^1 \quad (A.2)$$

- (2)  $2 > h \geq 3/2$  middle quantum potential; the integrand of (15) as well as the quantum force may be vanishing at large distance to read

$$\text{Const} \geq \lim_{q \rightarrow \infty} |q^{-1} \partial V^{qu}/\partial q| \sim q^{-1} \quad (A.3)$$

but  $\lambda_q$  may be still infinite (*under-ballistic* free PDF expansion).

- (3)  $h < 3/2$  weak quantum potential leading to quantum force that becomes vanishing at large distance following the asymptotic behavior

$$\lim_{q \rightarrow \infty} |q^{-1} \partial V^{qu}/\partial q| \approx q^{-(1+\epsilon)}, \quad (\epsilon > 0) \quad (A.4)$$

with a finite  $\lambda_q$  for  $\Theta \neq 0$  (*asymptotically vanishing* free PDF expansion).

## A.2. Free Pseudo-Gaussian Particles in a Gas Phase In Presence of Noise

Gaussian particles generate a quantum potential that has an infinite range of interaction and hence they do not admit macroscopic local dynamics.

Nevertheless, imperceptible deviation by the perfect Gaussian PDF may possibly lead to finite quantum non-locality length [see Appendix D]. Particles that are inappreciably less localized than the Gaussian ones (let's name them as pseudo-Gaussian) own  $\partial V^{qu}(q)/\partial q$  that can sensibly deviate by the linearity so that the quantum non-locality length may be finite.

In the case of a free pseudo-Gaussian particle we can say that  $\lambda_q$  extends itself at least up to the Gaussian core (where the quantum force is linear). At a distance much bigger than  $\lambda_q$  for  $h < 3/2$ , the expansive quantum force becomes vanishing.

On short distance, for  $q \ll \lambda_c$ , the noise is progressively suppresses (i.e., the deterministic quantum dynamics is established). Therefore, it follows that:

- (1) For  $q \ll \lambda_c < \lambda_q$ , the evolution is quantum ballistic.
- (2) For  $q \gg \lambda_q > \lambda_c$  the evolution is classically stochastic.
- (3) For  $\langle \Delta q^2 \rangle^{1/2} \ll \lambda_c < \lambda_q$ , the quantum deterministic state with  $h = 2$  is approached by the free pseudo-Gaussian particle.
- (4) For  $\langle \Delta q^2 \rangle^{1/2} \gg \lambda_q > \lambda_c$  and for  $h < 3/2$  the expansion dynamics of the free pseudo-Gaussian PDF are almost diffusive.

If at the initial time, we have the pseudo Gaussian PDF confined on a micro-scale (i.e.,  $\langle \Delta q^2 \rangle^{1/2} \ll \lambda_c < \lambda_q$ ), the expansion of the particle PDF is always very fast (ballistic).

For  $\lambda_c \ll \langle \Delta q^2 \rangle^{1/2} < \lambda_q$  the noise will add diffusion to the PDF ballistic enlargement.

Then, when  $\langle \Delta q^2 \rangle^{1/2} \gg \lambda_q$ , the expansion dynamics slow down toward the diffusive one.

When the (pseudo-Gaussian) PDF has reached the mesoscopic scale ( $\langle \Delta q^2 \rangle^{1/2} \sim \lambda_q$ ), we can infer that its core expands ballistically while its tail diffusively.

Since the outermost expansion is slower than the innermost, there is an accumulation of PDF ( $\rho$  is a conserved quantity) in the middle region ( $q \sim \lambda_q$ ) generating, as time passes, a slower and slower (than the Gaussian one) PDF decrease so that (for a free particle) the quantum potential and  $\lambda_q$  decrease (and cannot increase) in time.

In force of these arguments (i.e., the core quantum ballistic enlargement is faster than the diffusive outermost classical one), the free pseudo-Gaussian states (with  $h < 3/2$ ) are self-sustained and remain pseudo-Gaussian in time.

As far as it concerns the particle de-localization at very large times, the asymptotically vanishing quantum potential does not completely avoid such a problem since the ( $\Theta$ -noise driven) diffusion spreading of the molecular PDF remains (even if it is much slower than the quantum ballistic one).

If the particle PDF confinement cannot be achieved in the case of one or few molecules, on the contrary, in the case of a system of a huge number of structureless particles (with a repulsion core as in the case of the Lennard-Jones (L-J) potentials) the PDF localization can come from the interaction (collisions) between the molecules.

More analytically, we can say that in a rarefied gas phase at the collision, when two particles get at the distance of order of the L-J potential minimum  $r_0$ , the PDF is squeezed by the harmonic L-J potential well and the quantum non-locality length increases and becomes bigger than the inter-particle distance of interaction  $r_0$  (since for a L-J well the potential is approximately quadratic, the associated state largely Gaussian) [24]

After the collision, when the molecules are practically free, the PDF starts to expand again and  $\lambda_q$  decreases again. It will never reach the flat Gaussian configuration since, in a finite time, the molecule undergoes another collision taking a bit of PDF squeezing leading to a new increase of the  $\lambda_q$ . The overall effect of this process is that the random collisions among the huge number of free particles in a gas phase, with L-J type intermolecular potential, maintain their localization.

### A.3. Condensed Phase and He<sup>4</sup><sub>I</sub>→He<sup>4</sup><sub>II</sub> Transition

When both the lengths  $\lambda_c$  and  $\lambda_q$  are much smaller than the smallest physical length of the system (so that the resolution of the descriptive scale can be of order or bigger than  $\lambda_q$ ) the macroscopic classical description arises. This for instance happens in a rarefied gas phase of L-J interacting particles where  $\lambda_q$  as well as  $\lambda_c$  are very small compared to the intermolecular mean distance (except for few colliding molecules).

On the contrary, when the mean inter-particle distance becomes comparable with the quantum non-locality length, the classical description may break down because the quantum potential enters in the particle interaction. Furthermore, if the wave function of the interacting particles is localized on a length of order or smaller than the quantum coherence length  $\lambda_c$ , the quantum deterministic description takes place for the bounded states of the couples of molecules.

In the classical regime, the Virial expansion furnishes an elegant conceptual understanding for passing from a gas to a condensed phase for molecules having finite range of interaction *even in non-equilibrium condition* [21].

In the classical treatment of the Virial expansion, the

energy function does not include the quantum potential and hence converges to the classical value failing, for instance, to predict the law of the specific heat for solids where the quantum dynamics enters in the atoms interaction.

In the frame of the QHA description, the quantum potential energy (that changes at each stationary state) added to the classical value of the energy, leads to the variety of the quantum energy eigenvalues. This is very clearly shown in Ref. [9], the energy of the quantum eigenstates is composed by the sum of the two terms: one steams from the classical Hamiltonian while the other one by the quantum potential, leading to the correct eigenvalue  $E_n$ . Therefore, in principle the Virial approach can be applied (in the SQHA model) both for quantum as well classical molecular interactions

Since in a crystal the atoms fall in the linear range of interaction, the quantum non-locality  $\lambda_q$  is larger than the inter-molecular distance [24] and the system shows quantum characteristics (in those properties depending by the molecular state).

Usually, for crystalline solids the inter-atomic distance lies in the harmonic range of the L-J interaction even at temperature higher than the room one due to the great deepness of the potential well [see Appendix C].

When, at higher thermal oscillations, the mean molecular distance starts to increase by the equilibrium position  $r_0$  toward the non-linear range of the L-J inter-molecular potential, we have a transition from the solid phase to the liquid one [22, 24]. During this process, the inter-particle wave function extends itself more and more in the non-linear L-J zone so that the quantum potential weakens and  $\lambda_q$  decreases [see Appendix C].

For deep L-J intermolecular potential well, this happens at high temperature and we have a direct transition from the solid to the classical fluid phase.

For small potential well, the liquid phase can persist down to a very low temperature. In this case, even if  $\lambda_q$  may result smaller than the inter-particle distance (so that the liquid phase is maintained), decreasing the temperature (the amplitude  $\Theta$  of fluctuations and  $\lambda_c$  grow and become of order of the mean molecular distance and even bigger than  $\lambda_q$  (see appendix C)) the liquid phase may acquire quantum properties (about those depending by the molecular interaction such as the viscosity). The fluid-superfluid transition can happen if the temperature of the fluid can be lowered up to the transition point before the solid phase takes place.

Therefore, the mechanism that brings to the quantum atomic interaction in a solid is different from that one in a superfluid: in the former the linearity of the interaction leads to a quantum non-locality length  $\lambda_q$  larger than the typical atomic distance while in the latter is the decrease of  $\Theta$ , by lowering the temperature, that increases  $\lambda_c$  up to the inter-atomic distance.

Even if the relation between the PDF noise fluctuations amplitude  $\Theta$  and the temperature  $T$  of an ensemble of particles is not straight [10], it can be easily acknowledged that when we cool a system toward the absolute zero (with

steps of equilibrium) also the noise amplitude  $\Theta$  reduces to zero since the energy fluctuations of the system must vanish. Thence, even there is not a fix linear relation between the fluctuation amplitude  $\Theta$  and the temperature we expect lower values of  $\Theta$  for lower values of the temperature [10].

## Appendix B

### *The Virial Expansion Applied to the He Fluid*

From the standard Virial expansion [13] the state equation of (classical) real gas accounting only for double collisions, reads:

$$P V = n k T \{1 - (n (a/kT - b)/ V)\} \quad (\text{B.1})$$

that under the standard substitution [14]

$$\{1 + n b / V\} \cong \{1 - n b / V\}^{-1} \quad (\text{B.2})$$

leads to the van der Waals equation

$$\{P + a n^2 / V^2\} (V - n b) = n k T \quad (\text{B.3})$$

where  $P$  is the pressure,  $V$  the volume,  $n$  the number of molecules,

$$b = \frac{2}{3} \pi r_0^3 = V_{cr} / 3N_A \quad (\text{B.4})$$

is the fourfold atomic volume [15], where  $N_A$  is the Avogadro's number and  $V_{cr}$  is the critical molar volume, and

$$a = -2 \pi \int_{r_0}^{\infty} V(r) r^2 dr \quad (\text{B.5})$$

is the mean inter-molecular potential energy. By using the rigid sphere approximation [13] that reads

$$V(r) = \infty, \quad r < r_0 \quad (\text{B.6})$$

$$V(r) = V_{LJ}(r) = 4U [(\sigma/r)^{12} - (\sigma/r)^6], \quad x > r_0 \quad (\text{B.7})$$

where  $U = -V_{LJ}(r_0)$  is the well depth of the L-J intermolecular potential, we obtain that

$$a \cong 4\pi r_0^3 U / 3 = 2U V_{cr} / 3N_A \quad (\text{B.8})$$

that, by using the relation[15]

$$a = 9 k T_{cr} V_{cr} / 8 N_A \quad (\text{B.9})$$

for  $\text{He}^4$  reads to

$$U / k = 27 T_{cr} / 16 = 8.77^\circ\text{K} \quad (\text{B.10})$$

satisfactory close to the value  $U / k = 10.9$  given by quantum Monte Carlo models [16] and to the value  $U / k =$

11.07 given by  $\text{He}^4$ - $\text{He}^4$  scattering [17].

Moreover, by using for helium [18] the value of

$$V_{cr} = 5.7 \times 10^{-5} \text{ m}^3/\text{mole} \quad (\text{B.11})$$

it follows that

$$r_0 \cong 2.56 \times 10^{-10} \text{ m} = 4.8 \text{ bohr} \quad (\text{B.12})$$

where

$$r_0 = 2^{1/6} \sigma \quad (\text{B.13})$$

is the point of minimum for the L-J intermolecular potential with

$$\sigma = 2^{-1/6} r_0 = 2.32 \times 10^{-10} \text{ m} \cong 4.35 \text{ Bohr}.$$

## Appendix C

### *Quantum non-Locality Length $\lambda_q$ of L-J Bounded States*

In order to calculate the quantum potential and its non-locality length for a L-J potential well, we can assume the harmonic approximation

$$V_{LJ}(q) = \frac{1}{2} k (q - r_0)^2 + C, \quad (\text{C.1})$$

where

$$k = 4 K_0^4 \hbar^2 / m \quad (\text{C.2})$$

where  $K_0 = (2m(U + E_0)/\hbar^2)^{1/2}$ , and where the constant  $C$  can be calculated by the energy eigenvalue of the fundamental state

$$C = E_0 - V_{qu} \big|_{(q-q=0)}, \quad (\text{C.3})$$

leading to a Gaussian wave function whose series expansion at second order coincides with that one of eqs. (21-22) having the same eigenvalue  $E_0$  and mean position  $q = \sigma + \Delta$  that reads

$$\begin{aligned} \psi_0 &= B \exp[-K_0^2(q - q)^2] \cong B [1 - K_0^2(q - q)^2] \\ &\cong B \sin[K_0(q - \sigma)] \quad |q - r_0| \ll 2\Delta/\pi. \end{aligned} \quad (\text{C.4})$$

The convex quadratic quantum potential associated to the wave function  $\psi_0$  reads

$$\begin{aligned} V_{qu} &= -(\hbar^2/2m)|\psi|^{-1}\partial^2|\psi|/\partial q\partial q \\ &= -(2\hbar^2/m) K_0^4 (q - q)^2 + (\hbar^2/m) K_0^2 \end{aligned} \quad (\text{C.5})$$

that leads to the quantum force

$$-\partial V_{qu} / \partial q = 2 K_0^4 (\hbar^2/m) (q - q) \quad (\text{C.6})$$



and to

$$C = E_0 - V_{qu}(q=0) = \frac{1}{2} \hbar (k/m)^{1/2} - (\hbar^2/m) K_0^2 = 0.$$

Given the simple exponential PDF decrease of (21-22) for  $x > \sigma + 2\Delta$  (that leads to a vanishing quantum potential as well as to vanishing small quantum force), we can disregard the contribution to the quantum non-locality length for  $x > \sigma + 2\Delta$ .

Thence, by (13) it follows that,

$$\lambda_q = \lambda_c \frac{\int_0^\infty |q^{-1} \frac{dV_{qu}}{dq}| dq}{\left| \frac{dV_{qu}}{dq} \right| (q=\lambda_c)} \quad (C.7)$$

$$|dV_{qu}/dq| = 2 K_0^4 (\hbar/2m) \lambda_c$$

$$|-q^{-1} \partial V_{qu} / \partial q| = 2 K_0^4 (\hbar/2m)$$

$$\lambda_q \equiv \int_0^{\sigma+2\Delta} dq = \sigma + 2\Delta \quad (C.8)$$

so that, since for  $T < T_\lambda$   $\lambda_c > \sigma + 2\Delta$ , it follows that

$$\lambda_c > \lambda_q$$

Since for distances smaller than  $\lambda_c$  the quantum deterministic dynamics take place and even vanishing quantum potentials must taken into account [10, 24],  $\lambda_c$  becomes the reference length for quantum behavior.

## Appendix D

### Pseudo-Gaussian PDF

If a system admits the large-scale classical dynamics, the PDF cannot acquire an exact Gaussian shape because it would bring to an infinite quantum non-locality length.

In appendix A we have shown that for  $h < 3/2$  the PDF decreases slower than a Gaussian and a finite quantum non-locality length is possible.

The Gaussian shape is a physically good description of particle localization but irrelevant deviations from it, at large distance, are decisive to determine the quantum non-locality length.

For instance, let's consider the pseudo-Gaussian function type

$$n = \exp[-(q-q)^2 / <\Delta q^2> [1 + [(q-q)^2 / \Lambda^2 f(q-q)]]], \quad (D.1)$$

where  $\Lambda$  here  $f(q-q)$  is an opportune regular function obeying to the conditions

$$\Lambda^2 f(0) \gg <\Delta q^2>$$

and

$$\lim_{|q-q| \rightarrow \infty} f(q-q) \ll (q-q)^2 / \Lambda^2.$$

For small distance  $(q-q)^2 \ll \Lambda^2 f(0)$  the above PDF is physically indistinguishable from a Gaussian, while for large distance we obtain the behavior

$$\lim_{(q-q) \rightarrow \infty} n(q,t) = \exp[-\Lambda^2 f(q-q) / <\Delta q^2>]. \quad (D.3)$$

For instance, we may consider the following examples

a)  $f(q-q) = 1$

$$\lim_{|q-q_0| \rightarrow \infty} n(q,t) = \exp[-\Lambda^2 / <\Delta q^2>]; \quad (D.4)$$

b)  $f(q-q) = 1 + (|q-q|/\Lambda)$

$$\lim_{|q-q_0| \rightarrow \infty} n(q,t) \propto \exp[-\Lambda |q-q| / <\Delta q^2>]; \quad (D.5)$$

c)  $f(q-q) = 1 + \ln[1 + (|q-q|/\Lambda)^h] \quad (0 < h < 2)$

$$\lim_{|q-q_0| \rightarrow \infty} n(q,t) \propto \Lambda^{-1} |q-q|^{-h \Lambda^2 / <\Delta q^2>}; \quad (D.6)$$

d)  $f(q-q) = 1 + (|q-q|/\Lambda)^h \quad (0 < h < 2)$

$$\lim_{|q-q_0| \rightarrow \infty} n(q,t) \propto \exp[-\Lambda^{(2-k)} |q-q|^h / <\Delta q^2>]. \quad (D.7)$$

All cases (D.4-D.7) lead to a finite quantum non-locality length  $\lambda_q$ . Given that for the PDF (D.7)

$$\begin{aligned} \lim_{|q-q| \rightarrow \infty} |\psi| &= \lim_{|q-q| \rightarrow \infty} n^{1/2} \\ &= \exp[-\Lambda^{(2-k)} (q-q)^h / 2 <\Delta q^2>], \end{aligned}$$

the quantum potential for  $|q| \gg |q|$  reads:

$$\begin{aligned} \lim_{(q-q) \rightarrow \infty} (2m/\hbar^2) V_{qu} &= -|\psi|^{-1} \partial^2 |\psi| / \partial q \partial q \\ &= -[(\Lambda^{(2-k)} \hbar^2 (q-q)^{2(h-1)} / 4 <\Delta q^2>)^{-h} h(h-1) (q-q)^{(h-2)}], \end{aligned} \quad (D.9)$$

leading, for  $h \neq 2$ , to the quantum force

$$\begin{aligned} \lim_{(q-q_0) \rightarrow \infty} (2m/\hbar^2) \partial V_{qu} / \partial q &= -[(\Lambda^4 (2h-1) \hbar^2 (q-q)^{2h-3} / 4 <\Delta q^2>) \\ &\quad - \Lambda^2 h(h-1) (h-2) (q-q)^{(h-3)} / 2 <\Delta q^2>], \end{aligned} \quad (D.10)$$

that for  $h < 3/2$  gives  $\lim_{(q-q) \rightarrow \infty} \partial V_{qu} / \partial q = 0$ .

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