Nucleation of a vapour bubble or liquid drop by the self-trapping of a quantum particle in a fluid

LETTER TO THE EDITOR

Nucleation of a vapour bubble or liquid drop by the self-trapping of a quantum particle in a fluid

John P Hernandez and L W Martin

Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255, USA

Abstract. The conditions which allow the self-trapping of a quantum particle to nucleate a local heterophase region in the host fluid are explored theoretically. A previously neglected aspect is emphasized: the curvature of the surface separating the coexisting liquid and vapour leads to a surface pressure difference across that surface which has contributions from the surface tension and the quantum particle. Results of calculations for an electron in liquid neon, for conditions in which a stable vapour bubble is nucleated, are used to give an example of the phenomena explored.

A quantum particle interacting via short-range forces with the atoms of a fluid may self-trap through a local distortion of the fluid structure. This general phenomenon is now well known, both theoretically and in its experimental consequences [1]. For example, under appropriate conditions, excess electrons self-trap in 'bubbles' in helium and neon [2] fluid hosts. In helium, the bubbles may be trapped by vortices [3], their mobility phonon limited [4], their acceleration measured [5], and their optical absorption determined [6]. However, the conditions in which such self-trapping leads to a heterophase region in the fluid have not been investigated theoretically in detail. The problem, which has been ignored until now, is the pressure difference which is necessary to maintain equilibrium of a curved surface separating coexisting phases, in the presence of the quantum particle. A simplified treatment of this problem is discussed in this letter. First we give the context of the present approach and derive the conditions required for the self-trapping under consideration. Then as an example, results appropriate to an excess electron in liquid neon are obtain from an application of the formalism.

The problem is discussed using the following variables for a thermodynamic fluid: temperature (T), density (ρ), pressure (P), chemical potential (μ) and surface tension (γ). For $T < T_c$ (where T_c is the vapour–liquid critical temperature) an interfacial region may be formed, i.e. one in which the local fluid density takes on values between those of the homogeneous fluid at coexistence ($\rho_V < \rho < \rho_L$). Ignoring its detailed nature and approximating the density by a constant (ρ_V or ρ_L) with a jump at a 'surface of coexistence' is a procedure often used in connection with the 'equimolecular dividing surface' [7]. This surface is defined as the one for which the piecewise constant-density approximation conserves the total number of atoms in the system. In what follows, the above procedure will be used to describe the

interfacial region; the curvature dependence of the surface tension [8] will be ignored for simplicity.

In this approach to the self-trapping problem, consider a homogeneous fluid of density ρ and temperature T with a quantum particle in its lowest-energy delocalized state, as a reference system. In the reference system, the particle–fluid interaction is characterized by a uniform potential, V_ρ, which is a function of the fluid density. A density-functional model is now sought to describe the most probable state of the (ρ, T) particle–fluid system, which is described by a particle wavefunction, $\psi(r)$, and an inhomogeneous fluid density, $\rho(r)$. A $\rho(r)$ which is slowly varying everywhere except in an interfacial region, if one exists, can be taken to imply local values for μ, P, and V, which correspond to a homogeneous fluid of that density at the temperature in question.

The most probable state sought for the particle–fluid system can then be described by the Schrödinger equation for the particle (of mass m and energy E):

$$[-(\hbar^2/2m)\Delta^2 + (V(r) - V_\rho) - E]\psi(r) = 0 \tag{1}$$

and by the difference in the Helmholtz free energy between this system and the reference one:

$$\Delta F = E + \int [\rho(r)(\mu(r) - \mu_\rho) - (P(r) - P_\rho)] \, \mathrm{d}r + \gamma \int \mathrm{d}A. \tag{2}$$

The subscripted variables correspond to the reference system and the local ones to the system of interest. Assuming spherical symmetry, the last term in (2) is $4\pi R^2\gamma$, where R is the radius of the 'equimolecular dividing surface' (if an interfacial region exists). The state sought must be the reference system ($E_\rho = 0 = \Delta F$) or another for which ΔF is a lower energy minimum (with $E < 0$).

Extremization of $\Delta F[\rho(r), R]$ is carried out in two steps. For all r, except in a possible interfacial region (where $\rho_V < \rho(r) < \rho_L$), the requirement $\delta\Delta F/\delta\rho(r) = 0$ implies

$$[\rho(r) \, \delta\mu(r)/\delta\rho(r) - \delta P(r)/\delta\rho(r)] + [\mu(r) - \mu_\rho$$
$$+ (\delta V(r)/\delta\rho(r)) \, |\psi(r)|^2/\langle\psi|\psi\rangle] = 0 \tag{3}$$

where the last denominator is the particle normalization. The local relation between density, chemical potential and pressure guarantees that the first square bracket in (3) vanishes and any equation of state may be used. Thus, the requirement gives an implicit relation between $\rho(r)$ and $\psi(r)$:

$$(\mu(r) - \mu_\rho)/(\delta V(r)/\delta\rho(r)) = |\psi(r)|^2/\langle\psi|\psi\rangle. \tag{4}$$

Within the interfacial region (where $\mu(r) = \mu(\rho_V) = \mu(\rho_L)$), the choice of $\rho(r) = \rho_V$ or ρ_L, with a jump at R, defines $V(r)$. It may be noted that if $V(r) \propto \rho(r)$ then equation (4) and the continuity of $\psi(r)$ imply that the interfacial region is indeed a surface and R is uniquely specified.

The extremization of (2) with respect to R is to be accomplished at constant μ, P, T, total number of atoms, and total volume [9]. Thus it yields a pressure difference across the curved surface at R:

$$-[P(R^-) - P(R^+)] + [V(R^-) - V(R^+)]|\psi(R)|^2/\langle\psi|\psi\rangle + 2\gamma/R = 0 \tag{5}$$

where the last term is the well known classical effect due to the surface tension and the middle term is a surface pressure difference due to the quantum particle ($V(R^\pm)$ corresponds to densities $\rho_{V,L}$, with R^- being in the heterophase region). Equation (5) only causes a pressure change at R and thus does not affect (3). The free-energy difference (2) may be separated into the sum of a term due to the surface pressure and energy—a 'surface' term—and the rest—a 'bulk' term:

$$\Delta F|_s = (4\pi/3)R^3\{[V(R^+) - V(R^-)]|\psi(R)|^2/\langle\psi|\psi\rangle + \gamma/R\} \tag{6}$$

$$\Delta F|_s = E + \int [\rho(r)(\mu(r) - \mu_\rho) - (P(r) - P_\rho)] \, dr. \tag{7}$$

Note that (7) explicitly excludes the surface pressure, which is in (6) with the surface tension part of it having cancelled two-thirds of the last term in (2). Furthermore, as $T \to T_c$ from below, both terms in (6) tend to zero: as ρ_V and ρ_L tend to the common value (ρ_c) the potential difference vanishes and also $\gamma \to 0$.

The problem of defining R operationally still remains to be resolved. Its definition as the radius of the 'equimolecular dividing surface' is not useful as $\rho(r)$ is unknown in the interfacial region. A method for bracketing R, and all functions depending on it, uses (4) as follows. As the relation between $\rho(r)$ and $\psi(r)$ outside the interfacial region is given by (4), extreme brackets for R may be obtained by choosing its values to be at either extreme of the interfacial region (r_V or r_L, corresponding to the fluid just reaching the coexistence densities). The usefulness of this bracketing may be investigated numerically. The problem consists in the jump of $\delta V/\delta\rho$ at the phase change; the required variation in $\psi(r)$ from r_V to r_L (see (4)) may depend so strongly on the choice of R that substantial uncertainties result.

To clarify and quantify the preceding discussion, results will now be given for an excess electron in *liquid* neon, as the particle–fluid interaction is repulsive in this case. $V(r)$ is obtained from electron–atom interactions, which are assumed to be non-overlapping, and cast as an s-wave pseudopotential, as in our previous work which focussed on experiments at $T > T_c$ [10]:

$$V(r) = -(\hbar^2/2m)4\pi[(\tan \delta_0(k))/k]\rho(r) \tag{8}$$

where the s-wave scattering phase shifts $\delta_0(k)$ are taken from O'Malley and Crompton [11] and correspond to a scattering energy of $\hbar^2 k^2/2m$. This energy, in turn, is related to $\rho(r)$ through the Wigner–Seitz model, in which the appropriate boundary condition in a fluid yields

$$\tan[kr_s + \delta_0(k)] = kr_s \tag{9}$$

with $\rho(r)^{-1} = 4\pi r_s^3/3$. This approximation is in the same spirit as that of a local pressure and chemical potential for a slowly varying $\rho(r)$. Fluid neon is described with the van der Waals equation of state, parametrized to the experimental critical point: $T_c = 44.38$ K and $\rho_c = 1.443 \times 10^{22}$ cm^{-3}. The self-consistent calculation using (1) and (4) can now be carried out numerically. γ is only required to obtain the surface free energy in (6).

We shall use an empirical fit to a scaled surface tension [12]:

$$\gamma/k_B T_c \rho_c^{2/3} = 2(1 - T/T_c). \tag{10}$$

Table 1. Coexistence densities, at selected temperatures, of fluid neon [15] and, in parentheses, those of the van der Waals model. Densities scaled to ρ_c; temperatures to T_c.

T^*	1	0.95	0.90	0.85	0.80
ρ_V^*	1	0.41	0.37	0.18	0.12
	(1)	(0.579)	(0.426)	(0.320)	(0.240)
ρ_L^*	1	1.65	1.85	2.00	2.13
	(1)	(1.462)	(1.657)	(1.807)	(1.933)

The constant has been deliberately chosen to be fairly small to account for the reduction of γ from that appropriate to a flat surface to that for a curved surface [8]. Other estimates may be used [13].

Full discussion of our calculations for T above and below T_c will be given elsewhere [14]. Here, we report examples, for the temperature range $0.95 \geqslant T/T_c \geqslant 0.80$, in which electron self-trapping nucleates a vapour bubble in the van der Waals model liquid which approximates neon. The stability trends in this regime are the same for calculations above the critical point at comparable densities: the stability of self-trapping increases as the temperature is lowered at constant density or as the density is lowered at constant temperature. As shown below, this increase of stability is achieved on approaching the coexistence line; the bubble radius grows under these conditions. These stability trends are mainly due to the 'bulk' contributions to the free energy (7). The 'surface' contributions (6) are substantial and tend to destabilize self-trapping (since they are non-negative), but show a less pronounced density and temperature dependence than the bulk contributions. In the cases for which stable self-trapping is obtained, the widths of the interfacial regions are of the order of 10% of R and the bracketing of R gives uncertainties in the values of R and the total free energy of less than 20%.
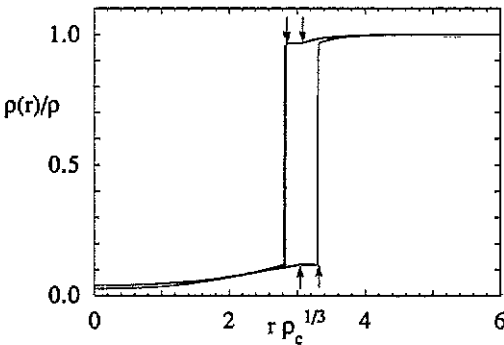
Figure 1. $\rho(r)/\rho_c$ against $r\rho_c^{1/3}$ for a reference fluid with $\rho = 2\rho_c$ and $T = 0.8T_c$. Bracketing cases for R are shown—innermost and outermost edges of the interfacial regime; the vertical arrows mark the edges of the interfacial regions (r_V and r_L) for both bracketing cases.

A typical example of the results obtained for $\rho(r)$, for the bracketing choices of R, is given by the two curves in figure 1. These results correspond to a reference fluid of density of $2\rho_c$ at a temperature of $0.8T_c$. Note that these conditions correspond to a single-phase fluid in the van der Waals model, but not to real neon; see table 1 for the coexistence data [15]. The example has been chosen as one in which the reference fluid is relatively close to the liquid at coexistence in the van der Waals model.

Table 2. Results for the most probable self-trapped state of an excess electron in a van der Waals model for neon, with bracketing choices for R. The reference fluid is characterized by $\rho^* = \rho/\rho_c$ and $T^* = T/T_c$. Radii are in units of $\rho_c^{-1/3}$ (i.e. 4.11 Å). The density at the localization centre is scaled to the saturated vapour density. ΔN is the number of atoms expelled by the trapped electron. The particle binding energy $-E, \Delta F|_b$ (from (7)), and total ΔF (from (2)) are in units of $k_B T$. The penultimate column gives the ratio of the first to the second term in (6), i.e. the quantum particle pressure contribution to the contribution from the surface tension.

ρ^*	T^*	R	r_V	r_L	$\rho(0)/\rho_V$	ΔN	$-E$	$-\Delta F|_b$	Ratio	$-\Delta F$
1.70	0.95	2.91	2.91	3.05	0.21	155	48	29.9	3.29	13.9
		3.12	2.97	3.12	0.23	165	50	29.9	2.56	14.6
1.80	0.95	2.49	2.49	2.63	0.17	112	46	24.3	5.03	7.8
		2.68	2.55	2.68	0.18	118	49	24.5	4.01	8.7
1.90	0.95	2.16	2.16	2.30	0.14	84	43	18.4	7.30	1.3
		2.34	2.20	2.34	0.15	87	46	18.6	5.75	2.2
1.80	0.90	2.90	2.90	3.08	0.22	167	59	40.8	1.99	17.4
		3.22	3.02	3.22	0.27	186	64	41.2	1.40	18.0
1.90	0.90	2.38	2.38	2.57	0.17	106	53	30.8	3.86	5.2
		2.67	2.46	2.67	0.20	116	60	31.1	2.73	6.4
1.90	0.85	2.89	2.89	3.11	0.23	177	71	53.2	1.72	19.6
		3.30	3.06	3.30	0.31	208	79	53.8	1.10	20.0
2.00	0.85	2.27	2.27	2.49	0.16	98	60	36.8	3.47	2.8
		2.61	2.37	2.61	0.21	111	71	37.6	2.24	4.9
2.00	0.80	2.84	2.84	3.08	0.24	181	84	65.4	1.19	28.5
		3.32	3.04	3.32	0.33	121	95	66.6	0.72	27.2
2.10	0.80	2.13	2.13	2.38	0.13	88	66	41.0	2.74	5.3
		2.52	2.24	2.52	0.21	101	82	42.8	1.67	7.2

Table 2 shows self-consistent results calculated for various reference conditions at which stable self-trapping is obtained. At higher densities than those shown, on isotherms, self-trapping becomes metastable, then unstable due to the increasing stiffness of the fluid. The features previously discussed are illustrated and it is noteworthy that $\Delta F/k_B T|_s$ (equation (6)) is dominated by the contribution from the quantum particle, when compared to that of the surface tension, unless the coexistence curve is closely approached.

In conclusion, a model has been presented for calculating conditions in which a heterophase region may be stably nucleated by the self-trapping of a quantum particle in a fluid. The free-energy minimization must take into account the curvature of the interfacial surface and the resulting surface pressure contributions. In the example given, these contributions appear to be dominated by those due to the quantum particle, rather than by those due to the surface tension, unless the coexistence curve is closely approached. The model presented is certainly susceptible to detailed improvement but we believe it gives the core of the physical processes involved.

It had been noted [6] that surface tension contributions, used to obtain a bubble radius (R) for electrons in liquid helium, required an altered pressure dependence in some cases for calculations to agree with experimental observations. It is now apparent that, in previous calculations where a heterophase region was nucleated, theoretical estimates usually did not have an appropriately minimized free energy. It may be worthwhile to re-examine such theoretical results [1] regarding the self-trapping of electrons and positronium in simple fluids.

References

[1]   See reviews:
      Schwarz K W 1975 *Advances in Chemical Physics* vol 33, ed I Prigogine and S A Rice (New York: Wiley) p 1
      Fetter A 1975 *The Physics of Liquid and Solid Helium, Part 1* ed K H Bennemann and J B Ketterson (New York: Wiley) p 207
      Hernandez J P 1991 *Rev. Mod. Phys.* at press
[2]   Borghesani A F and Santini M 1990 *Phys. Rev.* A **42** 7377
[3]   Springett B E 1967 *Phys. Rev.* **155** 139
[4]   Ostermeier R M 1973 *Phys. Rev.* A **8** 514
[5]   Ellis T, McClintock P V E and Bowles R M 1983 *J. Phys. C: Solid State Phys.* **16** L485
[6]   Grimes C C and Adams G 1990 *Phys. Rev.* B **41** 6366
[7]   Hirschfelder J O, Curtiss C F and Bird R B 1954 *Molecular Theory of Gases and Liquids* (New York: Wiley) p 339
[8]   Tolman R C 1949 *J. Chem. Phys.* **17** 333
[9]   Landau L D and Lifshitz E M 1980 *Statistical Physics, Part 1* 3rd edn (Oxford: Pergamon) p 522
[10] Hernandez J P and Martin L W 1991 *Phys. Rev.* A **43** 4568
[11] O'Malley T F and Crompton R W 1980 *J. Phys. B: At. Mol. Phys.* **13** 3451
[12] McCarty R D 1972 *NBS Technical Note* 631 (US Dept of Commerce, NBS) and [15] quotes fits of this type to experimental data. The coefficient in equation (11) is 1.543 for He, 2.02 for Ar and ~3.5 to fit the low-temperature Ne data.
[13] Guggenheim E A 1945 *J. Chem. Phys.* **13** 253
[14] Martin L W 1991 *PhD Thesis* University of North Carolina at Chapel Hill
      Martin L W and Hernandez J P unpublished
[15] Johnson V J 1960 *WADD Technical Report* 60-56, Part 1 (US Department of Commerce, NBS)