Calculation of Hydrodynamic Mass for Atomic Impurities in Helium

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Abstract

We present a simple numerical procedure for calculating the irrotational hydrodynamic flow in a helium solvation structure around a spherical solute in linear motion through superfluid helium. The calculation requires only the radial helium density around the impurity as input. From the resulting irrotational flow, the helium contribution to the effective mass of the solute is calculated. The results for alkali cations are compared to recent many-body Variational Monte Carlo (VMC) calculations by M. Buzzacchi, D. E. Galli, and L. Reatto (Phys. Rev. B., 64 094512 (2001)). The helium contribution to the effective masses calculated by the two methods are 12.9(4.6) versus 9.4 u for Li+, 48.2(5.6) versus 52.1 u for Na+, 69.6(4.8) versus 70.1 u for K+, and 6.4(8.8) versus 6.8 for Cs+, with the VMC result listed first (with one σ statistical error estimate) and the hydrodynamic result listed second. For the cases of Na+ and K+, the hydrodynamic calculation treated the first helium solvation shell as a rigid solid, as suggested by the VMC calculations; treating the first solvent layer as part of the superfluid lead to considerable underestimate, ≈ 50%, of the mass increase in both cases. In all cases, the agreement of the two results are in within the error estimate of the VMC calculation, demonstrating the accuracy of hydrodynamic treatment of helium motion even on the atomic length scale.

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The study of atomic ions as microscopic probes of superfluidity in helium-4 has a rich history [1]. Recent progress on both the injection of neutral metal atoms into bulk liquid helium [2, 3] and the study of doped helium nanodroplets [4] have caused a renewed interest in the dynamical behavior of solutes in this unique quantum liquid. In particular, concerning the rotational degrees of freedom, here have recently been several papers that try to provide a microscopic explanation for the observed sizable fractional increase in the rotational moments of inertia of all but the fastest rotors when dissolved in superfluid helium [5, 6, 7, 8, 9, 10]. In all of the proposed models, the extra moment of inertia arises from helium kinetic energy induced by rotation of the molecule, but there is disagreement about the way this should be calculated, and about the physical description of the helium motion [11].

A closely related problem is that of the change in the effective translational mass of a solute in superfluid helium, which also arise from helium kinetic energy induced by the requirement that the helium solvation structure must ‘follow’ a moving impurity. In the quantum hydrodynamic model [8, 12], one calculates the classical velocity potential that describes the irrotational flow which maintains a constant helium solvation structure in the frame of a moving impurity. By a theorem of Lord Kelvin [8, 13], this irrotational flow will provide the minimum kinetic energy flow that satisfies the equation of continuity. A simple example is the case of a moving spherical “hole” in the liquid, for which the hydrodynamic flow is a dipole field that carries a kinetic energy equal to one half of that of the liquid mass displaced by the sphere moving at the velocity of the hole [13]. For the general case of an inhomogeneous density, Barrera and Baym [14] have presented a solution to the equation of continuity, based upon a transformation of dipole solution. However, this transformed solution is not irrotational, and if fact has a continuously varying vorticity, and thus is not appropriate for flow in a superfluid, where vorticity must be quantized.

This paper presents a general numerical scheme for finding the irrotational solution of the equation of continuity given a solvation density around a moving spherical solute. The hydrodynamic equation can be solved by separation of variables, and reduces to one dimensional quadrature of the radial homogeneous and inhomogeneous equations, allowing the mixed boundary conditions to be satisfied without need for iteration. In the limit of infinitesimal solute velocity, the given solution can be shown [12] to provide a variationally optimized helium ground state wave function, assuming a one-body phase function. As such,
it should provide a rigorous lower bound on the true increase in effective mass.

In order to test the quantitative accuracy of this approximation, we have compared the calculated mass increase for Li$^+$, Na$^+$, K$^+$, and Cs$^+$ with those calculated by Buzzacchi, Galli, and Reatto [15] using a Variational Monte Carlo (VMC) treatment of the explicit many-body problem [16, 17]. The input to the hydrodynamic calculations were the helium radial densities calculated by these same authors using the same method; thus the comparison provides a direct test of the accuracy of the one-particle hydrodynamic treatment on atomic length scales.

I. CALCULATION METHOD

Consider an atomic solute in superfluid He that has a solvation structure with radial number density $\rho(r)$. We assume that the solute is moving with velocity $V$ (in a direction we take as the $z$ axis), and that the solvation structure adiabatically moves with the atom. This generates an irrotational flow in the helium of velocity $v = -\nabla \phi$, where $\phi$ is the velocity potential, which must satisfy the equation of continuity:

$$\nabla (\rho \nabla \phi) = \frac{d\rho}{dt} = -(\nabla \rho) \cdot (V \hat{z})$$  \hspace{1cm} (1)

If we write $\phi = \tilde{\phi}(r) V \cos(\theta)$ where $r$ is the distance from the impurity atom and $\theta$ is the angle with the $\hat{z}$ axis, we find that the hydrodynamic equation of continuity is solved if $\tilde{\phi}$ satisfies the following radial equation:

$$\frac{d^2 \tilde{\phi}}{dr^2} + \frac{2}{r} \frac{d \tilde{\phi}}{dr} - \frac{2}{r^2} \tilde{\phi} + \left( \frac{d \ln \rho}{dr} \right) \left( \frac{d \tilde{\phi}}{dr} \right) = - \left( \frac{d \ln \rho}{dr} \right)$$  \hspace{1cm} (2)

At long range from the atom, the density must approach the bulk value, $\rho_e$, and $\tilde{\phi} \rightarrow A/r^2$. On the inner wall of the solvation structure, $r_i$ (where the helium density vanishes rapidly), $\frac{d \tilde{\phi}}{dr} \rightarrow -1$. The general solution to the inhomogeneous equation (2) can be written as a sum of any inhomogeneous solution plus any linear combination of the homogeneous solutions. The homogeneous equation is found by setting the right hand side of Eq. (2) equal to zero. The inhomogeneous solution that satisfies the boundary conditions was found as follows. At large $r_o$, inhomogeneous and homogeneous solutions were started assuming the asymptotic form. The value of $A = r_i^3/2$, which is the correct value for the uniform density case, was used to start the solutions. The two solutions are numerically integrated until $r = r_i$, at which
point the derivatives of the homogeneous solution, $\bar{\phi}_h$ and the inhomogeneous solution, $\bar{\phi}_{inh}$ are used to determine the constant $B$, equal to:

$$B = -\frac{1 + \left(\frac{d\bar{\phi}_{inh}}{dr}\right)_{r_i}}{\left(\frac{d\bar{\phi}_h}{dr}\right)_{r_i}}$$

(3)

The inhomogeneous solution satisfying the boundary conditions is:

$$\bar{\phi}(r) = \bar{\phi}_{inh}(r) + B \bar{\phi}_h(r)$$

(4)

The hydrodynamic kinetic energy is found by integrating the helium kinetic energy, which is proportional to $V^2$. This allows us to define a hydrodynamic mass, $M_h$, by

$$\frac{M_h}{M_{He}} = V^{-2} \int \rho |\nabla \phi|^2 dV$$

$$= \frac{4\pi}{3} \int \rho(r) \left[ \left(\frac{d\bar{\phi}}{dr}\right)^2 + \frac{2\bar{\phi}(r)^2}{r^2} \right] r^2 dr$$

(5)

This integral is evaluated from the numerical solution over the domain $r_i \leq r \leq r_o$. If we assume that the solution for $r > r_o$ is given by the asymptotic form, then this gives an additional contribution of $(8\pi/3) M_{He} \rho_e \bar{\phi}(r_o)^2 r_o$ to the integral defining $M_h$. It has been checked that this definition of $M_h$ gives the correct value of one half the displaced helium mass for the case of a hole in helium of uniform density.

It is also possible to use the hydrodynamic equation to transform the integral for the effective mass to give:

$$\frac{M_h}{M_{He}} = V^{-2} \left[ -\int \phi \left(\frac{d\rho}{dr}\right) dV + \int \rho \phi \nabla \phi \cdot dS \right]$$

$$= \frac{4\pi}{3} \left[ \int_{r_i}^{r_o} \bar{\phi}(r) \left(\frac{d\rho}{dr}\right) r^2 dr + \rho(r_i) \bar{\phi}(r_i) r_i^2 \right]$$

(6)

There is no contribution to the volume integral in the region $r > r_o$ because by assumption, $(\frac{d\rho}{dr}) = 0$ in this region. The two estimates for $M_{He}$ need agree only if $\bar{\phi}$ is a solution of the continuum hydrodynamic equation, and thus a comparison between them provides a test of the convergence of the numerical solution and the size of spacing used for integration.
II. APPLICATION TO ALKALI CATIONS

Figure 1 shows the helium solvation densities around Li\(^+\), Na\(^+\), K\(^+\), and Cs\(^+\), as calculated by VMC \cite{15} using a trial function of the “shadow function” form. This technique treats solids, liquids, and solid-liquid mixtures with a single functional form \cite{Pederniza94,Duminuco00}. It can be noted that the solvation density goes almost to zero between the first and second solvent layers for K\(^+\), and is highly structured in the case of Na\(^+\). The VMC calculations find that the first solvation layer has a highly solid-like order for the Na\(^+\) and K\(^+\) cases with little to no exchange of these atoms between solvent layers \cite{15,17}. This suggests that the first solvation layer not be treated as part of the fluid but as a fixed mass that moves rigidly with the cation, as in the snowball model of Atkins \cite{18}. In contrast, the VMC find substantial mobility between solvation layers for Li\(^+\) and Cs\(^+\), suggesting that in these cases that even the highly compacted first solvation layer should be treated as part of the superfluid, and thus be treated as part of the hydrodynamic flow.

Table I contains comparisons of the effective mass for each cation calculated using a hydrodynamic treatment and estimated from the VMC calculations. It is seen that in all four cases, the agreement of the two estimates is excellent, being within the VMC statistical error estimate. For the cases of Na\(^+\) and K\(^+\), the first solvation shell, with 10 and 12 helium atoms respectively, was treated as a rigid solid and the hydrodynamic calculations were begun at the minimum density point between the first and second solvent shells. In both these cases, treating the entire density with the hydrodynamic approach yielded a substantial underestimate for the translational mass; 21.7 u for Na\(^+\) and 36.0 u for K\(^+\). The hydrodynamic calculations are vastly less computationally expensive than the many-body treatment \cite{19}.

It is useful to compare our present results with that of the widely used model of the cation “snowball” due to Atkins \cite{18}. In this electrostrictive model, the helium is treated as a continuum dielectric material, whose density is increased near the cation due to the ion-induced dipole interaction. For a radius less than \(b\), on the order of 5-6 Å (whose value depends upon the helium liquid-solid surface tension assumed but is independent of the specific singly charged cation \cite{1}), the helium is predicted to form a solid “snowball” that moves rigidly with the ion. This snowball contributes a mass of \(\approx 150\) u to the ion effective mass \cite{1}. In addition, there is a hydrodynamic contribution to the mass, expected to be
on the order of the hard sphere value $m_{HS} = \frac{2\pi}{3} b^3 \rho_e m_{He} \approx 40 \text{ u}$. Taking into account the increased helium density for $r$ slightly larger than $b$, using the model used by Barrera and Baym [14] ($\rho - \rho_e = \rho_e \lambda (b/r)^4$ with $\lambda = 0.186$), the above hydrodynamic treatment predicts the hydrodynamic contribution to the mass to be $0.932m_{HS}$, which can be compared to the value $0.97m_{HS}$ reported by Barrera and Baym [14] for their proposed velocity solution which is not irrotational. In agreement with the Kelvin minimum energy principle [13], their solution is higher in kinetic energy and thus predicts a higher mass. Comparison with the both the VMC and hydrodynamic results show that the effective masses, even for the case of rigid first solvation shells, is considerably less than those predicted by the snowball model of Atkins.

III. CONCLUSIONS

The present work demonstrates that the hydrodynamic treatment of the linear motion of a solute through superfluid helium predicts the solvent contributions to the effective mass of the impurity in quantitative agreement with more exact many-body approaches, yet requires only a trivial additional computational cost once the solvent density has been calculated. This applies to helium density well inside the predicted 5-6 Å radius of the liquid-solid surface in the “snowball” model of Atkins [18]. However, the highly ordered first solvent layer around some ions must be treated as a solid that rigidly moves with the ion. The present results compliment our recent hydrodynamic calculations of solvent contributions to the moments of inertia of molecules solvated in helium, which were found to be in good agreement with experiment [8]. The present results have been directly compared to higher levels of theory and thus provide a more critical test of the hydrodynamic model, since uncertainties in the solute-helium potentials do not enter. We therefore demonstrate that the hydrodynamic treatment of superfluid helium motion can be accurate on the atomic scale, directly refuting recent criticisms of its use [9].

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required approximately four days on a 16 PC Beowulf cluster. In contrast, given the helium
solvation density (which is much less expensive to calculate by Monte Carlo methods than the
excitation energies), the hydrodynamic calculation took on the order of one second.

TABLE I: Helium contribution to the effective translational mass, in atomic mass units, for four
cations calculated by VMC [15] compared to the hydrodynamic calculation of the same quantity
(this work). For the cases of Na\(^+\) and K\(^+\), the hydrodynamic calculation treated the first helium
solvation shell as crystalline, as predicted by the VMC calculations.

| Cation | VMC       | Hydrodynamic |
|--------|-----------|--------------|
| Li\(^+\) | 12.9 (4.6) | 9.4          |
| Na\(^+\) | 48.2 (5.6) | 52.1         |
| K\(^+\)  | 69.6 (4.8) | 70.1         |
| Cs\(^+\) | 6.4 (8.8)  | 6.8          |
FIG. 1: The radial density of $^4$He around the alkali ions. This figure is reproduced from Ref. 15.