

Model-independent bounds for the potential and kinetic energy of liquid ${}^4\text{He}$ at zero temperature

J. Boronat

Departament d'Estructura i Constituents de la Matèria, Universitat de Barcelona, E-08028 Barcelona, Spain

A. Fabrocini

Dipartimento di Fisica and Istituto Nazionale di Fisica Nucleare, Università di Pisa, I-56100 Pisa, Italy

A. Polls*

Department of Physics, Washington University, St. Louis, Missouri 63130

(Received 16 September 1988)

Using the experimental values of the chemical potentials of liquid ${}^4\text{He}$ and of a ${}^3\text{He}$ impurity in liquid ${}^4\text{He}$, we derive a model-independent lower (upper) bound to the kinetic (potential) energy per particle at zero temperature. The values of the bounds at the experimental saturation density are 13.42 K for the kinetic energy and -20.59 K for the potential energy. All the theoretical calculations based on the Lennard-Jones potential violate the upper-bound condition for the potential energy.

The theoretical study of one isolated ${}^3\text{He}$ atom in liquid ${}^4\text{He}$ provides the basis for understanding the dilute ${}^3\text{He}$ - ${}^4\text{He}$ mixtures¹⁻³ and in addition can provide useful information on the host medium. In this paper we are concerned with the second aspect, and the main purpose is to use the experimental values of the chemical potentials of the ${}^3\text{He}$ impurity (μ_I^{expt}) and of the liquid ${}^4\text{He}$ (μ_4^{expt}) to obtain model-independent bounds to the kinetic and potential energies per particle of the liquid ${}^4\text{He}$ at zero temperature. These bounds are useful in testing (a) the basic interactions used in microscopic calculations, and (b) experimental determinations of the kinetic energy.

The system we study consists of A ${}^4\text{He}$ atoms and one ${}^3\text{He}$ atom enclosed in a volume Ω . The Hamiltonian of the system is given by

$$H(A+1) = H_4(A) + H_I(A+1), \quad (1)$$

where

$$H_4(A) = -\frac{\hbar^2}{2m_4} \sum_{i=1}^A \nabla_i^2 + \sum_{\substack{i,j=1 \\ i < j}}^A V(r_{ij}) \quad (2)$$

is the Hamiltonian of the host medium and

$$H_I(A+1) = \frac{-\hbar^2}{2m_I} \nabla_I^2 + \sum_{i=1}^A V(r_{Ii}) \quad (3)$$

is the Hamiltonian of the impurity. We work in the limit $A \rightarrow \infty$ and $\Omega \rightarrow \infty$, keeping the density $\rho = A/\Omega$ constant.

The chemical potential is defined by the following difference of expectation values:

$$\mu_I(\rho) = \frac{\langle \Psi_{A+1} | H(A+1) | \Psi_{A+1} \rangle}{\langle \Psi_{A+1} | \Psi_{A+1} \rangle} - \frac{\langle \Psi_A | H_4(A) | \Psi_A \rangle}{\langle \Psi_A | \Psi_A \rangle}, \quad (4)$$

where Ψ_{A+1} and Ψ_A are the wave functions describing the system of $A+1$ and A particles, respectively. This

difference is difficult to evaluate in general. However, its evaluation is greatly simplified if we take the trial wave function Ψ_{A+1} to be the wave function used to describe the liquid ${}^4\text{He}$ but with $A+1$ particles. This approximation, known as average-correlation approximation (ACA), is based in the fact that the interaction is the same for all pairs of particles. In this case $\mu_I(\rho)$ is given by Baym's formula^{4,5} for the impurity chemical potential

$$\mu_I^{\text{ACA}}(\rho) = \mu_4(\rho) + \left(\frac{m_4}{m_I} - 1 \right) t(\rho), \quad (5)$$

where $\mu_4(\rho)$ and $t(\rho)$ are the chemical potential and the kinetic energy per particle of the liquid ${}^4\text{He}$ associated with the wave function Ψ_A .

The crucial step in establishing the bounds is to analyze the upper-bound properties of μ_I^{ACA} . If we use arbitrary trial wave functions to calculate $\mu_I^{\text{ACA}}(\rho)$, we are confronted with the fact that the difference of two upper bounds is not necessarily an upper bound. However, when we assume the trial wave function to be the unknown exact wave function of liquid ${}^4\text{He}$, $\mu_I^{\text{ACA}}(\rho)$ provides an upper bound to $\mu_I^{\text{expt}}(\rho)$,

$$\mu_4^{\text{expt}}(\rho) + \left(\frac{m_4}{m_I} - 1 \right) t(\rho) \geq \mu_I^{\text{expt}}(\rho). \quad (6)$$

Therefore,

$$t(\rho) \geq t^{\text{LB}}(\rho) \equiv \left[\frac{m_I}{m_4 - m_I} \right] [\mu_I^{\text{expt}}(\rho) - \mu_4^{\text{expt}}(\rho)]. \quad (7)$$

Once a lower bound to the kinetic energy has been established, it is straightforward to determine an upper bound to the potential energy per particle,

$$v(\rho) \leq v^{\text{UB}}(\rho) \equiv e^{\text{expt}}(\rho) - t^{\text{LB}}(\rho), \quad (8)$$

where $e^{\text{expt}}(\rho)$ is the ${}^4\text{He}$ binding energy per particle.

In Fig. 1 we report the bounds to the kinetic and potential energies and the experimental binding energy in

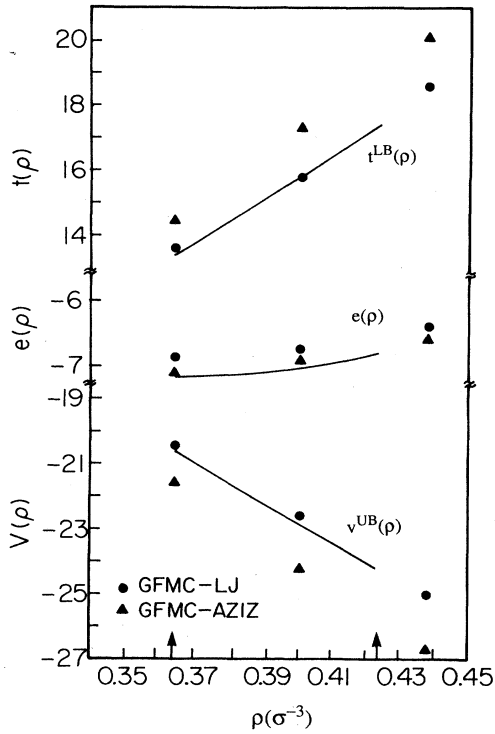


FIG. 1. Upper bound to the potential energy, experimental binding energy and lower bound to the kinetic energy as functions of the density. Also shown are GFM-C values for the LJ (filled circles) and the Aziz (filled triangles) potentials. The two arrows indicate the densities corresponding to $P=0$ and $P=20$ atm.

a density range between $0.365\sigma^{-3}$ and $0.424\sigma^{-3}$ ($\sigma=2.556$ Å) corresponding to a pressure range between 0 and 20 atm. The Green's-function Monte Carlo method (GFM-C) results^{6,7} for the Lennard-Jones (LJ) and the Aziz potentials are also shown. The values of $e^{\text{expt}}(\rho)$, $\mu_4^{\text{expt}}(\rho)$, and $\mu_1^{\text{expt}}(\rho)$ necessary to evaluate the bounds have been taken from Refs. 2 and 8. For the ratio m_4/m_3 we use 1.327. At the experimental saturation density ($\rho_0=0.365\sigma^{-3}$), $t^{\text{LB}}(\rho_0)=13.42$ K, and $v^{\text{UB}}(\rho_0)=-20.59$ K.

Figure 1 points out the different balance of potential and kinetic energies produced by the two potentials. Due to the cancellation between kinetic and potential energy, the differences between the two potentials are less sizable in the calculation of the total energy. As it is well known, both potentials give a reasonable equation of state, that for the Aziz potential being slightly better. The kinetic energies of the LJ potential are systematically smaller than for the Aziz potential and very close to the lower bound. The LJ potential energies are less attractive and violate the upper bound for all densities.

Table I collects a variety of theoretical predictions of the kinetic and potential energy per particle at the saturation density. These are to be compared with $t^{\text{LB}}(\rho_0)$ and $v^{\text{UB}}(\rho_0)$. The variational calculations referred to in the table were performed with trial wave functions containing two- and three-body correlations. The elementary diagrams were calculated using the scaling approximation.⁹

TABLE I. Theoretical calculations of the kinetic and potential energy per particle (in kelvin) of liquid ^4He at the experimental saturation density and at zero temperature. The relevant bounds are $v^{\text{LB}}(\rho_0)=13.42$ K and $t^{\text{UB}}(\rho_0)=-20.59$ K. SJ and SJT refer to a Jastrow-type wave function with two- and three-body correlations respectively.

Reference	Potential	Method	e	t	v
5,9	LJ	Variational SJ	-5.71	14.14	-19.85
5,9	LJ	Variational SJT	-6.55	13.51	-20.06
6	LJ	GFM-C	-6.85	13.62	-20.77
9	Aziz	Variational SJ	-5.94	15.25	-21.29
9	Aziz	Variational SJT	-6.93	14.72	-21.65
7,20	Aziz	GFM-C	-7.11	14.47	-21.58

All calculations with the LJ potential give a potential energy which is insufficiently attractive, i.e., higher than $v^{\text{UB}}(\rho_0)$. By contrast, the Aziz potential produces, in all the approximations, energies that do not violate the bounds. With the improvement of the wave function (i.e., upon inclusion of three-body correlations), the kinetic energy becomes less repulsive and the potential energy more attractive. In the case of the LJ potential, the resulting kinetic energy moves very close to the $t^{\text{LB}}(\rho_0)$, while the potential energy does not become attractive enough to drop below $v^{\text{UB}}(\rho_0)$. Contributions to the potential energy from the Axilrod-Teller three-body interaction¹⁰ estimated in Ref. 6 to be repulsive and of the order of 0.16 K do not help in bringing the LJ potential energy below $v^{\text{UB}}(\rho_0)$.

All the calculations referred to in Table I were performed at the experimental saturation density ρ_0 . Usually the minimization of the energy expectation value with respect to an approximate trial wave function (e.g., containing only two-body correlations) yields a saturation density (ρ_{eq}) that is different than ρ_0 . The upper-bound property of the variational energy applies to both $e(\rho_{\text{eq}})$ and $e(\rho_0)$; consequently $e(\rho_{\text{eq}})$, being the lowest, is taken as the estimate of $e^{\text{expt}}(\rho_0)$. On the other hand, as the variational principle applies only to the total energy, the separate theoretical evaluations of the kinetic and potential energies should be performed at ρ_0 . The results $\rho_{\text{eq}}=0.330\sigma^{-3}$, $t(\rho_{\text{eq}})=12.05$ K, $v(\rho_{\text{eq}})=17.87$ K, and $e(\rho_{\text{eq}})=-5.82$ K, for the LJ case which two-body correlations may be compared with the results of the table.

Several authors have already used $t^{\text{LB}}(\rho)$ and $v^{\text{LB}}(\rho)$ as approximations, estimated to be good at least to 10%, to the kinetic and potential energy per particle of liquid ^4He without exploiting their properties as bounds. In Ref. 11, Davison and Feenberg improved the estimate of the kinetic energy at ρ_0 by adding to $t^{\text{LB}}(\rho_0)$ a perturbative correction calculated in a correlated basis. The resulting kinetic energy, $t(\rho_0)=14.3$ K,¹² no longer has the lower-bound property. In Ref. 13, Mantz and Edwards mentioned that $t^{\text{LB}}(\rho_0)$ should be considered a lower bound, but did not proceed further.

We can also compare $t^{\text{LB}}(\rho_0)$ with experimental determinations of the kinetic energy, which are usually based on analysis of the dynamic structure function. Several authors¹⁴⁻¹⁶ have used the impulse approximation to extract

the kinetic energy from $S(Q, \omega)$. The resulting kinetic energies range between 10.9 and 13.2 K and hence violate the lower bound. The reason is that in practice the values of Q used to analyze $S(Q, \omega)$ are not large enough for the impulse approximation to be valid, so it is necessary to take account of the final-state-interaction effects.¹⁷

Recently, Sears^{18,19} has analyzed different ways to obtain $t(\rho_0)$ from experimental data. He reports a kinetic energy of 14.0 ± 0.5 K, which, in addition to respecting the lower-bound condition, agrees with the GFMC calculation^{6,20} and with the perturbative estimate.¹¹

It is also interesting to study the density dependence of $t^{\text{LB}}(\rho)$ or equivalently that of $\mu_l^{\text{expt}}(\rho) - \mu_4^{\text{expt}}(\rho)$. It turns out that the difference of the chemical potentials $\Delta\mu$ is well fitted by a straight line. Using a least-squares fit to adjust a straight line to the $\Delta\mu$ reported by Ebner and Edwards² at eleven equidistant pressures between 0 and 20 atm, we find that $\Delta\mu$ can be approximated by

$$\Delta\mu(\rho) \text{ (K)} = (4.38 \text{ K}) + (8.09 \text{ K}) \left[\frac{\rho - \rho_0}{\rho_0} \right], \quad (9)$$

with an error less than 0.3%. The linear correlation coefficient is 0.999897. To understand this approximate linear behavior we consider the derivative

$$\frac{d(\mu_l(\rho) - \mu_4(\rho))}{d\rho} = \frac{m_4 s^2 \alpha}{\rho}, \quad (10)$$

where s is the sound velocity in ${}^4\text{He}$ and α is the excess ${}^3\text{He}$ volume parameter in liquid ${}^4\text{He}$. This derivative is the product of an increasing function of the density ($m_4 s^2$) times a decreasing one (α/ρ), resulting in very little change as ρ varies over the liquid range. To be more precise, the derivative is an increasing function of the density running from $21.25 \pm 0.1 \text{ K}\sigma^3$ at $P=0$ atm to $23.00 \pm 0.8 \text{ K}\sigma^3$ at $P=20$ atm, implying that $\Delta\mu$ should be a slightly concave function of the density. To calculate the error in the derivative we have considered s to be well known, and taken the estimated error of α reported in Ref. 2. Actually, Eq. (10) is the relation conventionally used

to determine $\mu_l^{\text{expt}}(\rho)$ by numerical integration, direct vaporization heat measurements being available only at zero pressure.

It is interesting, if perhaps not significant, that the Aziz GFMC results for the kinetic energy are also well fitted by a straight line,

$$t^{\text{GFMC}}(\rho) \text{ (K)} = (14.49 \text{ K}) + (28.15 \text{ K}) \left[\frac{\rho - \rho_0}{\rho_0} \right]. \quad (11)$$

The linear correlation coefficient is 0.999995 and the slope is larger than that for the lower bound. As three points are not enough to draw any firm conclusion, and there is not apparent theoretical reason to expect a linear behavior, this approximate linearity should be viewed with caution.

The fact that the density expansion of the potential energy around the equilibrium density has no linear term (zero-pressure condition) implies that the density expansion of the potential energy has a linear term with a coefficient opposite to that of the linear term in the kinetic energy. The other terms of the expansion bend up the potential energy slightly, defining the minimum for the total-energy curve.

To summarize briefly, we have derived model-independent bounds for the potential and kinetic energy per particle of liquid ${}^4\text{He}$. These bounds have been used to test the basic interactions used in microscopic theory. Evidence is obtained for the inadequacy of the Lennard-Jones potential for quantitative prediction of observables other than the total energy.

We are in debt to S. Stringari and P. Whitlock for helpful discussions and to J. W. Clark for critical reading of the manuscript. This work has been supported in part by La Comisión Asesora de Investigación Científica y Técnica (CAICYT) (Spain), Grant No. PB85-0072-C02-00 and by the agreement between CAICYT (Spain) and Istituto Nazionale de Fisica Nucleare (INFN) (Italy).

*Permanent address: Departament d'Estructura i Constituents de la materia, Universitat de Barcelona, E-08028, Barcelona, Spain.

¹J. Bardeen, G. Baym, and D. Pines, Phys. Rev. **156**, 207 (1967).

²C. Ebner and D. O. Edwards, Phys. Rep. **2**, 77 (1970).

³A. Fabrocini and A. Polls, Phys. Rev. B **25**, 4533 (1982); A. Fabrocini, S. Fantoni, S. Rosati, and A. Polls, *ibid.* **33**, 6057 (1986).

⁴G. Baym, Phys. Rev. Lett. **17**, 952 (1966).

⁵J. Boronat, A. Fabrocini, and A. Polls, J. Low Temp. Phys. (to be published).

⁶P. A. Whitlock, D. M. Ceperley, G. V. Chester, and M. H. Kalos, Phys. Rev. B **19**, 5598 (1979).

⁷M. H. Kalos, M. A. Lee, P. A. Whitlock, and G. V. Chester, Phys. Rev. B **24**, 115 (1981).

⁸R. deBruyn Ouboter and C. N. Yang, Physica B **144**, 127 (1987).

⁹Q. N. Usmani, S. Fantoni, and V. R. Pandharipande, Phys. Rev. B **26**, 6123 (1982).

¹⁰B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 293 (1943).

¹¹T. B. Davison and E. Feenberg, Phys. Rev. **178**, 306 (1969).

¹²G. E. Watson, J. D. Reppy, and R. C. Richardson, Phys. Rev. **188**, 384 (1969).

¹³I. B. Mantz and D. O. Edwards, Phys. Rev. B **20**, 4518 (1979).

¹⁴H. W. Jackson, Phys. Rev. A **10**, 278 (1974).

¹⁵L. J. Rodriguez, H. A. Gersch, and H. A. Mook, Phys. Rev. A **9**, 2085 (1974).

¹⁶H. A. Mook, Phys. Rev. Lett. **32**, 1167 (1974).

¹⁷R. N. Silver, Phys. Rev. B **37**, 3794 (1988).

¹⁸A. D. B. Woods and V. F. Sears, J. Phys. C **10**, L341 (1977).

¹⁹V. F. Sears, Phys. Rev. B **28**, 5109 (1983).

²⁰P. Whitlock and R. Panoff, Can. J. Phys. **65**, 1416 (1987).