Helium mixtures in nanotube bundles

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Helium atoms are strongly attracted to and absorbed within nanotube bundles\textsuperscript{[1]}\textsuperscript{[2]}. For tubes at the experimentally observed diameter of $\sim$14 Angstroms, the most energetically favorable sites lie within interstitial channels bounded by three nanotubes; these tubes form a hexagonal array. For a system of adsorbed $^4$He atoms, the individual atoms are highly localized by the periodic potential due to the surrounding nanotubes\textsuperscript{[3]}. The $^4$He atoms’ mutual interactions induces a condensation which is well-described by an anisotropic lattice gas model. Because of the well-localized atomic states, the transition temperature to the condensed state is nearly the same for $^3$He and $^4$He. Here we analyze a mixture of these isotopes and show that the system forms an ideal solution, wherein the ratio of the partial pressures of the coexisting vapors of the two components satisfies an analogue of Raoult’s law\textsuperscript{[5]}.

An analogue to Raoult’s law is determined for the case of a $^3$He–$^4$He mixture adsorbed in the interstitial channels of a bundle of carbon nanotubes. Unlike the case of $^4$He mixtures in other environments, the ratio of the partial pressures of the coexisting vapor is found to be a simple function of the ratio of concentrations within the nanotube bundle.

\begin{equation}
\frac{p_{^3\text{He}}}{p_{^4\text{He}}} = \exp\left(\frac{-\beta N f_1(\theta)}{N_3 + N_4}\right),
\end{equation}

where $f_1(\theta)$ is the Helmholtz free energy per atom for such a system of interacting indistinguishable particles. We need not specify the form of $f_1(\theta)$ here; its behavior was described in previous work\textsuperscript{[4]} using an anisotropic lattice gas model (based in turn on studies by Fisher and Graim and Landau\textsuperscript{[8]}).

The equilibrium number of $^3$He atoms, $\langle N_3 \rangle$, follows from maximizing $p(N_3, N_4)$:

\begin{equation}
\left[\frac{\partial}{\partial N_3} \ln p(N_3, N_4)\right]_{T,\mu_{^3\text{He}},\mu_{^4\text{He}}} = 0.
\end{equation}

Hence we obtain the condition for the chemical potential:

\begin{equation}
\mu_{^3\text{He}} = \epsilon_{^3\text{He}} + \beta^{-1} \ln x + f_1(\theta) + \theta f_1'(\theta) = \epsilon_{^3\text{He}} + \beta^{-1} \ln x + g(\theta)
\end{equation}

where $x = N_3/(N_3 + N_4)$ is the $^3$He concentration and a prime refers to differentiation with respect to $\theta$. The coexisting three dimensional vapor (assumed ideal) satisfies\textsuperscript{[6]}
\[ \mu_3 = \beta^{-1} \ln(n_3 \lambda_3^3) = \beta^{-1} \ln(\beta P_3 \lambda_3^3), \] (5)

where \( n_3 \) is the \(^3\)He particle density in the vapor phase, \( P_3 \) is the \(^3\)He partial pressure, and \( \lambda_3 = (2\pi \hbar^2 / \beta m_3)^{1/2} \) is the de Broglie wavelength for the \(^3\)He atoms. The resulting isotherm is then

\[ P_3 \lambda_3^3 = x \exp[\beta(\epsilon_3 + g'(\theta))]. \] (6)

In similar fashion,

\[ P_4 \lambda_4^3 = (1 - x) \exp[\beta(\epsilon_4 + g'(\theta))], \] (7)

which yields a remarkably simple relation between the isotope partial pressures:

\[ \frac{P_3}{P_4} = \left( \frac{3}{4} \right)^{3/2} \frac{x}{1-x} e^{\beta(\epsilon_3 - \epsilon_4)}. \] (8)

The ratio of partial pressures is independent of both \( \theta \) and the form of the interaction between the atoms. These quantities disappear from the pressure ratio since the interaction between \(^3\)He atoms is nearly isotope-independent due to the strong atomic localization. This ratio is an expression of Raoult’s law of solutions. Because \( \epsilon_3 - \epsilon_4 \approx 17 \text{ K} \), \( P_3 > P_4 \) except at small \( x \) and high \( T \).

This result coincides with that obtained from a noninteracting (band) model. In this case the average number of \(^3\)He particles is

\[ N_4 = \int d\epsilon \frac{N(\epsilon)}{e^{\beta(\epsilon - \mu_4)} - 1} \] (9)

where \( N(\epsilon) \) is the density of states as a function of the single-particle energy \( \epsilon \). In the limiting case of very low coverage relevant to this noninteracting model (i.e. \( \exp(-\beta \mu) \ll 1 \)),

\[ N_4 \approx e^{\beta \mu_4} \int d\epsilon N(\epsilon) e^{-\beta \epsilon}. \] (10)

For the present case of a very narrow band we can approximate the density of states by a delta function to obtain

\[ N_4 \approx e^{\beta \mu_4} \frac{L}{a}, \] (11)

where \( a \) is the lattice constant and \( L \) is the total length of interstitial channel. The chemical potential is then:

\[ \mu_4 = \epsilon_4 + \beta^{-1} \ln \left( \frac{N_4 a}{L} \right). \] (12)

Taking the same vapor chemical potential as before, and following a similar analysis for \(^3\)He, one again obtains Eqn. 8 as the isotopic ratio of the partial pressures. This confirms our expectation that the pressure ratio in a localized lattice gas model with arbitrary interactions coincides with that obtained in the appropriate noninteracting band model. At high density the noninteracting model fails, so a comparison is not appropriate.

These results depend upon the isotope-independence of the He–He interaction, a property which we now address in detail. Three effects could contribute to an isotope dependence in the He–He interaction: differences in zero point motion (primarily along the axis of the channel), the magnetic interaction in \(^3\)He, and the exchange interaction. The contribution from zero point motion can be described by a Hartree interaction,

\[ V_H(a) = \int d\vec{r}_1 \ n_1(\vec{r}_1) \int d\vec{r}_2 \ n_2(\vec{r}_2) \ u(\vec{r}_{12}), \] (13)

where \( n_1(\vec{r}_1) \) and \( n_2(\vec{r}_2) \) are the densities at neighboring sites separated by a distance \( a \) in the same channel, and \( u(\vec{r}_{12}) \) is the interaction potential between two atoms. Since the densities are well-confined, we can Taylor expand
the integrand (with $z_{1,2}$ the axial coordinate and $\rho_{1,2}$ the transverse radial coordinate). Keeping second order terms, we obtain

$$V_H(a) = u(a) + \frac{1}{2a}u'(a)(<\rho_1^2> + <\rho_2^2>) + \frac{1}{2}u''(a)(<z_1^2> + <z_2^2>).$$  \hspace{1cm} (14)$$

Using the single-particle wavefunctions for $^3$He and $^4$He in the interstitial channel of an (18,0) tube lattice, we obtain a correction $\Delta V \equiv V_H(a) - u(a)$ of -0.488 K, -0.490 K and -0.489 K respectively for the $^4$He–$^4$He, $^3$He–$^3$He and $^3$He–$^4$He interactions. Although the magnitude of this correction reaches 25% of the bare He–He interaction, it introduces only a tiny distinction between the isotopes.

The magnetic energy of $^3$He is also negligible ($\sim$ nK) on this scale due to the very small nuclear moment of $^3$He. As to the exchange of He atoms between different sites, one might expect this to be significantly different for the two species. However, the very similar effective masses and band widths for the two isotopes suggests that the effects of exchange are not significantly different for the two species.

In summary, we have found a simple expression for the ratio of partial pressures of the ambient vapor of He isotopes when exposed to adsorption sites within bundles of carbon nanotubes. To our knowledge, this expression has no precedent in the field of $^3$He–$^4$He mixtures. In other known adsorption situations, the single-particle wave functions are not sufficiently localized to justify the present assumption that the effects of interactions are nearly isotope-independent. One can contrast the localized wave functions in the present case with those of He on graphite wherein the states are quite delocalized. The band masses are $m^*/m \sim 18$ in the nanotube environment and $\sim 1.05$ on graphite. In the case of He on graphite one cannot employ the present simple analysis because the effect of interparticle interactions depends on the species degree of localization, which differs for the two isotopes. It is plausible that other nanoscale porous media, such as zeolites, exhibit similar behavior of adsorbed He isotopic mixtures.

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[6] For simplicity, we consider spinless particles throughout this paper. Final results, however, apply to the general case of atoms with spin.
[9] The reader recognizes that the Hartree interaction is divergent because of the omission of the pair correlation function; this spurious divergence disappears in the present expansion.
[10] Nanotubes are labelled according to the lattice coordinates of the circumference vector. See, for example, R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. 60, 2204 (1992).