Peas in a pod: quasi-one-dimensional $C_{60}$ molecules in a nanotube

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“How luscious lies the pea within the pod…”
Emily Dickinson

We evaluate the equation of state of the quasi-one-dimensional (1D) phase of $C_{60}$ molecules in small carbon nanotubes, nicknamed “peas in a pod”. The chemical potential and 1D pressure are evaluated as functions of the temperature and density, initially with the approximation of nearest neighbor interactions and classical statistical mechanics. Quantum corrections and long-range interaction corrections are discussed, as are the effects of interactions with neighboring peapods. Transition phenomena involving the 3D coupling are evaluated.

I. INTRODUCTION

Carbon nanotubes have been found to exhibit a wide range of remarkable properties, concomitants of intriguing systems is that created when $C_{60}$ molecules within nanotubes of small radius ($R \approx 7 \, \text{Å}$) experience potentials confining them to the vicinity of the tube axis. This paper employs the potentials developed by Girifalco and coworkers. Transition phenomena involving the 3D coupling are evaluated.

II. MODEL CALCULATIONS

Girifalco and coworkers have shown how $C_{60}$ molecules separated a distance $\rho$ experience potentials confining them to the vicinity of the tube axis. The potential $U(\rho)$ is the molecule-tube interaction that determines the molecules’ degree of localization near the axis, which depends also on the temperature $T$. The other interaction in Eq. (1), $V(z)$, is that between a pair of $C_{60}$ molecules separated a distance $z$ along the tube axis. Girifalco et al have shown that both interactions, $U(\rho)$ and $V(z)$, can be expressed in a universal way by the following reduced function:

$$V_{total}(\rho_{i}, z_{i}) = \sum_{i} U(\rho_{i}) + \sum_{i<j} V(|z_{i} - z_{j}|) \quad (1)$$

Here, $\mathbf{r}_{i} = (\rho_{i}, z_{i})$ is the position of the $i$-th molecule’s center, written in terms of its coordinate $z_{i}$ parallel to the tube axis and its transverse displacement from the axis, $\rho_{i}$. The potential $U(\rho)$ is the molecule-tube interaction of the following reduced function:

$$\Phi(r) = \frac{\Phi(r_{0})}{|\Phi(r_{0})|} = \frac{5}{3} \left( \frac{3.41}{3.13 \bar{r} + 0.28} \right)^{4} - \frac{2}{3} \left( \frac{3.41}{3.13 \bar{r} + 0.28} \right)^{10} \quad (2)$$

where $|\Phi(r_{0})|$ is the well depth at the equilibrium spacing $r_{0}$, and $\bar{r} \equiv (r - r_{1})/(r_{0} - r_{1})$. The distance parameter $r_{1}$ for each system ($C_{60}$-tube) is chosen so that the interactions fit the universal function (2). Table I indicates the values of the used parameters. The function in Eq. (2) is obtained using a continuum model for...
the carbon surfaces. The carbon-carbon interatomic potential is integrated over the interacting surfaces assuming a mean surface density of carbon atoms and different Lennard-Jones parameters for atoms in C_{60}-C_{60} and C_{60}-graphene systems. Therefore, we ignore any dependence of the interactions on the atomic structure of either the tubes or the C_{60} molecules. Similarly, the neglect of any interactions that depend on the C_{60} orientation means that the molecular rotational problem is not affected by the environment. This means that the rotational degree of freedom may be omitted completely from the present analysis.

Concerning the C_{60}-C_{60} interaction, there has been some discussion in the literature of the value of the asymptotic van der Waals coefficient \( C_6 \), the coefficient of \( r^{-6} \), with values varying over the range 16.6 \( N_0^2 \) eV \( \AA^6 \) to 29.05 \( N_0^2 \) eV \( \AA^6 \). The value used in Girifalco’s calculations \( \Delta \) (Eq. (2)) is 20.0 \( N_0^2 \) eV \( \AA^6 \).

In reality, the intermolecular interaction \( V \) ought to depend on the full 3D separation. By neglecting this interaction’s dependence on \( \rho_i \) and \( \rho_j \), Eq. (1) implicitly assumes that the molecules’ rms transverse displacement \( d = \sqrt{\langle \rho_i^2 \rangle} \) is small compared to the mean separation \( a = L/N \) along the axis. We discuss the regime of validity of that approximation below. Also implicit in Eq. (1) is the assumption that both the nanotube and the C_{60} molecules are rigid, since otherwise their shape fluctuations would affect the nanotubes’ potential energy. While conventional in this field, this assumption deserves future attention in the case of such strongly interacting molecules as C_{60}.

With Eq. (1), the properties of the system may be evaluated in terms of independent transverse and longitudinal contributions to the Hamiltonian. For example, the partition function \( Z \) of the C_{60} molecules factorizes into transverse and longitudinal factors, \( Z = Z_t Z_z \), so that the Helmholtz free energy \( F \) is an additive function of these separate parts of the problem: \( F = F_t + F_z \). We may therefore write the chemical potential \( \mu \) of the set of \( N \) molecules as a sum of a transverse part \( \mu_t \) and a longitudinal part \( \mu_z \):

\[
\mu = \mu_t + \mu_z \quad (3)
\]

One may immediately evaluate \( \mu_t \) from the transverse partition function \( Z_t \) because that part of the problem consists of independent motions of individual molecules:

\[
-\beta \mu_t = \frac{1}{N} \ln Z_t = \ln \left( \sum_{\alpha} e^{-\beta E_\alpha} \right) \quad (4)
\]

Here \( \beta^{-1} = k_B T \) and the sum is over all eigenvalues \( E_\alpha \) of the Schrodinger equation for transverse motion of a single molecule. This equation may be evaluated analytically in the case when the transverse potential is nearly harmonic, i.e. when \( U \) includes just a small quartic term, involving a parameter \( \gamma \):

\[
U(\rho) = U_0 + \frac{k}{2} \rho^2 + \gamma \rho^4 \quad (5)
\]

The resulting transverse chemical potential is given by perturbation theory, assuming that the value of \( \gamma \) is small:

\[
\mu_t = U_0 + \frac{\hbar \omega}{\beta} + \frac{2}{\beta} \ln(1-e^{-x}) + 2\gamma \left[ \frac{\hbar}{m\omega} \coth \left( \frac{x}{2} \right) \right]^2 \quad (6)
\]

Here \( x = \beta \hbar \omega \) with \( \omega = \sqrt{k/m} \), and the regime of validity of this expression is that range of \( T \) for which the rightmost term in \( \mu_t \) is small compared to the middle term (i.e., \( k_B T < k_B T_1 \equiv k^2/\gamma \)). In the case of (10,10) nanotubes, the upper limit to the \( T \) range for which this expression is valid is about 13,000 K (based on our fits to the Girifalco potential \( U(\rho) \): \( k = 1.32 \) eV/ \( \AA^2 \) and \( \gamma = 1.58 \) \( \AA^{-4} \)). Thus, the expansion suffices in practice throughout the relevant range of \( T \).

The present case corresponds to \( x \approx 32 \) K/T, which is much less than 1 at room temperature. Therefore, it is appropriate to substitute the fully classical expression for \( \mu_t \):

\[
-\beta \mu_t = \ln \left( \frac{1}{\lambda_T} \int d^2r e^{-\beta(U(\rho))} \right) \quad (7)
\]

Here \( \lambda_T = (2\pi \beta \hbar^2/m)^{1/2} \) is the de Broglie thermal wavelength of the molecule, which is about 0.04 \( \AA \) at room temperature. The resulting expression for \( \mu_t \) in the case of a harmonic potential with a small quartic term coincides with the classical limit (\( x \ll 1 \)) of the preceding quantum expressions for both \( \mu_t \) and the transverse contribution to the specific heat (per molecule), \( C_t/N \):

\[
\mu_t = U_0 + \frac{2}{\beta} \ln(x) + \frac{8\gamma}{(\beta\omega^2 m)^2} \quad (8)
\]

\[
\frac{C_t}{Nk_B} = 2 - \frac{16\gamma}{(\beta\omega^2 m)^2} = 2 - \frac{16}{T_1} \quad (9)
\]

This includes a constant contribution (expected for two harmonic motions in the classical regime of \( T \)), plus an anharmonic term proportional to \( T \).

Figure 1 shows \( \mu_t \) as a function of \( T \), computed using the different approximations described above. The full line is the quantum result (Eq. (6)) obtained assuming the nearly harmonic transverse potential of Eq. (5). It is interesting to note that the corresponding classical expression, Eq. (8), is extremely similar to the quantum one (they coincide in the figure), showing that quantum effects are really negligible. The dashed line shows the classical result Eq. (7) using the exact potential. For \( T > 500 \) K, the curves start to differ as the real shape of the potential deviates from the quartic approximation.
The solution of the remaining 1D problem of interacting buckyballs requires a numerical calculation, in general. Quantum calculations have been carried out for some 1D fluids (helium and hydrogen \(^2\)) in their ground states, but for classical systems at finite \(T\) the determination of the equation of state is more straightforward. Specifically, the equation of a 1D classical system assumes an analytic form in the case when nearest neighbor interactions adequately represent the total potential energy. We assume that to be the case here (and justify that in Section III) so that we may write down an expression relating the 1D density, \(N/L = 1/a\), in terms of the 1D pressure \(P\):

\[
\frac{1}{a} = \int_0^\infty dz \ e^{-\beta[V(z)+zP]} \int_0^\infty dz' \ e^{-\beta[V(z)+z'P]}
\]

where \(V(z)\) is the \(C_{60}-C_{60}\) interaction given by Eq. (2). Similar results were reported recently by Hodak and Girifalco.\(^{16,17}\)

Figure 2 shows the “compression ratio”, i.e. the ratio of \(P\) to the pressure of an ideal 1D gas (\(k_B T/a\)): the interaction effects can be clearly observed. The pressure is evidently reduced by interactions over an extended density range until the point when the molecules start to come nearly into contact (\(a \approx 12.5\, \text{Å}\) at \(T = 300\, \text{K}\)), above which density the pressure rises extremely rapidly. One observes that the \(C_{60}\) gas behavior is nearly ideal at \(T > 1000\, \text{K}\) while the effects of the interaction are quite significant below room temperature. The Boyle temperature is around 1400 K. The calculated behavior and high characteristic temperature are not surprising in view of the fact that the well depth of the pair potential is around 1400 K. The calculated behavior and high characteristic temperature are not surprising in view of the fact that the well depth of the pair potential is about \(1400\, \text{K}\). The calculated behavior and high characteristic temperature are not surprising in view of the fact that the well depth of the pair potential is around 1400 K. The calculated behavior and high characteristic temperature are not surprising in view of the fact that the well depth of the pair potential is about \(1400\, \text{K}\).

The 1D pressure can be integrated (according to the Gibbs-Duhem relation) to obtain the total chemical potential of the \(C_{60}\) fluid at temperature \(T\) and density \(1/a\):

\[
\mu(T, a) = \mu(T, a_0) + \int_{P_0}^P a(P', T) \, dP'
\]

Here \(\mu_{id}(T, a_0) = k_B T \ln(\lambda_T/a_0)\) is the chemical potential of a 1D ideal gas at a reference density (\(1/a_0\)) that is low enough for the fluid to be ideal.\(^{18}\) The integration domain extends from the reference pressure \(P_0 = k_B T/a_0\) to the pressure corresponding to the specified spacing \(a\). The result of this analysis appears in Figure 3 for a range of temperatures.

Figure 4 exhibits the effects of the interaction on the chemical potential, expressed in terms of the difference between the chemical potential of the (fully interacting) system and that of an ideal system which has the mutual interactions “turned off”:

\[
\Delta \mu_{int}(T, a) = \mu(T, a) - [\mu(T) + \mu_{id}(T, a)] = \int_{P_0}^P \left[a(P', T)' - \frac{1}{k(T', P)}\right] \, dP'
\]

The rightmost integral may alternatively be expressed in terms of the 1D compressibility, \(\kappa = -(\partial \ln a/\partial P)_T\) as follows:

\[
\Delta \mu_{int}(T, a) = \int_{P_0}^P \left(\frac{k_B T}{a'} - \frac{1}{\kappa(a', T)}\right) \, da'
\]

Because the attraction dominates the effect of the interaction over most of the density range shown in Figures 2 to 4, the chemical potential shift due to the interaction is negative unless one reaches high density.

### III. CORRECTIONS TO THE MODEL

We assess three corrections to the preceding section’s results. One is the long range correction to the thermodynamic properties. This is the energy shift associated with the neglect of interactions other than nearest neighbors and could be written in terms of the probability per unit length \(P_z(x)\) that a second, third or other (than first) nearest neighbor is present at distance \(x\). Since we seek only an estimate of its effect, we take \(P_z(x)\) to be a Heaviside step function for \(|x| > 2\sigma\), where \(\sigma\) is the hard core diameter (7.1 Å) of the \(C_{60}\) molecule. Then, our approximate energy correction per molecule due to this neglect is given by

\[
\Delta E_{zp}/N = \int_{2\sigma}^\infty \frac{dz}{a} V(z)
\]

Note that a “missing” factor of \((1/2)\) is cancelled by the omission of the region \(z < 0\). If the potential \(V(z)\) were the familiar Lennard-Jones 6-12 interaction, the result of this integration would be \(\Delta E_{zp}/(N\epsilon) = -\sigma/(40a)\) (where \(\epsilon\) is the well depth), which represents a negligible correction of the energy.

The second correction we assess is the quantum correction. To do this, we introduce a phonon model as a means of characterizing the dynamics of the fluid. As was shown recently, for a Lennard-Jones system in its ground state, the ratio of the zero-point energy \(E_{zp}\) to the pair potential well depth \(\epsilon\) is

\[
\frac{E_{zp}}{\epsilon} = 2^{4/3} \frac{3}{\pi^2} \Lambda^\ast
\]

Here \(\Lambda^\ast = h/\sigma(m\epsilon)^{1/2}\) is the de Boer quantum parameter. In the case of a \(C_{60}\) modeled by such an interaction, \(\Lambda^\ast \approx 0.003\), so this ratio is 0.002. This indicates that the quantum effects are small even in the ground state. They become even smaller (relatively speaking) with increasing \(T\) and can be neglected at \(T > E_{zp}/k_B\), which is of order 10 K for \(C_{60}\).

\[
\frac{E_{zp}}{k_B T} = \frac{\epsilon}{k_B T}\]

we estimate the effect on the mutual interaction energy of the molecules’ motion perpendicular to the axis. To do so, we evaluate the expectation value of the
 difference in potential energy due to changing the approximate separation of a pair of molecules \((z_{ij})\) used in Eq. (1) into their fully 3D separation \(r_{ij} = (\rho_{ij}^2 + z_{ij}^2)^{1/2}\). To lowest order in the transverse separation, the difference in potential energy is \(\Delta V(z) = V'(z)[\rho_{ij}^2/(2z_{ij})]\), where the prime means a derivative. Substituting the mean value \((\rho_{ij}^2) = 2d^2\), the energy shift per molecule due to this substitution is obtained from the radial distribution function \(g_{1D}(z)\):

\[
\frac{\Delta E_t}{N} = \int dz \, g_{1D}(z) \frac{V'(z)d^2}{z} (16)
\]

For this estimate, we substitute for \(g_{1D}(z)\) a step function at \(z = \sigma\). The result for a Lennard-Jones potential is

\[
\frac{\Delta E_t}{N\varepsilon} = -\frac{24}{91} \frac{d^2}{a\sigma} \quad (17)
\]

For a \((10,10)\) tube in a high density case, with \(a = \sigma \approx 9.5 \ \text{Å}\), for example, at room temperature \((d = 0.5 \ \text{Å})\), we obtain \(\Delta E_t/(N\varepsilon) = 6\times10^{-3}\), which is negligibly small (using \(\varepsilon \approx 3200 \ \text{K}\)). Although this is a relatively crude estimate, the order of magnitude is plausible in view of the small ratio of \(d/a\). Evidently, the small value of \(\Delta E_t\) implies that the 1D approximation is adequate for the present circumstances.

IV. TRANSITIONS DUE TO INTERACTIONS WITH NEIGHBORING TUBES

In this section we evaluate an interesting possibility—transitions of the \(C_{60}\) fluid as a result of molecular interactions between buckyballs in neighboring tubes. In our analysis, we assume an infinite array of perfectly parallel and identical tubes and chemical equilibrium among the \(C_{60}\) molecules. Under these circumstances, molecules in nearby tubes can undergo a cooperative transition, a condensation to a 3D liquid. A qualitatively similar problem (condensation of helium confined within interstitial channels of a carbon nanotube bundle) was studied previously by our group, using a Monte Carlo evaluation of a lattice gas model\(^2\).

The present analysis is carried out first by perturbation theory; then, a comparison is made with an exactly solved model that captures the essential physics but employs a number of simplifications. Although neither model is completely satisfactory, we will see that the two sets of results are quite similar because the key predictions (parameters of the critical point) turn out to be only weakly dependent on the assumptions.

The perturbation theory is based on the shift in free energy of the system due to interactions between molecules in neighboring tubes, \(\Delta F_{\text{inter}}\):

\[
\Delta F_{\text{inter}} = \frac{N\nu}{2a} \int_{-\infty}^{\infty} dz \, V[(b^2 + z^2)^{1/2}] \quad (18)
\]

Here \(b\) is the separation between tubes and \(\nu\) is the number of nearest neighbor tubes. This expression assumes a simple form in the case when \(b\) is sufficiently large that the interaction may be approximated by the asymptotic form \(V(r) \approx -C_6/r^6\), in which case the integration yields

\[
\Delta F_{\text{inter}} = -\nu N \frac{3\pi}{16} \frac{C_6}{b^6} \frac{1}{a} \quad (19)
\]

Including this term in the equation of state yields a relation for the shift of the 1D pressure proportional to \(1/a^2\):

\[
P = P_{1D} - \frac{\alpha}{a^2} ; \quad \alpha = \frac{3\pi}{16} \frac{C_6}{b^6} \quad (20)
\]

Note that \(\alpha = (3\nu\pi/16)bV(b)\); thus it is proportional to the product of the strength of the transverse interaction and the number of neighbors interacting with a molecule (\(\approx b/a\)).

Figure 5 shows the effect on the isotherms of including the intertube interaction term. One observes that van der Waals loops develop, indicating the appearance of a phase transition. Figure 6 shows how the critical temperature \(T_c\) varies with the parameter \(\alpha\). For a typical lattice of \((10,10)\) tubes with \(b = 17 \ \text{Å}\) and \(\nu = 6\), \(\alpha \approx 2180 \ \text{K}\) which yields \(T_c \approx 530 \ \text{K}\). There is a singular rise of \(T_c\) for small \(\alpha\), followed by a region of weaker dependence. We may understand this behavior by examining an alternative model, the anisotropic Ising model applied to the lattice gas version of this problem. As shown by Fisher\(^2\), for the case of such a model with nearest neighbor interactions \(J_i\) along the 1D chains and transverse interactions \(J_t\), the critical temperature is given by the expression

\[
k_B T_c = \frac{2J_t}{\ln(1/c) - \ln[\ln(1/c)]} \quad (21)
\]

where \(c = J_t/J_i\). This is an asymptotic formula valid when \(c < 0.1\) (weak transverse interaction). Figure 6 shows the dependence derived from this expression when the values \(J_i = 800 \ \text{K}\) and \(J_t = 18.2 \ \text{K}\) are substituted in the Fisher formula. The result is seen to track the perturbation theory behavior well. This similarity is surprising, at first sight, because the perturbation theory is a mean field theory, neglecting density fluctuations in adjacent tubes. We rationalize this agreement by noting that the exact calculation yields critical exponents (3D Ising model) that are, in fact, different from those of the mean field perturbation theory. On the other hand, in 3D, one does not expect a large error in the mean field theory value of the critical temperature\(^2\).
TABLE I: Parameters of the universal function Eq. (2) for the carbon structures investigated.

| System         | $|\Phi(r_0)|$ (eV) | $r_0$ (Å) | $r_1$ (Å) |
|----------------|-----------------|----------|----------|
| C$_{60}$-C$_{60}$ | 0.278           | 10.05    | 7.10     |
| C$_{60}$-(10,10) tube | 0.537     | 13.28    | 10.12    |

Finally, we note that Carraro has described the possibility of a crystallization transition for such a problem. To estimate the onset temperature for this freezing, we simply evaluate the energy difference $\Delta E_f$ between the ground state crystal and the energy of the alternative fluid state. This is determined by comparing the energy computed above ($\Delta E_{\text{inter}}$) for the intertube interaction energy. The difference is just the difference between the integral and the sum that arises when the buckyballs are located in lattice sites, separated by $a$:

$$
\Delta E_f = -\frac{\nu C_6}{2a^6} \left[ \sum_n \frac{1}{(\delta^2 + n^2)^3} - \int_{-\infty}^{\infty} \frac{dz}{(\delta^2 + z^2)^3} \right]
$$

where $\delta = b/a$. The difference would be identically zero if the Euler-MacLaurin theorem were analytically evaluated to evaluate it. The integral can be analytically evaluated yielding $3\pi/(8\delta^5)$. Hence, we compute the sum numerically and find the difference. It is negligible small when $b/a > 2$ and increases as $b/a$ goes to zero. This is shown in Figure 7, expressed as a freezing temperature

$$
T_f = \Delta E_f/k_B
$$

In the case of C$_{60}$ inside (10,10) tubes, $b/a = 1.7$ and $T_f \approx 0.5K$. Such small values of $T_f$ imply that such a transition will be difficult to observe in the laboratory.

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21. The choice of this reference is arbitrary because the $a_0$ term cancels out after the integral is performed.
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FIG. 1: The transverse chemical potential $\mu_t$ as function of temperature. The full line corresponds to the quartic approximation of the potential (Eq. 5); quantum and classical results (Eqs. (6) and (8)) are so similar that they cannot be distinguished over the whole range of $T$. The dashed line shows the classical result using the full potential, Eq. (7).
FIG. 2: Compression ratio at various temperatures of the 1D pressure $P$ to that of an ideal 1D gas, $P_{\text{ideal}} = k_B T/a$, as a function of the density $1/a$. 
FIG. 3: Total chemical potential $\mu(T, a) = \mu_e(T) + \mu_z(T, a)$ of the C$_{60}$ fluid as a function of molecular density $1/a$ and temperature $T$. 
FIG. 4: Chemical potential shift due to the intermolecular interactions $\Delta \mu_{\text{int}}(T,a)$ as a function of $1/a$. 
FIG. 5: Effects of the interaction between C$_{60}$ molecules in nearest neighbor tubes ($\alpha = 2180$ $\text{K} \, \text{Å}$). The isotherms develop van der Waals loops as a function of the temperature, with a critical temperature around 530 K.
FIG. 6: Dependence of the critical temperature $T_c$ on the strength of the transverse interaction and geometry of the tube lattice, given by the parameter $\alpha$. The full curve corresponds to the perturbation theory results and the dashed one indicates the anisotropic lattice model predictions (see text).
FIG. 7: Energy difference $\Delta E_f$ between the ground state crystal and the fluid state as a function of the dimensionless separation between tubes $\delta = b/a$. 