

Potential-energy-landscape-based extended van der Waals equation

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The inherent structures (IS) are the local minima of the $3N$ -dimensional potential energy surface, or landscape, of an N -atom system. Stillinger has given an exact IS formulation of thermodynamics. Here the implications for the equation of state are investigated. It is shown that the van der Waals (vdW) equation, with density-dependent a and b coefficients, holds if the averaged IS energy is close to its high-temperature plateau value. The density-dependence alone significantly enriches the equation of state. Furthermore, an additional “landscape” contribution to the pressure is found at lower T . The resulting extended vdW equation is capable of yielding a waterlike density anomaly, flat isotherms in the coexistence region vs vdW loops, and several other desirable features. The plateau IS energy, the width of the distribution of IS, and T_{TOL} , the “top of the landscape” temperature at which the plateau is reached, are simulated over a broad reduced density range, $2.0 \geq \rho \geq 0.20$, in the Lennard-Jones fluid. Fits to the data yield an explicit equation of state, which is argued to be plausible at high density. Nevertheless, $a(\rho_c)$ and $b(\rho_c)$, where ρ_c is the critical density, are in excellent agreement with the standard values obtained by fitting the vdW equation at the critical point.

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I. INTRODUCTION

Classical thermodynamics and dynamics are ultimately governed by the potential energy, $U(\mathbf{r})$, where \mathbf{r} represents the $3N$ coordinates of an N -atom system. The potential may be [1] regarded as a surface, or *landscape*, the potential-energy landscape (PEL), defined over the $3N$ -dimensional configuration space available for a given constant volume. The canonical partition function is determined by the configurational integral of the Boltzmann factor over the space.

Stillinger and Weber [1] proposed a PEL-based approach to this long standing theoretical challenge. The space is partitioned into the basins of attraction of the local minima, named [1] inherent structures (IS), with energy U_{IS} . The integral becomes a sum over basins of intrabasin integrals, which determine the “vibrational free energy,” A_v ; its average, for basins in a U_{IS} band, is $A_v(U_{IS}, T, V)$. Knowledge of the distribution in energy of distinguishable IS then allows [1,3,2] a further transformation to an integral over the IS energies, evaluation of which yields the Helmholtz free energy, $A(T, V)$, and thence all of thermodynamics. Of course, obtaining A_v and the distribution of IS is challenging, and detailed implementation of the IS formalism is in its infancy.

Intensive quantities are defined [1,3] as $\phi = U_{IS}/N$ and $a_v = A_v/N$. The IS distribution is $\Omega(\phi) = C \exp(N\sigma(\phi))$, where C has dimensions of inverse energy, and, identifying the logarithm of the integrand of the partition function with $-A(U_{IS}, T, V)/k_B T$,

$$A(N\phi, T, V)/N = \phi + a_v(\phi, T, V) - k_B T \sigma(\phi, V). \quad (1)$$

Contributions from the momentum integrals are incorporated into a_v . With the plausible, but not unique [4], attitude that the meaningful configurational states in liquids are the IS, with multiplicity determined by σ , the configurational entropy/particle obeys $S_c(N\phi, V)/N = k_B \sigma(\phi, V) \equiv s_c(\phi, V)$. In the limit of large N the IS energy which mini-

mizes A , the thermodynamic average, $\phi(T, V)$, is overwhelmingly dominant. The thermodynamic A is obtained by replacing ϕ with $\phi(T, V)$.

The equation of state [3,5] is determined by the relation, $P = -(\partial A/\partial V)_T = +\rho^2(\partial(A/N)/\partial\rho)_T$, where ρ is the number density; we will use density instead of volume in the following. Given $\phi(T, \rho)$, $\sigma(\phi, \rho)$, and $a_v(\phi, T, \rho)$, one can simply evaluate Eq. (1) and differentiate. For additional insight, note that the density derivative acts both on the explicit ρ dependence of σ and a_v , and on that implicit in $\phi(T, \rho)$. Using the extremal condition, $(\partial A/\partial\phi) = 0$ when $\phi = \phi(T, \rho)$, it may be seen that the implicit contributions sum to zero, and

$$P = \rho^2 \left[\left(\frac{\partial a_v}{\partial \rho} \right) (\phi(T, \rho), T, \rho) - k_B T \left(\frac{\partial \sigma}{\partial \rho} \right) (\phi(T, \rho), T, \rho) \right], \quad (2)$$

including the explicit ρ -dependence only.

Little is currently known about the fundamental PEL functions. A Gaussian approximation,

$$\sigma(\phi, \rho) = \alpha - [\phi - \phi_0(\rho)]^2 / 2\delta^2(\rho), \quad (3)$$

where ϕ_0 is the band center and δ^2 is the standard deviation squared/atom, is reasonable for fluids if one believes [6–9] that the IS are built up from weakly interacting local regions. The total number of distinguishable IS is [1] $\propto \exp(\alpha N)$, defining the parameter α .

A harmonic approximation to a_v —that is, to the intrabasin configurational integral—is natural at higher densities, and could be quite good at low T ,

$$\begin{aligned} a_v(\phi, T, \rho) &= \frac{k_B T}{N} \left\langle \sum_{i=1}^{3N} \ln(\beta \hbar \omega_i) \right\rangle (\phi) \\ &= k_B T \left[3 \ln(\beta \hbar \omega_0) + \frac{1}{N} \left\langle \sum_{i=1}^{3N} \ln(\omega_i/\omega_0) \right\rangle (\phi) \right], \end{aligned} \quad (4)$$

where ω_i is the i th normal mode frequency at the IS, ω_0 is the frequency unit, and the averages are over representative IS with energy ϕ . Sastry [10] found that the frequency sum has a linear ϕ dependence,

$$\frac{1}{N} \left\langle \sum_{i=1}^{3N} \ln(\omega_i/\omega_0) \right\rangle (\phi) \equiv f = f^0(\rho) + f^1(\rho)\phi, \quad (5)$$

for some liquid states of the Lennard-Jones (LJ) mixture.

La Nave *et al.* [5] reached the same conclusion for OTP, and obtained and tested the Gaussian linear harmonic (denoted GLH) equation of state. With these approximations,

$$\phi(T, \rho) = [\phi_0(\rho) - f^1(\rho)\delta^2(\rho)] - \frac{\delta^2(\rho)}{k_B T}. \quad (6)$$

The pressure has the form [5]

$$P(T, \rho) = TP_T(\rho) + P_{const}(\rho) + T^{-1}P_{1/T}(\rho), \quad (7)$$

where

$$P_T = -\rho^2 \frac{\partial}{\partial \rho} (s_{c,\infty} - k_B(f^0 + f^1\phi_\infty)), \quad (8)$$

$$P_{const} = \rho^2 (\partial\phi_\infty/\partial\rho), \quad (9)$$

$$P_{1/T} = -\rho^2 \frac{\partial}{\partial \rho} \left(\frac{\delta^2}{2k_B} \right). \quad (10)$$

The high- T plateau of the IS energy is $\phi_\infty = \phi_0 - f^1\delta^2$, and, correspondingly, $s_{c,\infty} = k_B\sigma(\phi_\infty, \rho)$.

The [5] ‘‘potential-energy-landscape equation of state,’’ evaluated via computer simulation, was shown to accurately reproduce the true pressure for a range of liquid-state ρ and T in OTP. Here we attempt to reach some more general conclusions. We identify the origin of the van der Waals (vdW) equation in the IS formalism, and obtain expressions for density-dependent a and b coefficients. The vdW-like terms are P_T and P_{const} . However, an additional contribution, which we call the ‘‘landscape pressure,’’ does not have a vdW analog; in the GLH approximation it is simply $P_{1/T}$.

Combining everything gives an extended van der Waals equation with the possibility of yielding a waterlike density anomaly (already pointed out by Sciortino [11]), flat isotherms in the coexistence region, as opposed to vdW loops, a positive derivative $(\partial U/\partial\rho)_T$ at high density, and a critical anomaly in C_V . In the GLH approximation our theory may be characterized as further interpretation of Eq. (7), but we also attempt to go beyond GLH, and we determine relevant PEL quantities by computer simulations on the single-component LJ fluid for a wide range of densities including the coexistence region. Fits to the data at high density, where the harmonic approximation is most apt, lead to an analytic equation of state. Perhaps surprisingly, the resulting $a(\rho_c)$ and $b(\rho_c)$, where ρ_c is the critical density, are in excellent agreement with the usual values obtained by fitting the vdW equation to the critical point.

II. THE EXTENDED VAN DER WAALS EQUATION OF STATE

In the vdW equation the pressure,

$$P(T, \rho) = \frac{k_B T \rho}{1 - b\rho} - a\rho^2, \quad (11)$$

is the sum of a T -independent term and a linear term. Here a and b are the well-known coefficients expressing the reduction of P from the ideal gas value by the attractive forces and the increase due to repulsions, respectively.

1. The Gaussian linear harmonic approximation

Identification of the attractive and repulsive/ideal gas contributions with P_{const} and P_T is obvious, and holds up upon further consideration. The standard expression is $a = -(\partial(U/N)/\partial\rho)_T$, where U is the total potential energy. In the GLH approximation, $U(T, \rho) = U_{IS}(T, \rho) + \frac{3}{2}Nk_B T$ and $(\partial(U/N)/\partial\rho)_T = (\partial\phi/\partial\rho)$. In general the derivative is T -dependent but the plateau value, $(\partial\phi_\infty/\partial\rho)$, is a function of density only and allows identification of an explicit T -independent contribution to P . Thus [Eq. (9)] we propose a density-dependent extended vdW a coefficient,

$$P_{const} = -a(\rho)\rho^2, \quad (12)$$

$$a(\rho) = - \left(\frac{\partial\phi_\infty}{\partial\rho} \right), \quad (13)$$

and the less familiar IS energy is related to a textbook parameter.

The vdW repulsive/ideal gas pressure is conventionally derived from the entropy. The total entropy/particle is the sum of the configurational and vibrational contributions, $s = s_c + s_v$, and $s_v = (e_v - a_v)/T$ where e_v is the vibrational energy/particle. In the harmonic approximation $e_v = 3k_B T$, so Eqs. (4) and (5) give $s_v = k_B[3 - f(\phi(T, \rho))]$. The derivative in Eq. (8) is indeed that of the total plateau entropy, which contributes a term linear in T to the free energy, and thence to P , that is, TP_T . We propose

$$P_T = -\rho^2 \frac{\partial}{\partial \rho} (s_\infty) \equiv \frac{\rho k_B}{1 - \rho b(\rho)}, \quad (14)$$

with a density-dependent b coefficient. Note that the density dependence of a_v occurs via $-Ts_v$; the nontrivial aspect of the harmonic vibrational free energy is the harmonic vibrational entropy.

Equation (14) does not look terribly transparent. For clarification consider that, if

$$s_\infty = k_B \ln \left(\gamma \frac{1 - \rho b}{\rho} \right), \quad (15)$$

where γ is a ρ -independent constant, the vdW P_T is obtained so long as $\rho^2(\partial b/\partial\rho) \ll 1$, which obviously holds at low density. Equation (15) is plausible, with entropy/particle properly varying as $\ln(1/\rho)$ at low density and vanishing as ‘‘close packing’’ is approached, $\rho \rightarrow 1/b$. Specifically, s_∞

vanishes at $\rho = (b + 1/\gamma)^{-1}$. However, real molecules with soft cores retain positive entropy as they are compressed to very high density, so any vanishing must be understood as an extrapolation from a particular density range. We anticipate that $b(\rho)$ defined in Eq. (14) will decrease at high ρ , keeping the entropy positive and the pressure finite. This expectation will be explicitly realized in Sec. IV.

There is considerable interest [12–15] in the variation of the parameter α , which determines the total number of IS, with density and from substance to substance. If the ρ dependence of α [entering $s_{c,\infty}$ via $\sigma(\phi_\infty)$] dominates that of s_∞ , then Eqs. (14) and (15) give

$$\alpha \approx \ln \left(\gamma \frac{1 - \rho b}{\rho} \right). \quad (16)$$

This is consistent with Stillinger's [15] conclusion that $\alpha(\rho)$ has a logarithmic divergence as ρ approaches zero, thus providing some support for our assumption about $\alpha(\rho)$. On the other hand, Stillinger has also [14] observed that α is independent of ρ for systems with inverse-power law repulsions only, and at high density repulsive forces dominate even if attractions are present. Equation (16) is not expected to hold at high density.

To summarize so far, the free energy evaluated on the high- T plateau of the PEL yields an equation of state with more complicated density dependence than the vdW equation, but the same T dependence. The extended vdW equation also takes into account the deviation of $\phi(T)$ from its plateau value, measured by $d\phi(T, \rho) \equiv \phi_\infty(\rho) - \phi(T, \rho)$. In the GLH approximation, where $d\phi(T) = \delta^2/k_B T$, the resulting landscape pressure is $-\rho^2[\partial(\delta^2/2k_B T)/\partial\rho]$; the entire deviation of A from its plateau value is proportional to $d\phi$. Adding the landscape pressure yields the extended vdW equation in the GLH approximation,

$$P(T, \rho) = \frac{k_B T \rho}{1 - b(\rho)\rho} - a(\rho)\rho^2 - \rho^2 \frac{\partial}{\partial\rho} \left(\frac{\delta^2}{2k_B T} \right). \quad (17)$$

2. Beyond the GLH approximation

Simulation shows that the GLH expression for $\phi(T)$ is only a crude representation; what is the source of the error? The Gaussian approximation, taken literally, has no upper or lower bound on possible IS energies, but is a good representation for the contributing fluidlike states over a substantial range of T and ρ , and has [6,7,9] some theoretical justification. More physically, the energy below which S_c is negative may be considered [6,7] a lower cutoff.

The harmonic approximation is valid for a particular normal coordinate when the system remains close to the IS. This suggests high density, where in fact the harmonic $\phi(T)$ is better, and deterioration as ρ is decreased towards the coexistence region. Increasing anharmonicity with decreasing density may be seen directly via the increase of the number of imaginary frequency instantaneous normal modes [16], which are completely anharmonic vibrational coordinates. Their number is proportional [16–19] to the self-diffusion coefficient D .

Thus we aim to retain a Gaussian density of states, but to abandon the linear harmonic approximation for a_v . Deriving specific expressions for a_v is a current focus of our research but we will now try to draw some general conclusions.

As a first step consider the form

$$a_v(\phi, T, \rho) = [e_v^0(\rho) + e_v^1(\rho)\phi] - T[s_v^0(\rho) + s_v^1(\rho)\phi] + g(T \text{ only}). \quad (18)$$

Note that e_v and s_v are defined in terms of density-dependent quantities that contribute to the pressure. Equation (18) is hardly the most general possibility but it does include linear ϕ dependence and arbitrary ρ dependence of both the vibrational energy and entropy, while the linear harmonic approximation has ϕ - and ρ -dependent entropies only [discussion surrounding Eq. (14)]. Of course, a function of T (which includes a constant) only in a_v does not influence P or $\phi(T)$. With the Gaussian density of states, Eq. (18) constitutes the Gaussian linear (GL) approximation.

Calculations in the GL approximation are straightforward. The IS energy is

$$\phi(T) = \left(\phi_0 + \frac{s_v^1 \delta^2}{k_B} \right) - \frac{(1 + e_v^1) \delta^2}{k_B T}; \quad (19)$$

vibrational entropy influences the plateau IS energy, vibrational energy influences the T dependence. The T dependence of P is unchanged from the GLH approximation and

$$P_{const} = \rho^2 \frac{\partial}{\partial\rho} (e_v^0 + (1 + e_v^1)\phi_\infty) = \rho^2 \frac{\partial e_\infty}{\partial\rho}, \quad (20)$$

$$P_T = -\rho^2 \frac{\partial}{\partial\rho} (s_{c,\infty} + s_v^0 + s_v^1\phi_\infty) = -\rho^2 \frac{\partial s_\infty}{\partial\rho}, \quad (21)$$

$$P_{1/T} = -\rho^2 \frac{\partial}{\partial\rho} \left(\frac{(1 + e_v^1)^2 \delta^2}{2k_B} \right). \quad (22)$$

The corresponding GL extended vdW equation is

$$P(T, \rho) = \frac{k_B T \rho}{1 - b(\rho)\rho} - a(\rho)\rho^2 - \rho^2 \frac{\partial}{\partial\rho} \left(\frac{(1 + e_v^1)^2 \delta^2}{2k_B T} \right). \quad (23)$$

Equation (14) still holds for b , but, defining the total energy/particle $e = \phi + e_v$,

$$a(\rho) = -\frac{\partial}{\partial\rho} ((1 + e_v^1)\phi_\infty + e_v^0) = -\frac{\partial e_\infty}{\partial\rho}. \quad (24)$$

With the introduction of a nontrivial vibrational free energy, a is expressed in terms of the total plateau energy, just as the total plateau entropy was previously seen to determine b . Along with the parameter definitions, the entire equation of state may be rewritten using only quantities which are well defined with no reference to the GL approximation,

$$P(T, \rho) = \frac{k_B T \rho}{1 - b(\rho) \rho} - a(\rho) \rho^2 - \rho^2 \frac{\partial}{\partial \rho} \left(de(T, \rho) - \frac{k_B T d\phi^2(T, \rho)}{2\delta^2} \right), \quad (25)$$

where $de = d\phi + de_v$.

Equation (25) is easily verified with Eqs. (18) and (19), and will be motivated shortly. It rests upon a particular choice of a_v but suggests greater generality. And, a more general treatment of anharmonicity is necessary to discuss densities and temperatures where $\phi(T)$ is not described by Eq. (19). In the GLH and GL approximations there is no characteristic temperature at which the plateau is reached; $d\phi(T)$ vanishes smoothly as $1/T$. Simulation, however, shows [10] a characteristic [20] “top of the landscape” temperature, T_{TOL} , at typical liquid densities, and only the final approach to the plateau at $T \geq T_{TOL}$ obeys a $1/T$ law. Near the critical density, the $1/T$ regime is nonexistent, or very small.

We take the point of view that a complex, anharmonic a_v is reflected in the behavior of $\phi(T, \rho)$. Determination of $\phi(T, \rho)$ by simulation is much easier than a comprehensive theory of a_v . Thus, in light of Eq. (25), we seek an equation of state with vdW-like P_{const} and P_T terms determined by the exact plateau energy and entropy, and a landscape pressure, of arbitrary T dependence, determined by the drop from the plateau. The drop is expressed through de_v and ds_v , as well as $d\phi$, but we further postulate that their most interesting behavior arises from their dependence on $d\phi$.

It is necessary to characterize the plateau more carefully. The vibrational free energy is a function of both ϕ and T . The character of the relevant basins, on average, is determined by ϕ ; given the basins, the calculation of a_v —the basin-constrained configurational integral—is fully T dependent. A plateau free energy, then, must be defined in terms of the high-temperature limit for plateau-type basins. The first step is to establish the existence of a well-defined free energy as $T \rightarrow \infty$.

For a given basin

$$a_v(T) = \frac{k_B T}{N} \left[3N \ln(\Lambda(T)) - \ln \left(\int d\{\mathbf{r}\} e^{-\beta \Delta U(\{\mathbf{r}\})} \right) \right], \quad (26)$$

where $\Delta U = U - U_{IS}$ and Λ is the thermal de Broglie wavelength, expressing the role of the kinetic energy. Since $\Lambda \propto T^{-1/2}$, $\ln[\Lambda(T)]$ does not reach a high- T plateau value but, since it is independent of density, it does not contribute to the pressure.

Escape from a basin occurs along “reaction pathways” which lead to transition states. On the other hand, the potential keeps increasing as the system moves away from the IS in a nonreactive direction. Taking the high- T limit of the configurational integral is complicated by the possibility of finding very large ΔU . The most important anharmonicity of the basins is, very simply, their finite extent. We suggest that the principal features of a_v at high T may be determined by

dividing the coordinates into $3N - N_u$ approximately harmonic coordinates and N_u (u for unstable) reaction pathways. The energy remains finite for the latter, and $\beta \Delta U \rightarrow 0$ as $T \rightarrow \infty$. Characterizing the i th reaction pathway for plateau IS with extent ℓ_i and energy ϵ_i , which will be somewhat less than the barrier height, and expanding the Boltzmann factor, the high- T limit for one basin is

$$a_v(T \rightarrow \infty) = \frac{k_B T}{N} \left[(3N - N_u) \ln(\beta \hbar \omega_0) + N_u \ln(\Lambda(T)/\ell_0) + \sum_{i=1}^{3N - N_u} \ln(\omega_i/\omega_0)(\phi_\infty) - \sum_{i=1}^{N_u} \ln \left(\frac{\ell_i}{\ell_0} (1 - \beta \epsilon_i) \right) \right], \quad (27)$$

where ℓ_0 is the length unit, and we have used Eq. (4) for the $3N - N_u$ harmonic coordinates. The terms on the first line are [Eq. (18)] $g(T)$, the part of a_v that does not contribute to the pressure.

Expanding $\ln(1 - \beta \epsilon_i)$ and decomposing the remainder of Eq. (27) into the form $e_v - Ts_v$,

$$e_{v,\infty} = \frac{1}{N} \sum_{i=1}^{N_u} \epsilon_i = 3 \left(\frac{N_u}{3N} \right) \bar{\epsilon}, \quad (28)$$

$$s_{v,\infty} = \frac{k_B}{N} \left[\sum_{i=1}^{N_u} \ln(\ell_i/\ell_0) - \sum_{i=1}^{3N - N_u} \ln(\omega_i/\omega_0)(\phi_\infty) \right], \quad (29)$$

where in Eq. (28) we indicate that the nontrivial plateau vibrational energy is determined by the plateau fraction of reaction coordinates, $N_u/3N$ times an averaged barrier height. We anticipate that fraction of reaction coordinates is closely related to the high- T limit of the [16] fraction of imaginary-frequency instantaneous normal modes, offering the prospect of combining INM and IS thermodynamics. The vibrational entropy has the harmonic part already discussed for the harmonic coordinates, and a new contribution from the reaction coordinates.

While further development of these ideas may lead to detailed expressions for a_v , the key point for now is that both e_v and s_v reach well defined high-temperature plateau values. The temperature requirements are both that $T > T_{TOL}$, so $\phi \approx \phi_\infty$ (which is all that “plateau” meant previously), and that $k_B T$ is greater than all the barrier heights, to make the high- T expansion in the configurational integral over the reaction coordinates. It would be pleasing if T_{TOL} sufficed for both conditions, but that remains to be seen.

Accordingly, we rewrite the free energy,

$$A(T, \rho)/N = g(T) + [\phi_\infty + e_{v,\infty} - T(k_B \sigma(\phi_\infty) + s_{v,\infty})] - [d\phi(T) + de_v(T) - k_B T d\phi^2(T)/2\delta^2] + T[ds_v(T) + k_B(\phi_0 - \phi_\infty)d\phi(T, \rho)/\delta^2], \quad (30)$$

suppressing the ρ dependence on the right-hand side; everything except $g(T)$ and k_B is density dependent. Equation (30) has three distinct groups of terms, enclosed by square brackets. The first group is the plateau free energy, with constant and linear T dependence, which yields P_{const} and P_T in the GLH and GL approximations. Now that we have established the existence of the plateau quite generally, we assert that the exact, true plateau free energy yields a contribution to the equation of state of form $P_{const} + TP_T$, given by Eqs. (20) and (21). Considering the plateau only, the equation of state is a vdW equation with density-dependent coefficients, given by Eqs. (14) and (24).

The second group contains the effect of the drop of $e = \phi + e_v$ from the plateau, plus the $d\phi^2$ term in $[\phi_0 - \phi(T)]^2 = [(\phi_0 - \phi_\infty) + d\phi(T)]^2$ which arises in evaluating the configurational entropy contribution, $-k_B T \sigma(\phi(T))$; it yields the landscape pressure $P_{1/T}$ in the GLH and GL approximations. The current derivation shows that the group may be identified without any approximation, yielding whatever T dependence is given by the true $d\phi$ and de_v . The proposed Eq. (25) is seen to correctly reproduce the first two groups in Eq. (30). Thus our aim of including anharmonic, complex a_v through easily simulated quantities is realized.

The third group consists of the drop of s_v from the plateau plus the cross term in $(\phi_0 - \phi_\infty + d\phi(T))^2$, and vanishes in the GLH and GL approximations. This conclusion holds even if the GL coefficients are made T dependent, $e_v^i(T)$ and $s_v^i(T)$, $i = 1, 2$. It seems interesting that part of the drop in the configurational entropy exactly cancels the drop in the vibrational entropy, considerably simplifying the equation of state.

We have no argument that the third group should vanish in general. Our most complete equation of state, subject only to the arguments about the existence of the plateau, is

$$\begin{aligned}
 P(T, \rho) = & \frac{k_B T \rho}{1 - b(\rho) \rho} - a(\rho) \rho^2 \\
 & - \rho^2 \frac{\partial}{\partial \rho} \left(de(T, \rho) - \frac{k_B T d\phi^2(T, \rho)}{2 \delta^2} \right) \\
 & + T \rho^2 \frac{\partial}{\partial \rho} [ds_v(T, \rho) + k_B(\phi_0 - \phi_\infty) d\phi(T, \rho) / \delta^2].
 \end{aligned}
 \tag{31}$$

Nonetheless, we propose Eq. (25) as a tractable approximation. The essence of the extended vdW equation is an exact treatment of the plateau free energy, plus the landscape pressure resulting from the drop from the plateau. Equation (25) incorporates these features, and allows an arbitrary T dependence for the drop. The GLH and GL approximations for $d\phi(T)$ can be quite poor, so it is important to incorporate the true $d\phi(T)$. Even if the contribution of group three is non-zero, it will not change the qualitative behavior of the landscape pressure too much, if ds_v resembles $d\phi$.

While finding the most comprehensive equation of state is the ultimate goal, the GLH is not to be scorned. At high density the harmonic approximation makes good sense, es-

pecially at low temperature, and the linear ϕ dependence has been verified [4,5,10] in simulation for several systems and conditions.

III. SOME GENERAL PROPERTIES OF THE EXTENDED VAN DER WAALS EQUATION

On the plateau the pressure is described by the vdW-like $P = TP_T + P_{const}$, with density-dependent a and b coefficients. In the Angell classification of liquids on a strong-fragile scale [20–23], the more complex behavior of fragile liquids is associated with a more pronounced drop $d\phi(T)$ from the plateau. Thus incorporating $a(\rho)$ and $b(\rho)$, and ignoring the landscape pressure, may be a good approximation for strong liquids. We further suggest that the ordinary vdW equation should be most useful for strong liquids.

1. Isotherms

Perhaps the most-discussed features of the vdW equation are the loops in the isotherms below the critical temperature T_c . They are a consequence of treating the fluid as homogeneous in the coexistence region. There is no provision for the phase separation which yields the true, flat isotherms.

There are two simple scenarios for crossing the liquid-gas coexistence curve, $T_{lg}(\rho)$, from above in the (ρ, T) plane: the system may phase separate in thermal equilibrium, with flat isotherms, or it may remain a metastable, homogeneous fluid, with loops. Intermediate cases with incomplete phase separation are also possible. Similarly, above the triple point density, cooling below the melting temperature may lead to liquid-solid phase separation or a metastable supercooled liquid. One cannot assume that equilibrium is maintained, in simulation or in the laboratory.

At a given density, there will exist IS representative of all the possible thermodynamic states. Under the coexistence curve, there will be both homogeneous fluid and phase-separated liquid-gas and gas-solid IS. Above the triple point density the IS types will be homogeneous liquid, liquid-solid phase separated, and crystal with varying amounts of disorder. Due to surface effects, phase-separated IS may be difficult to observe, and/or modified in character, in finite- N simulation. A PEL-based calculation in a metastable state is achieved by including only the IS to which the system is restricted, while equilibrium results from keeping all the IS.

Phase separation causes a large drop in $\phi(T)$, i.e., a strong increase in $d\phi(T)$. On the other hand, $d\phi(T)$ varies more gently when the system remains homogeneous. Thus the landscape pressure in Eq. (25) behaves quite differently for the two scenarios. We suggest that, consequently, the extended vdW equation can give either loops or flat isotherms, as appropriate for the degree of equilibration. Specifically, the landscape pressure is negligible for a homogeneous fluid, reproducing the vdW equation with $a(\rho)$ and $b(\rho)$, and loops. However, it is large if phase separation occurs, and contributes “antiloops” which cancel or partially cancel the vdW loops, *leading to flat or flatter isotherms*, for complete or partial equilibration, respectively.

To demonstrate this idea, assume that de_v is either negligible or has the same qualitative behavior as $d\phi$ in Eq. (25)

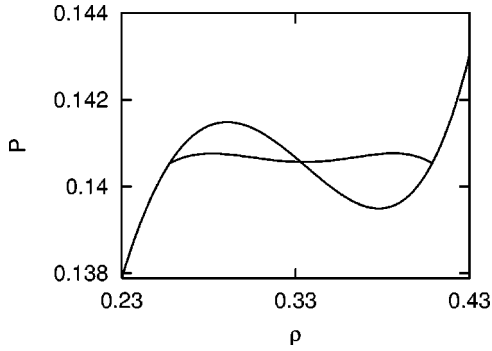


FIG. 1. Ordinary and extended vdW pressure vs density for $(T_c - T) = 0.015$, $a = 4$, $b = 1$ ($\rho_c = 1/3$); all quantities in LJ units. Outside the coexistence region the two pressures are identical, inside the flatter curve is the extended vdW equation with the illustrative form of $d\phi(T, \rho)$ from the text.

(recall $de = d\phi + de_v$). Let phase separation at a given ρ , and the corresponding strong growth in $d\phi(T)$, begin at $T_{lg}(\rho)$. For $T < T_c$, the distance to the coexistence curve, $[T_{lg}(\rho) - T]$, is an increasing function of ρ for $\rho < \rho_c$ and a decreasing function for $\rho > \rho_c$; the density derivative changes from positive to negative at ρ_c . If $d\phi(T)$ is a monotonic function of $[T_{lg}(\rho) - T]$, its derivative $[\partial d\phi(T)/\partial \rho]$ will have the same behavior. Then the landscape pressure in Eq. (25) will be negative below ρ_c and positive above, i.e., the antiloop.

As an illustration only, consider the simple ansatz $d\phi(T, \rho) = c[T_{lg}(\rho) - T]^2$, with T_{lg} estimated from the ordinary vdW equation. We use ρ independent $a = 4$ and $b = 1$ for an approximate description of the LJ fluid and ignore de_v . All quantities are expressed in natural LJ units. The landscape pressure is nonzero within the vdW coexistence curve only, so we assume it does not change the critical point from $T_c = 1.185$, $\rho_c = 0.333$. Figure 1 shows vdW and extended vdW isotherms at $T = 1.170$ for the choices $c = 1.91$, $\delta^2 = 1$. We do not claim to have the correct $d\phi(T)$ but the point is that any model in which its growth begins at the coexistence curve will yield an antiloop and potentially a flat isotherm. On the other hand, if the fluid remains in a metastable homogeneous phase, $d\phi$ has no relation to $[T_{lg}(\rho) - T]$, there are no antiloops, and the vdW loops remain.

2. Some thermodynamic derivatives

There is considerable current interest in the phenomenon of a positive $(\partial \rho / \partial T)_P$, the “density anomaly” well known in water, which may or may not be associated [24] with the existence of multiple critical points. Some textbook manipulations show that equivalent conditions are $(\partial S / \partial \rho)_T > 0$ or $(\partial P / \partial T)_\rho < 0$.

It is immediately apparent that the vdW equation cannot have a density anomaly, since

$$(\partial P / \partial T)_\rho = \frac{k_B \rho}{1 - b\rho} > 0 \quad (\text{van der Waals}). \quad (32)$$

However, [11] adding the landscape pressure in the GL approximation,

$$(\partial P / \partial T)_\rho = \frac{k_B \rho}{1 - b(\rho)\rho} + \rho^2 \frac{\partial}{\partial \rho} \left(\frac{(1 + e_v^1)^2 \delta^2}{2k_B T^2} \right) \quad (33)$$

and thus, if the density derivative is negative and large enough, there will be an anomaly. A more complicated condition can be expressed with the true $d\phi(T)$ via Eq. (25).

There exists a clear physical interpretation of why the extended vdW equation can have a density anomaly. One expects that entropy should decrease with increasing density, as the system becomes more congested and/or ordered, but this is only true on the high- T plateau where S is a maximum. In the GL approximation, the deviation of $\phi(T)$ from the plateau at constant T is proportional to δ^2 . If δ^2 decreases with increasing density, the system gets closer to the maximum plateau entropy, which may compensate for the decrease in S_∞ itself, leading to $(\partial S / \partial \rho)_T > 0$.

For the vdW equation the energy decreases with increasing density; the relation $(\partial(U/N)/\partial \rho)_T = T(\partial P / \partial T)_\rho - P$ yields $(\partial(U/N)/\partial \rho)_T = -a$, corresponding to the negative energy of attraction. This is because repulsions enter via the entropy only, i.e., there is no true positive repulsive energy contribution to the pressure, no matter how high the density. The situation is different in the extended vdW equation, however. Simulation (Sec. IV) shows that $(\partial \phi_\infty / \partial \rho)$ changes sign from negative to positive near the triple point, yielding a negative $a(\rho)$ and a positive contribution to $(\partial(U/N)/\partial \rho)_T$ at high density, barring some unexpected contrary behavior by $e_{v,\infty}$. Then, the “vdW attractive” term transforms into a repulsive pressure. Taking the landscape pressure into account, the GL approximation is

$$(\partial(U/N)/\partial \rho)_T = -a(\rho) - \frac{\partial}{\partial \rho} \left(\frac{(1 + e_v^1)^2 \delta^2}{k_B T} \right), \quad (34)$$

and the landscape term also changes from positive to negative near the triple point.

The critical behavior of the heat capacity is described [25] by the exponents α [different from α in Eq. (3)] and α' ,

$$(\partial U / \partial T)_{\rho_c} \propto (T - T_c)^{-\alpha}, \quad T > T_c$$

$$\propto (T_c - T)^{-\alpha'}, \quad T < T_c.$$

In the vdW approximation [25], $\alpha = \alpha' = 0$. Since we are obtaining P from the free energy the simplest consistent route to U is also through A ; statistical mechanics yields the exact relation

$$(U(T)/N) = \phi(T) - T^2 \left(\frac{\partial(a_v(T, \phi)/T)}{\partial T} \right)_{\phi(T)}, \quad (35)$$

where the derivative acts on the explicit T dependence of a_v/T only, not on that which enters implicitly through $\phi(T)$. For an equation of state based upon a particular approximation to a_v , use of that approximation, and the resulting $\phi(T)$, in Eq. (35) yields the corresponding potential energy. Since the vdW equation is obtained by ignoring the deviations of ϕ , e_v , and s_v from their plateau values, strong T dependence of $U(T)$, and even the mild harmonic $1/T$ be-

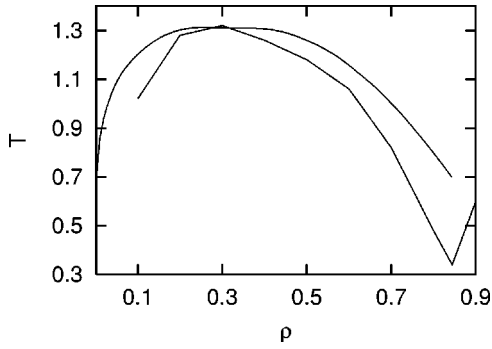


FIG. 2. Simulated $T_{TOL}(\rho)$ data (connected line segments) and coexistence curve from Ref. [26], LJ units.

havior, is discarded. That is why $\alpha = \alpha' = 0$; the critical anomaly is in the anharmonic landscape term.

IV. APPLICATION TO THE LENNARD-JONES LIQUID

Here we present some preliminary results on LJ. A careful prior study of phase equilibria [26] determined that the critical point and triple point are $\rho_c = 0.31$, $T_c = 1.31$, and $\rho_t = 0.84$, $T_t = 0.75$, LJ units. An estimate of $T_{TOL}(\rho)$, determined from $\phi(T)$, $N = 256$, is shown in Fig. 2, along with the coexistence curve from Ref. [26]. A minimum is found near the triple point density, and with decreasing density $T_{TOL}(\rho)$ runs below the coexistence curve, touching it at the critical point. Note that the phase diagram in our system may differ slightly from that of Ref. [26], as they used $N = 1372$, so quantitative comparisons should not be attempted.

Earlier we discussed the liquid-gas coexistence temperature T_{lg} as marking the onset of a rapid rise in $d\phi(T)$; T_{lg} is a “TOL” temperature for equilibrium states. In a finite-size simulation the metastable homogeneous phase can survive until the spinodal is reached. We do not claim to have an equilibrated simulation and our result, $T_{TOL} \leq T_{lg}$, is expected. What may be interesting is that the liquid-gas spinodal and the TOL temperature discussed in supercooled liquids, found at densities above the minimum, are thus connected. Leyvraz and Klein [28] have suggested that properties of supercooled liquids may be influenced by a spinodal.

We have obtained $\delta^2(\rho)$ and $\phi_\infty(\rho)$ (Fig. 3) for $2.0 \geq \rho \geq 0.20$, $N = 500$, from the distribution of IS visited at high T , where δ^2 becomes T independent, and from $\phi(T)$, respectively. Starting at low density both quantities, like T_{TOL} , decrease to minimum values near the triple point, and then begin to rise; the coefficient $a(\rho)$ changes sign from positive to negative. Similar behavior has been observed [2,27] for the IS pressure.

The higher the density the better we expect the harmonic approximation to perform. Thus we are going to use our data to evaluate the GLH equation of state over the entire available density range, but we do not make any claims of validity at low to intermediate density. Both $\delta^2(\rho)$ and $\phi_\infty(\rho)$ are well represented by a sum of two exponentials, particularly at high density, $2.0 \geq \rho \geq 1.2$. Taking density derivatives

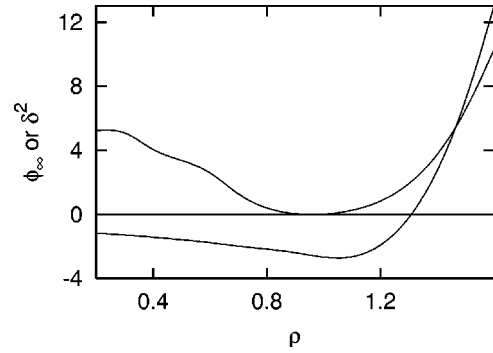


FIG. 3. Plateau energy ϕ_∞ (lower), shifted up by five energy units, and squared Gaussian width δ^2 vs reduced density, all in LJ units.

yields $P_{const}(a(\rho))$ and the landscape pressure $P_{1/T}$.

We do not at the moment have the information necessary to calculate $b(\rho)$ from first principles. This coefficient involves an extrapolation, i.e., in some small density range it appears that the pressure would diverge at a particular, higher “close packed” density, but since the cores are soft that density is never reached. Consequently b may appear to be constant at low density, but its ρ -dependence becomes essential at high density.

It is difficult to equilibrate the system at $\rho > 1.2$ without going to quite high T . To get some idea of the behavior of b we have calculated the $T = 25$ isotherm, and thence $b(\rho)$ from the GLH Equation (17). The results are shown in Fig. 4. Because of the soft cores, the quantity $(1 - b(\rho)\rho)$ can become small, but never zero. Thus we suggest a plausible behavior is exponential decay with ρ , giving

$$b(\rho) = (1 - e^{-b_0\rho})/\rho, \quad (36)$$

and the smooth curve in Fig. 4 is Eq. (36) with $b_0 = 1.31$. Combining everything,

$$P(T, \rho) = T\rho e^{1.31\rho} + \rho^2(9.15e^{1.95\rho} - 13.7e^{1.48\rho}) - \frac{\rho^2}{T}(0.00841e^{4.96\rho} - 17.7e^{-3.09\rho}), \quad (37)$$

anticipating that the analog of the vdW attractive term will be positive, and the landscape term negative, at high density.

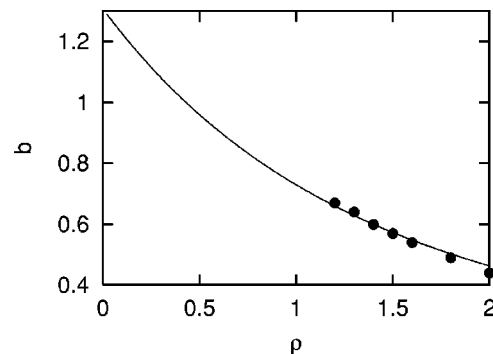


FIG. 4. High density b coefficient from simulation and fit to Eq. (36), $b_0 = 1.31$. Note $b(\rho_c = 0.31) = 1.08$.

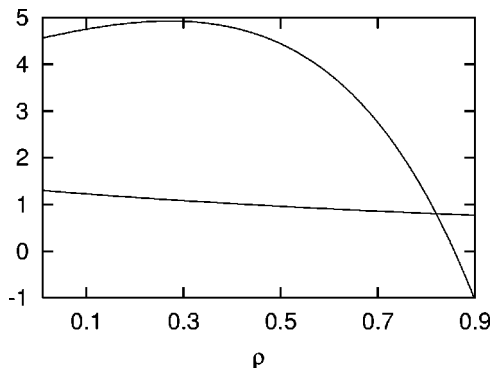


FIG. 5. a (upper) and b coefficients vs density.

Matching the [26] true ρ_c and T_c of LJ to the vdW equation gives $b=1.07$ and $a=4.73$. At the critical density we find $a(0.31)=4.92$ [negative of first parenthesis in Eq. (37)] and [Eq. (36)] $b(\rho)=1.08$. Again, we expect the missing anharmonicity to be important at the critical density and regard these results with some skepticism, but the agreement is remarkable. The density dependence of a , along with b , is shown for $\rho \leq 0.90$ in Fig. 5; note the sign change near the triple point density.

V. DISCUSSION

The equation of state is obtained from the density derivative of the Helmholtz free energy. The PEL approach provides a less traditional way to view the problem and generate approximations. Since a Gaussian approximation for the IS energy distribution is reasonable, the focus is on the vibrational free energy a_v . The GLH approximation was worked out [5] by La Nave *et al.*, and the starting point of this paper is simply the observation that their result resembles the van der Waals equation with density-dependent a and b coefficients, and an extra “landscape” term.

Recently Shell *et al.* [29] and Speedy [30] have exploited

the simplicity of the soft-sphere system, with [14] density-independent total number of IS (parameter α), by combining it with a vdW-like mean-field attraction, and a harmonic a_v . The resulting PEL equation of state thus has the same T dependence as the GLH and GL approximations, but with more explicit density dependence; the a coefficient (interpreting their results with the perspective of this paper) is ρ independent by construction. Various desirable properties are demonstrated but, despite the presence of a vdW attraction, their focus is different from that presented herein.

In addition to the GLH and GL calculations, we have tried to include anharmonicity with as few assumptions about a_v as is possible; in Eq. (25), anharmonicity is implicit in the T -dependent inherent structure energy, and in the plateau energy and entropy. The extended equation can reproduce, and provide PEL interpretations of, thermodynamic phenomena absent from the usual vdW equation. If the system phase separates in thermal equilibrium below the coexistence curve, the landscape pressure will have vdW antiloops, fully or partially canceling the vdW loops.

Computer simulation in the LJ fluid yields the quantities $T_{TOL}(\rho)$, $\phi_\infty(\rho)$, and $\delta^2(\rho)$; they all have minima near the triple point. The $a(\rho)$ coefficient becomes negative at $\rho \gtrsim 1.0$, as the vdW attractive pressure turns repulsive. The $b(\rho)$ coefficient is represented by a simple expression stemming from the idea that the pressure may become exponentially large, but not infinite. Since the harmonic approximation is best suited for high density, the resulting analytic GLH expression is suggested as a high density equation of state. Nevertheless, when evaluated at the critical density, $a(\rho_c)$ and $b(\rho_c)$ are remarkably close to the accepted values.

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