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Regarding the Theory of the Zeno Line

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The line of thermodynamic states with a unit value of the compressibility factor was calculated for a Lennard-Jones system using four different approaches. We show that all four approaches give rise to a straight line on the density−temperature plane. Thus, we theoretically confirm that the Lennard-Jones system satisfies Zeno line regularity.

Introduction

Presently, there is considerable experimental evidence confirming that states where the compressibility factor is a unit (i.e., $Z = P/nT = 1$, where P is pressure, n is density, and T is temperature) form a straight line on the density−temperature plane. This empirical regularity is referred to as the Zeno line.[1–3] Corresponding data are presented for noble gases, hydrocarbonates,[1]and for water and other non-metallic materials.[2,3] In our earlier work,[4,5] we studied experimental data for Hg and Cs and showed that the Zeno line is a straight line for these metals as well. Thus, some researchers suppose that this linearity on the density−temperature plane is a general law analogous to the corresponding states law. Some other researchers consider this line as a curious coincidence. (Detailed discussion of this question is discussed in ref 3.) The reason for the second opinion is the absence of theoretical support for the linear dependence in hand. Bachinskii[6] was the first to deduce the linear dependence of the unit compressibility factor for the van der Waals equation in 1906. It is one of the few theoretical confirmations for this regularity.[3]

In this work, we used three theoretical approaches for a Lennard-Jones (LJ) liquid to calculate the Zeno line. The first of them is the virial expansion. The second approach is a solution of integral equations of liquid theory. The third approach is the direct calculation of pressure using an analytical expression for the pair correlation function.[7]This analytical expression was obtained by fitting the data of molecular dynamics (MD) simulation.[8] The last approach is a direct Monte Carlo simulation. We show that all four temperature dependences of the density obtained by these distinct approaches are straight lines. Thus, Zeno line regularity is confirmed theoretically for the LJ liquid.

Virial Expansion

Let us consider the virial expansion for pressure

$$P = nT(1 + B(T)n + C(T)n^2 + D(T)n^3 + E(T)n^4 + ...) \tag{1}$$

Next, we use dimensionless units of the LJ system (LJ units). The dimensional parameters are as follows: for pressure, D/σ^3; for temperature, D; and for density, σ^{-3}. Here, D is the depth of the potential, and σ is the minimum distance at which the potential is zero. Virial coefficients B, C, D, and E are known for a LJ system.[9,10] The technique for approximate calculation of subsequent virial coefficients was developed in ref 11, and the convergence radius for eq 1 was determined.

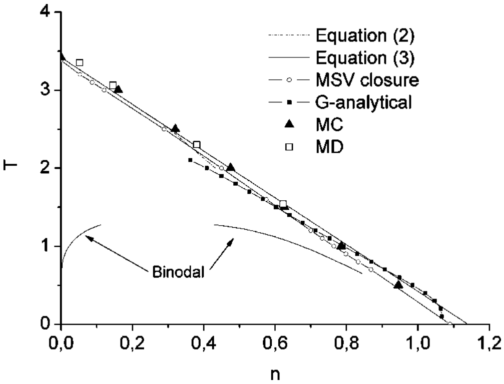

Figure 1. Zeno line calculated in different approaches. Equation 2: calculation by eq 2with 70 virial coefficients; Equation 3: calculation by eq 3with 2nd and 3rd virial coefficients; MSV closure: calculation by solution of integral equations; G-analytical: calculation by eq 8; MC: results of Monte Carlo calculations; MD: results of MD calculations of ref 3. We also present the binodal of the LJ system according to the data of ref 16.

It follows from eq 1 that $Z = 1$ if

$$(B(T) + C(T)n + D(T)n^2 + E(T)n^3 + ...) = 0 \tag{2}$$

The exact values for the 2nd to 5th virial coefficients were used to solve eq 2. The values of the 6th and higher coefficients were taken in accordance with the data of ref 11. The results are presented as eq 2 in Figure 1. At $T < 2$ and $n > 0.48$, the virial series diverges. Thus, the line obtained by the solution of eq 2 is limited by these values. At the limit of low densities, we can use only the $B(T)$ and $C(T)$ terms of eq 2. We know that at Boyle point $B(T_B) = 0$, consequently $n(T_B) = 0$. For the LJ potential,[5]$T_B = 3.418$.

Thus, at $n \to 0$ and $T \to T_B$, we have the following temperature dependence on the density:

$$T = -nA + T_B \tag{3}$$

In eq 3, the coefficient A is $C(T_B)/(dB(T_B)/dT)$ (refs 3–5). (If one sets $T = 0$ in eq 3, then for the LJ system $n(T = 0) =$

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1.14.) The dependence corresponding to eq 3 is presented in Figure 1 as Equation 3. The lines corresponding to the dependencies in eqs 2 and 3 are close to each other. They coincide for $n < 0.3$. The decay of the Equation 2 line for higher densities indicates the convergence limit of the virial series.

Integral Equations Approach

The pressure P of any one-component system can be calculated using a well-known formula[11–14]

$$P = nT + \frac{2\pi}{3}n^2\int_0^\infty r^3\frac{\mathrm{d}\Phi(r)}{\mathrm{d}r}G(r,n,T)\mathrm{d}r \tag{4}$$

Here, $\Phi(r)$ is the pair interaction potential, and $G(r, n, T)$ is the pair correlation function (PCF).

If the interaction potential is given, then it is sufficient to know the PCF to find the pressure. One of the most effective ways to find the PCF is the technique of integral equations in the theory of liquids. Details of this technique are described in many books and articles.[11–16] That is why here we present only the necessary definitions. Besides the PCF, one can introduce the following function: the total correlation function $h = G - 1$, the direct correlation function $c(r)$, and the indirect correlation function $\gamma(r) = h(r) - c(r)$. The first two of these are connected by the well-known Ornstein−Zernike equation[12,13,18]

$$h(\bar{r}) = c(\bar{r}) + n\int h(\bar{r} - \bar{r}_1)c(\bar{r}_1)\mathrm{d}\bar{r}_1 \tag{5}$$

This equation is the exact consequence of the Gibbs distribution function. To find h (and G), we need a second equation. This equation also is a consequence of the Gibbs distribution function

$$h(r) = \exp(-\Phi(r)/T + \gamma(r) + B(r)) - 1 \tag{6}$$

In eq 6, $B(r)$ is the bridge functional. Note that the sum $\gamma(r) + B(r)$ equals $\omega(r)$, where $\omega(r)$ is the thermal potential.[11–16] The bridge functional, as well as the thermal potential, is the sum of irreducible Mayer diagrams, which cannot be expressed in terms of simple functions of the distance.[12,13] Moreover, it is the functional of the potential Φ, (i.e., $B = B[\Phi]$). The functional B also can be considered as the functional of the PCF and $c(r)$. The exact form of this functional is unknown. To bypass this problem, the exact functional was changed to some approximate function of the coordinate. This function is referred to as the closure. This rather crude substitution of the functional notwithstanding, the solution of eqs 5 and 6 together with an appropriate closure produced very accurate results. (The errors with respect to the data of numerical simulation with Monte Carlo or MD techniques are on the order of a few percent or less.[12,13,17]) Here, we used the closure of Martynov−Sarkisov−Vompe[14](MSV)

$$B(r) = -1/2(\omega(r) - n\phi(r))^2 \tag{7}$$

In eq 7, $\varphi(r)$ is the perturbation part of the potential energy in agreement with the partitioning of the potential energy into reference and perturbation parts as introduced by Weeks et al.[15]The results of the calculation with MSV closure are presented in Figure 1 as the line MSV closure. One can see that this approach gives a straight line for $Z = 1$. This line is slightly shifted with respect to the Equation 3 line ($T_\mathrm{B}^\mathrm{MSV} = 1.38$, $n_\mathrm{B}^\mathrm{MSV}$ $(T = 0) = 1.09$; $|T_\mathrm{B} - T_\mathrm{B}^\mathrm{MSV}|/T_\mathrm{B} = 2.7$ %; and $|1 - n_\mathrm{B}^\mathrm{MSV}$ $(T = 0)/n_\mathrm{B}(T = 0)|$ = 4.4 %|).

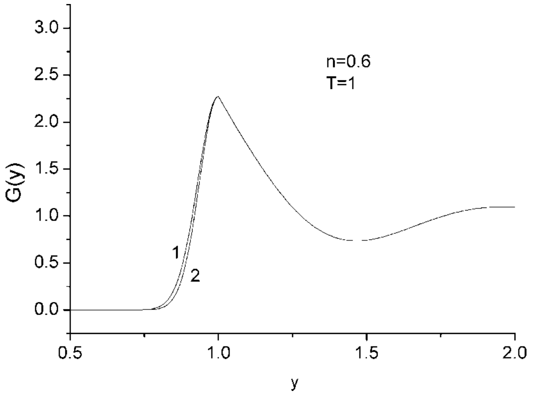

Figure 2. Pair correlation function at $T = 1$ and $n = 0.6$ calculated according to eqs 9and 10. Line l: with correcting multiplier and line 2: without it.

Calculation of Zeno Line by Means of Analytical $G(r)$

In accordance with eq 4, the equation for the Zeno line is

$$\int_0^\infty r^3\frac{\mathrm{d}\Phi(r)}{\mathrm{d}r}G(r,n,T)\mathrm{d}r = 0 \tag{8}$$

The simple analytical expression for $G(r, n, T)$ was obtained from ref 7. It satisfies the limiting conditions at zero density and at infinite distance imposed by statistical thermodynamics. Analytical $G(r, n, T)$ contains seven functions and 21 adjustable parameters (three parameters for each function). The functions and parameters were fitted with good accuracy to the extensive data of MD simulations.[8] The final expression is

$$\begin{aligned} &G(y,n,T) = 1 + y^{-m}[g(d) - 1 - \lambda] + [(y - 1 + \lambda)/y] \times \\ &\exp[-\alpha(y-1)]\cos[\beta(y-1)] \times \\ &y \geq 1; m \ \geq 1 \end{aligned} \tag{9}$$

$$G(y,n,T) = g(d)\exp[\theta(y-1)^2];\ y<1 \tag{10}$$

Here, $y = r/d$ is the dimensionless distance, and $d = h\sigma$ is the distance corresponding to the first maximum of the PCF. The formulas describing the dependence of the seven functions h, m, $g(d)$, λ, β, α, and θ on n and T are presented in ref 7. The limit of applicability of eqs 9 and 10 also was determined by the condition $m(n, T) \geq 1$.

If we use the dimensionless distance y from eq 9, then the equation for the LJ potential has the form

$$\int_0^\infty\left(\frac{1}{y^{10}h^6} - \frac{1}{y^4}\right)G(y,n,T) = 0 \tag{11}$$

The calculation carried out according to eq 11 shows that the result is highly sensitive to the behavior of $G(y, n, T)$ at $y < 1$, determined by eq 10 and described by the Gauss formula. We emphasize that the Gauss approximation is not quite adequate for PCF at $y < 1$ since the exact PCF must be equal to zero at small distances. Our calculations show that the best agreement with other approaches for the Zeno line is obtained if a correcting multiplier of 1.2 is introduced in the exponent in eq 10. Note that the function $G(y, n, T)$ is weakly sensitive to this procedure. Two functions of $G(y, n, T)$ are presented in Figure 2. Line 1 is calculated with this correcting multiplier. Line 2 is calculated without it. As is seen from Figure 2, the difference is not significant. This small difference also is conserved at different values of densities and temperatures.

The results of the latter calculation of the Zeno line are presented in Figure 1 as the line G-analytical. One can see that this approach gives a straight line for the unit Z approximately.

There are some deviations in the position of the Zeno line calculated with different methods. However, these deviations are small enough and lie within the limits of accuracy of using theoretical approaches.

Monte Carlo Simulation

We also carried out Monte Carlo simulations to calculate the Zeno line. We used the cut LJ potential on a system of 1000 particles and conventional NVT Monte Carlo. The detailed description of this technique is presented in refs 13 and 17. The cutoff radius was equal to the half-length of the simulation cell. We fixed the temperature and looked for the density to obtain $Z = 1$. The maximum error in the resulting pressure was $\sim 5\%$. The results of the Monte Carlo simulations are presented in Figure 1 as black triangles. One can see that the points of Monte Carlo simulation are in very good agreement with MSV results.

The LJ potential already was used in ref 3to describe the Zeno line for water. MD simulations were performed with 256 particles. The cutoff radius was equal to 2.5σ. The parameters σ and D were fit to reproduce the viscosity data of the water. We recalculated the data obtained in ref 3 in LJ units and presented them in Figure 1 as empty squares. Our calculations are more accurate because we used more particles in simulations and our cutoff radius was the maximum possible. (The errors of Monte Carlo as well as MD simulations decrease with growth of the particle number and cutoff radius.[13,17]) Nevertheless, the results of our simulation and data obtained in ref 3 are located on the same straight line.

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