

Application of the quasi-Gaussian entropy theory to molecular dynamics simulations of Lennard-Jones fluids

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The quasi-Gaussian entropy theory has been applied to reproduce the temperature dependence of the internal energy, pressure and isochoric heat capacity of a molecular dynamics simulated Lennard-Jones (LJ) fluid at density $\rho=1$ (reduced units). The results show that the gamma state level of the theory is an excellent approximation, able to predict the behavior of these properties over a large temperature range. This application of the theory to the simulated LJ fluid confirms previous results, obtained using experimental fluid data, and shows that the gamma state level of the theory, in combination with molecular simulation techniques, can be used as a general model to obtain accurate and physically consistent equations of state for fluid systems. © 1998 American Institute of Physics. [S0021-9606(98)50239-5]

I. INTRODUCTION

The theoretical study of the behavior of homogeneous fluids and fluid mixtures is important for many possible applications. The usual computational techniques are molecular dynamics (MD) and Monte Carlo (MC) simulations. These methods simulate the fluid system at the microscopic level, using simplified semiempirical models for the atomic interactions and a classical approach to describe the thermodynamics of the particles. In many ways these methods introduce different oversimplifications also in the case of simple fluids; nevertheless they are able to capture much of the essential physics of these systems.

The Lennard-Jones (LJ) potential is one of the most important interaction models for exploring the properties of simple apolar fluids and it has been used for a variety of theoretical computational studies. However, the model LJ Hamiltonian is still too complex to allow general theoretical derivations of the thermodynamic behavior for fluid conditions, although perturbation methods have been used.¹⁻⁵ Only by using a large set of simulation data it is possible to reconstruct the behavior of this system and in general semiempirical equations of state (EOS) are used in order to interpolate these data. The most successful of these EOS is a modified Benedict-Webb-Rubin (MBWR) equation with 33 parameters.^{6,7}

This EOS, based on pure fitting functions which require a large amount of input data, is clearly lacking a real physical basis and hence can only reproduce the data within the fitting range. This implies that extrapolations outside the fit-

ting range are questionable, and even within that range a good quality of the equation of state can be assured only for the properties which were directly used to fit these functions.

Recently a new theoretical approach based on statistical mechanics, the quasi-Gaussian entropy (QGE) theory, has been derived. Its application to the prediction of thermodynamical properties of real fluids provided results in excellent agreement with experimental data.^{8,9} In this paper we investigate the capability of the gamma level of the QGE theory to reproduce the temperature dependence of the thermodynamics at a given density for a LJ fluid. Furthermore we study different procedures to obtain the parameters of the gamma state model for the prediction of the LJ thermodynamics, using only a limited set of input simulation data. From MD simulations at different temperatures at one density, the excess internal energy, pressure and isochoric heat capacity are obtained and these properties are used to define in different ways the gamma state.

The paper is organized as follows. In Sec. II a summary of the QGE theory is presented. In Sec. III we describe the methods used to obtain the data; the results and discussions are reported in Sec. IV. Finally in Sec. V we give some conclusions.

II. QGE THEORY

The QGE theory, in the NVT ensemble, is based on the reformulation of the high-dimensional partition function of the system in terms of the potential energy distribution function, which is a special projection of the Hamiltonian in one-dimensional space. For monoatomic fluids the ideal reduced entropy of a system, S' , i.e., the entropy with respect to an

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ideal reference system with the same temperature and density but no intermolecular interactions, is given by¹⁰

$$S' = -k \ln \int e^{\beta \Delta \mathcal{U}'} \rho(\Delta \mathcal{U}') d\Delta \mathcal{U}' + k \ln \epsilon \quad (1)$$

with

$$\Delta \mathcal{U}' = \mathcal{U}' - \langle \mathcal{U}' \rangle = \mathcal{U}' - U', \quad (2)$$

where \mathcal{U}' is the instantaneous potential energy of the system, $\beta = 1/kT$, $\rho(\Delta \mathcal{U}')$ is the probability distribution of the energy fluctuation $\Delta \mathcal{U}'$, and $k \ln \epsilon$ is an entropic term due to a possible confinement of the system in configurational space associated with hard body excluded volume.¹⁰ We showed¹⁰ that for macroscopic systems, using the central limit theorem,¹¹ $\rho(\Delta \mathcal{U}')$ must be close to a Gaussian (“quasi-Gaussian”). In fact the distribution $\rho(\Delta \mathcal{U}')$ can be obtained from the generalized Pearson system for unimodal curves^{10,12} using specific physical constraints.

The parameters of these (model) distributions can be expressed in terms of central moments $M_n = \langle (\Delta \mathcal{U}')^n \rangle$ of the potential energy, where these potential energy moments are functions of the isochoric heat capacity (C'_V) and a limited number of its temperature derivatives.¹⁰ In this way from the general thermodynamic relation $(\partial S' / \partial T)_V = C'_V / T$ a closed differential equation, the *thermodynamic master equation* (TME) can be obtained.⁹ This is a completely defined differential equation with a unique, always existing solution that gives the temperature dependence of the ideal reduced isochoric heat capacity C'_V , once the values of C'_V and a limited number of its derivatives are known at one arbitrary temperature T_0 .

The knowledge of the potential energy distribution function at one temperature fully defines the whole ideal reduced thermodynamics of a system at every temperature at fixed density. Every potential energy distribution function therefore defines a different statistical state of the system with a thermodynamic complexity given by the number of heat capacity temperature derivatives, necessary to define the corresponding type of potential energy distribution function.

We showed^{8,9,10} that the first TME solution which satisfies all the basic mathematical and physical constraints, the gamma state solution, provides an excellent model for fluid systems. In contrast to macroscopic real systems, for simulated fluids the unimodal shape of the potential energy distribution functions is not necessarily accomplished, as the number of particles which is used in a simulation is still far from a real macroscopic condition. However, the model statistical states based on unimodal distributions can still be used assuming simply that at least the input molecular properties, that are required to define the statistical state, obtained from the simulations, are virtually identical to those which would be obtained from a real macroscopic size system.¹³

The gamma distribution, which defines the gamma state, is given by¹⁰

$$\rho(\Delta \mathcal{U}') = \frac{b_1 (1/b_1^2)^{b_0/b_1^2}}{\Gamma(b_0/b_1^2)} (b_0 + b_1 \Delta \mathcal{U}')^{b_0/b_1^2 - 1} \times \exp \left\{ - \frac{b_0 + b_1 \Delta \mathcal{U}'}{b_1} \right\} \quad (3)$$

with $\Gamma(\cdot)$ the gamma function,¹⁴ $b_0 = M_2$ and $b_1 = M_3 / (2M_2)$. Here M_2 and M_3 are the second and third moments of the potential energy fluctuation, respectively. For this distribution the TME reduces to the simple expression¹⁰

$$\left(\frac{\partial \delta}{\partial T} \right)_V = - \frac{\delta(1 - \delta)}{T} \quad (4)$$

where

$$\delta = \frac{M_3}{2kTM_2} = \frac{T(\partial C'_V / \partial T)_V}{2C'_V} + 1. \quad (5)$$

The solution of Eq. (4) provides $\delta(T)$, which can be expressed in terms of C'_V and $(\partial C'_V / \partial T)_V$, and hence this gives rise to a new differential equation in C'_V , the solution of which yields for a confined gamma state¹⁰

$$\delta(T) = \frac{T_0 \delta_0}{T(1 - \delta_0) + T_0 \delta_0}, \quad (6)$$

$$C'_V(T) = C'_{V0} \left(\frac{\delta(T)}{\delta_0} \right)^2, \quad (7)$$

$$U'(T) = U'_0 + (T - T_0) C'_{V0} \frac{\delta(T)}{\delta_0}, \quad (8)$$

$$A'(T) = U'_0 - \frac{T_0 C'_{V0}}{\delta_0} - \frac{T C'_{V0}}{\delta_0^2} \ln \{ 1 - \delta(T) \} - kT \ln \epsilon, \quad (9)$$

$$p'(T) = p'_0 + B_0 + B_1 \frac{T}{T(1 - \delta_0) + T_0 \delta_0} + B_2 \left(\frac{T}{T_0} \right) \ln \left\{ \frac{T(1 - \delta_0)}{T(1 - \delta_0) + T_0 \delta_0} \right\} + \xi T, \quad (10)$$

where

$$B_0 = A_{01} T_0 \left(\frac{\partial p'_0}{\partial T} \right)_V + A_{02} T_0^2 \left(\frac{\partial^2 p'_0}{\partial T^2} \right)_V + A_{03} T_0 \xi, \quad (11)$$

$$B_i = A_{i1} T_0 \left\{ \left(\frac{\partial p'_0}{\partial T} \right)_V - \xi \right\} + A_{i2} T_0^2 \left(\frac{\partial^2 p'_0}{\partial T^2} \right)_V, \quad i = 1, 2 \quad (12)$$

and

$$A_{01} = -\frac{2(1-\delta_0)\ln(1-\delta_0) + \delta_0}{D},$$

$$A_{02} = \frac{1}{\delta_0} \frac{(1-\delta_0)\ln(1-\delta_0) + \delta_0}{D},$$

$$A_{11} = \frac{\delta_0}{D}, \quad A_{12} = -\frac{1}{\delta_0} \frac{\ln(1-\delta_0) + \delta_0}{D}, \quad (13)$$

$$A_{21} = \frac{2(1-\delta_0)}{D}, \quad A_{22} = \frac{1}{D},$$

$$D = 2(1-\delta_0)\ln(1-\delta_0) + \delta_0(2-\delta_0), \quad (14)$$

and

$$A_{03} = -\frac{\delta_0(1-\delta_0)}{D}. \quad (15)$$

The zero subscript indicates the input properties evaluated at the reference temperature T_0 and $\xi = k(d\ln\epsilon/dV)$.

III. METHODS

The simulations were performed in the NVT ensemble and every property is expressed in reduced units.¹⁵ The system consisted of 864 atoms at a density $\rho=1$. Ten simulations were performed at temperatures 1.4, 2, 3, 4, 5, 6, 7, 8, 9, and 10. The temperature of the system was maintained at the reference value using the Gaussian isokinetic rescaling¹⁵ which should provide the correct Gibbs ensemble distribution in configurational space.¹⁶ Following Johnson *et al.*,⁶ a cutoff $r_c=4\sigma$ was used to avoid possible artifacts. Furthermore the potential was shifted to have a zero value at the cutoff distance. No shifting was applied to the force since the large cutoff makes this correction negligible.⁶ All the simulations were performed using a modified version of the GROMACS package¹⁷ that includes the Gaussian isokinetic rescaling. Note that in this paper we always use the energy and pressure values as obtained from the simulations, without applying the usual correction for the shift and long range interactions.

Each simulation was performed by equilibrating the system for 5×10^4 time steps and making a production run of 1.5×10^6 steps. The simulation at $T=6$ was extended up to 4.5×10^6 steps to increase the statistics for the third moment of the potential energy fluctuations. The time step was chosen according to the criteria described by Johnson *et al.*⁶ and a value $\delta t=0.002$ was used for all simulations.

The values of the heat capacity, C'_V , were obtained in two ways: from the second moment of the potential energy fluctuation, M_2 , using

$$C'_V = \frac{M_2}{kT^2} \quad (16)$$

and from the first derivative of a quadratic interpolation of the energy values at three subsequent temperatures. In Table I values of U' , p and the two estimates of C'_V together with the corresponding estimated errors are reported. The estimated standard deviations of the equilibrium properties were calculated using the block averaging method as described in

TABLE I. Potential energy, heat capacities (calculated from the second moment and from local interpolation) and pressure with the corresponding estimated errors.

T	U'	C'_V	C'_V	p
1.4	-5.520 ± 0.001	1.34 ± 0.01	1.34	11.105 ± 0.003
2	-4.776 ± 0.001	1.19 ± 0.01	1.23	15.472 ± 0.003
3	-3.707 ± 0.001	1.00 ± 0.01	1.00	21.771 ± 0.004
4	-2.767 ± 0.001	0.90 ± 0.01	0.90	27.344 ± 0.005
5	-1.911 ± 0.001	0.84 ± 0.01	0.83	32.364 ± 0.006
6	-1.105 ± 0.002	0.74 ± 0.01	0.78	37.250 ± 0.007
7	-0.349 ± 0.002	0.69 ± 0.01	0.73	41.995 ± 0.009
8	0.348 ± 0.002	0.71 ± 0.01	0.69	45.860 ± 0.009
9	1.042 ± 0.002	0.63 ± 0.01	0.66	50.35 ± 0.01
10	1.679 ± 0.002	0.65 ± 0.01	0.64	54.250 ± 0.015

previous articles.^{15,18,19} Note that the errors for C'_V , obtained from interpolation, are not reported in Table I as they are smaller than the reliable accuracy for the heat capacity obtained by a quadratic interpolation, and the deviations between the two heat capacity estimates are in the order of the error values. The fact that both methods yield almost identical values of the heat capacity confirms that the simulations used are really statistically mechanically consistent and well converged at least up to the second energy moment.

IV. RESULTS AND DISCUSSION

In order to evaluate the applicability of the gamma state model to LJ fluids, we investigated one high density isochore ($\rho=1$) in the temperature range 1.4–10. To obtain the best estimate of the gamma state we used the full energy data set in the temperature range studied. We did not use other properties since in general they cannot be obtained with the same accuracy as the energy by simulations. Choosing as a reference temperature $T_0=6$ we evaluated the gamma state parameters U'_0 , C'_{V0} and δ_0 by fitting the gamma state energy expression [Eq. (8)] to the energy data set. In Fig. 1 we compare the potential energy, the isochoric heat capacity (evaluated with the two methods described in Sec. III), and the pressure obtained by simulations with the corresponding properties predicted by this “best” gamma state (referred to as “reference gamma state,” Γ_{ref}). For the gamma state pressure expression [Eq. (10)] we used as p'_0 the actual pressure value at T_0 minus the corresponding ideal gas pressure. The first and second temperature derivatives of the pressure at T_0 , required in the same equation, were derived from a cubic fit of the pressure data. Finally the ξ parameter was adjusted to provide the best fit of the pressure data. The high accuracy of the gamma state in reproducing the energy values is evident from Fig. 1(a). Also the pressure, Fig. 1(c), is very well reproduced and only the lowest and the highest temperature data show slight deviations. In the case of the heat capacity, Fig. 1(b), the gamma state model can still provide a good description of the data but again there are deviations at both the extremes of the data set; in any case the maximum relative error (12%) which occurs at the highest temperature $T=10$ is still reasonably small. Note that the heat capacity data were not involved in the gamma state parametrization and usually it is a difficult task to reproduce

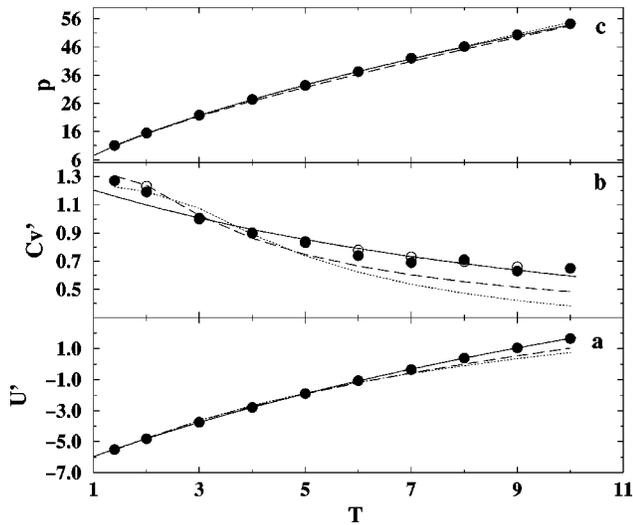


FIG. 1. Comparison of ideal reduced internal energy (a), heat capacity (b) and full pressure (c) (filled circles) obtained from the simulations, with the gamma state predictions (solid lines), obtained by the fitting of the complete energy data set, and the two MBWR EOS obtained by Johnson *et al.* (dotted line) and Sun and Teja (dashed line). In panel (b) the open circles represent the heat capacity evaluated from local interpolation.

them accurately. For comparison, also the predictions are given for the two MBWR EOS, which were parametrized in the temperature range $T \leq 6$, where they have a comparable accuracy as the gamma state. However, at $T \geq 5$ the gamma state predictions are better for energy and heat capacity.

Interestingly, using a simple hard sphere model for the confinement, from the ξ estimate we could evaluate the corresponding hard sphere volume per molecule v and from this obtain the hard sphere diameter σ_{HS} (Ref. 10). For the LJ fluid we obtained a volume $v \cong 0.19$ and a diameter $\sigma_{HS} \cong 0.71$ corresponding to an interaction energy $\mathcal{U}' \cong 261$. Note that the LJ potential does not have any exact confinement and hence this estimate must be considered as an ‘‘effective’’ hard sphere confinement which is valid, within our

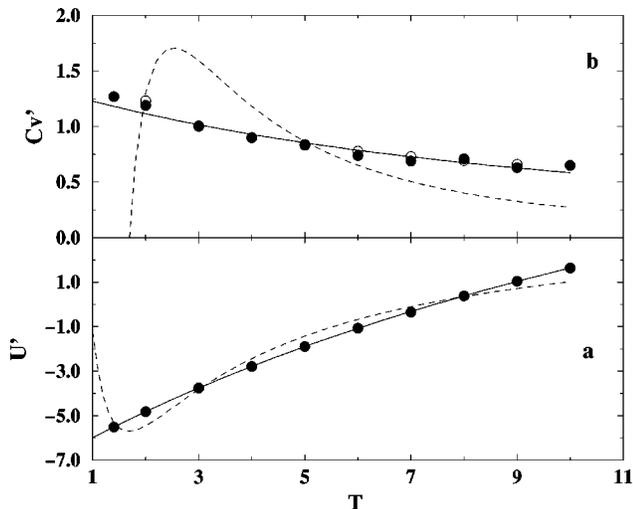


FIG. 2. Comparison of ideal reduced internal energy (a) and heat capacity (b) (filled circles) obtained from simulations with the gamma state prediction (solid line) as in Fig. 1 and the cumulant expansion CE model obtained from fitting the complete energy data set (dashed line).

physical model, in the whole temperature range of interest.¹⁰ In Fig. 2 we also compare the accuracy of the Γ_{ref} predictions for energy and heat capacity, with that of a model based on a cumulant expansion of the free energy^{3,20} of the same complexity of the gamma state (expansion of the cumulant generating function of the energy, in β , up to the third cumulant). This kind of expansion, usual in models based on perturbation theory, is in this case equivalent to a second order Taylor expansion of the energy in $1/T$, and provides for the energy and heat capacity temperature dependence:

$$U'(T) = U'_0 + (3C'_{V0} + T_0(\partial C'_{V0}/\partial T)_V) \left[1 - \frac{T_0}{T} \right] - \frac{1}{2} (2C'_{V0} + T_0(\partial C'_{V0}/\partial T)_V) \left[1 - \left(\frac{T_0}{T} \right)^2 \right],$$

$$C'_V(T) = (3C'_{V0} + T_0(\partial C'_{V0}/\partial T)_V) \left(\frac{T_0}{T} \right)^2 - (2C'_{V0} + T_0(\partial C'_{V0}/\partial T)_V) \left(\frac{T_0}{T} \right)^3.$$

The three parameters of the cumulant expansion model $[U'_0, C'_{V0}, (\partial C'_{V0}/\partial T)_V]$ were obtained fitting the whole energy data set, with $T_0 = 6$, as for the Γ_{ref} parameters. From Fig. 2 it is clear that the expansion model is very unsatisfactory being rather inaccurate and even providing unphysical behavior in the low temperature range (negative heat capacity). Note that the pressure prediction of the cumulant expansion model (not shown in Fig. 2) is also quite inaccurate (see Table III). Such a result in agreement with observations in previous papers^{9,21–23} is not surprising if we consider that in the QGE theory for a given model distribution the corresponding exact thermodynamics is derived. On the contrary the expansions are by definition local numerical approximations, and hence cannot in general provide physically exact behaviors.

In order to evaluate the possibility of using a restricted simulation data set and assess the most efficient procedure for the estimation of the gamma state parameters, we tried to use the least information necessary to obtain U'_0 , C'_{V0} and δ_0 . From three energy values at nearby temperatures ($T = 5, 6, 7$) using $T_0 = 6$ we could estimate the parameters of the gamma state (Γ_1). Alternatively we used at $T_0 = 6$ the energy and directly the second and third central energy moments, obtaining the values of C'_{V0} and δ_0 via Eqs. (16) and (5), to define the gamma state (Γ_2). In Figs. 3 and 4 we compare the predictions of these two gamma states with simulation data. From these figures it is clear that these

TABLE II. Parameters defining the three different gamma states with $T_0 = 6$.

Γ models	U'_0	C'_{V0}	δ_0	v
Γ_{ref}	-1.084	0.79	0.7717	0.19
Γ_1	-1.105	0.78	0.7960	0.19
Γ_2	-1.105	0.74	0.7622	0.19

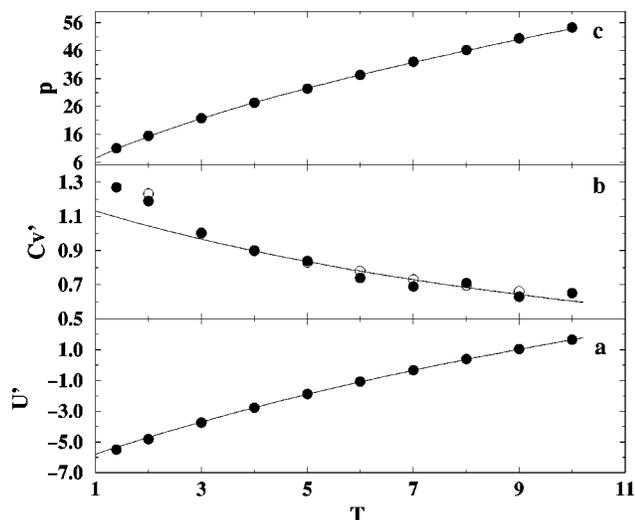


FIG. 3. Comparison of ideal reduced internal energy (a), heat capacity (b) and full pressure (c) (filled circles) obtained from the simulations, with the gamma state predictions (solid lines) obtained from three energy values. In panel (b) the open circles represent the heat capacity evaluated from local interpolation.

gamma states, based on the minimum amount of simulation data necessary, are good estimates of the “best” gamma state obtained from a large data set, and still reproduce well the LJ fluid behavior within the temperature range investigated. Obviously the heat capacity is now less accurate but the errors are still not large. In Fig 5 the running average of δ_0 at $T_0=6$, calculated from Eq. (5), shows that a direct measure of this property from the energy moments requires at least 4.5×10^6 steps and a full convergence is still not reached.

In Table II we show the parameters of the three gamma states. As expected, the estimates of the parameters obtained by the three different methods are very close, confirming the validity of the gamma state model. Finally in Table III we

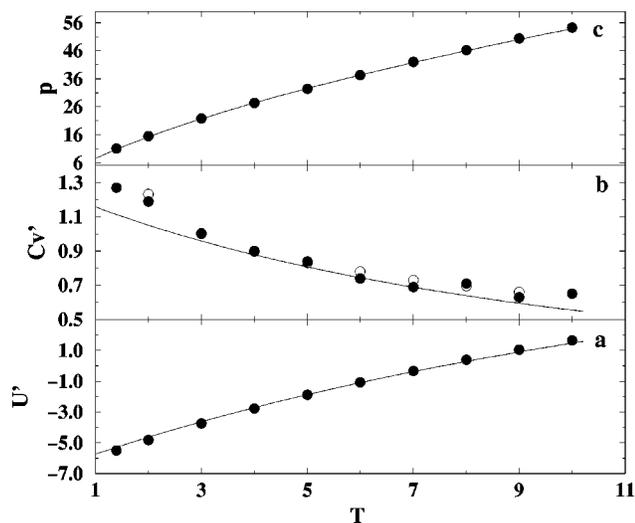


FIG. 4. Comparison of ideal reduced internal energy (a), heat capacity (b) and full pressure (c) (filled circles) obtained from the simulations, with the gamma state predictions (solid lines) obtained from the first three energy moments at $T=6$. In panel (b) the open circles represent the heat capacity evaluated from local interpolation.

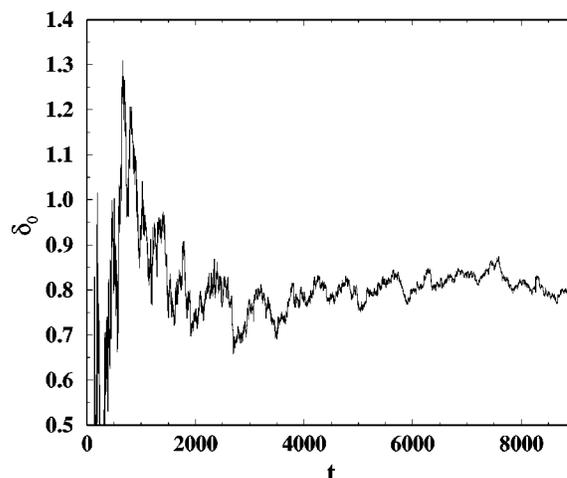


FIG. 5. Running average of δ_0 calculated from the second and third central energy moments at $T=6$.

summarize the results for the three gamma states, the two MBWR EOS, and the cumulant expansion (CE) model giving different overall measures of their accuracy. We use the root mean square deviation (rms) and the average relative error (%AAD) for energy, pressure and heat capacity, the latter obtained from local interpolation. The rms and %AAD for C_V^* obtained by M_2 are very similar to those obtained by local interpolation of the energy.

From the values of Table III it is evident that the gamma state obtained from the whole energy data set (Γ_{ref}) is the most accurate, and the CE model is clearly the worst, confirming the previous results. The comparison of the other two gamma states (Γ_1, Γ_2) shows that the use of the three energy moments from a single simulation results in a less accurate estimate of the gamma state parameters as expected from the fact that the full convergence of the second and especially the third central moment requires very long simulations. Interestingly the gamma state based on three energy values (Γ_1) is almost comparable to the “reference” gamma state (Γ_{ref}), and has even a smaller %AAD for the energy. In the case of pressure data the three gamma states are completely equivalent for the given accuracy, as expected from the similarity of the gamma state parameters in Table II. Note that the accuracy of the gamma state model Γ_{ref} for the isochore used is basically comparable to that of the MBWR EOS reported in the literature^{6,7} in the fitting range (1.4–6) of the latter, although in the temperature range that we cover the accuracy of the three gamma state models is considerably higher.

Finally it should be noted that, although the gamma state model, as shown, provides an accurate description of the LJ fluid behavior in the full temperature range, the small deviations between the model and the data obtained from simulations are still significant when compared to the extremely small error estimates. These remarkably small errors imply that LJ fluid simulations in the order of a few million time steps can provide virtually exact thermodynamic averages of energy and pressure, and hence the comparison of the simulation data with a model simply gives a measure of the accuracy of the model itself with respect to the “exact” system

TABLE III. Average relative errors (%AAD) and root mean square deviations (rms) of the different gamma states estimated from simulation data, of the MBWR EOS obtained by Johnson *et al.* (1) and Sun and Teja (2) and of the cumulant expansion CE model. Note that for the first five models the 1.4–10 temperature range was used while for the last CE model we used the 2–10 temperature range as the CE model at 1.4 has a negative heat capacity.

Γ Models	%AAD U'	rms U'	%AAD C'_V	rms C'_V	%AAD p	rms p
Γ_{ref}	2.6	0.038	4.0	0.058	0.8	0.25
Γ_1	1.3	0.073	4.3	0.082	0.8	0.25
Γ_2	7.3	0.134	7.7	0.087	0.8	0.25
MBWR EOS 1	34.1	0.406	18.1	0.158	0.3	0.16
MBWR EOS 2	26.4	0.292	11.8	0.102	1.9	0.78
CE	24.4	0.411	31.5	0.299	3.0	1.03

behavior. However it is still not fully clear if these errors could be partly underestimated because of very slow relaxation modes present in the simulations.

V. CONCLUSIONS

In this paper we assessed the use of the quasi-Gaussian entropy theory to model the thermodynamic properties of a LJ fluid as a function of temperature. The results showed that the gamma state level of the theory gives an excellent approximation of the thermodynamic properties over a large temperature range.

The comparison of the gamma state, obtained from a fitting procedure on all simulated energy data, with the gamma states obtained from three energy points and from the first three energy moments of a simulation at one temperature, shows only small differences. This result indicates that it is possible to obtain a good estimate of the gamma state parameters using a restricted amount of data. The first three energy moments at one temperature can be sufficient to derive a reliable gamma state; however, the faster convergence of the first potential energy moment implies that it is more accurate and convenient to reconstruct the gamma state using a limited set of energy data at different temperatures.

Finally the small deviations present at the extremes of the temperature range investigated, for the heat capacity, indicate that in order to describe the LJ fluid behavior over a larger temperature interval than the one used in this paper, some form of correction must be applied to the gamma state level of the theory. It is expected that only a small perturbation in the basic gamma state will suffice to construct a very accurate equation of state over a very large temperature and density range.

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- ¹D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).
- ²J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**, 587 (1976).
- ³J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986).
- ⁴J. Kolafa and I. Nezbeda, *Fluid Phase Equilibria* **100**, 1 (1994).
- ⁵M. Mecke *et al.*, *Int. J. Thermophys.* **17**, 391 (1996).
- ⁶J. K. Johnson, J. Z. Zollweg, and K. E. Gubbins, *Mol. Phys.* **78**, 591 (1993).
- ⁷T. Sun and A. S. Teja, *J. Phys. Chem.* **100**, 17365 (1996).
- ⁸M. E. F. Apol, A. Amadei, and H. J. C. Berendsen, *J. Chem. Phys.* **104**, 6665 (1996).
- ⁹A. Amadei, M. E. F. Apol, A. Di Nola, and H. J. C. Berendsen, *J. Chem. Phys.* **104**, 1560 (1996).
- ¹⁰A. Amadei, M. E. F. Apol, and H. J. C. Berendsen, *J. Chem. Phys.* **106**, 1893 (1997).
- ¹¹J. K. Patel, C. H. Kapadia, and D. B. Owen, *Handbook of Statistical Distributions* (Marcel Dekker, New York, 1976).
- ¹²J. K. Ord, *Families of Frequency Distributions* (Griffin, London, 1972).
- ¹³Note that this assumption which should be valid in the whole temperature range of interest, is always implicit at least for the properties which are investigated in molecular simulations studies. In any case the presence of a reasonably large number of particles in the simulation, provides in general a unimodal energy distribution which can be explained using an approximated form of the central limit theorem (Ref. 11).
- ¹⁴M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
- ¹⁵M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1989).
- ¹⁶D. J. Evans and G. P. Morriss, *Phys. Lett.* **98A**, 433 (1983).
- ¹⁷D. van der Spoel, R. van Drunen, and H. J. C. Berendsen, *Groningen MACHINE for Chemical Simulations*, Department of Biophysical Chemistry, BIOSON Research Institute, Nijenborgh 4 NL-9717 AG Groningen, 1994, electronic-mail to gromacs@chem.rug.nl.
- ¹⁸T. P. Straatsma, H. J. C. Berendsen, and A. J. Stam, *Mol. Phys.* **57**, 89 (1986).
- ¹⁹M. Bishop and S. Frinks, *J. Phys. Chem.* **87**, 3675 (1987).
- ²⁰R. W. Zwanzig, *J. Chem. Phys.* **22**, 1420 (1954).
- ²¹M. E. F. Apol, "The quasi-Gaussian entropy theory. Temperature dependence of thermodynamic properties using distribution functions," Ph.D. thesis, Rijksuniversiteit Groningen, The Netherlands, 1997.
- ²²A. Amadei, M. E. F. Apol, and H. J. C. Berendsen, *J. Chem. Phys.* **109**, 3009 (1998).
- ²³M. E. F. Apol, A. Amadei, and H. J. C. Berendsen, *J. Chem. Phys.* **109**, 3017 (1998).