Extensions of the quasi-Gaussian entropy theory

A. Amadei,^{a)} M. E. F. Apol, and H. J. C. Berendsen

Groningen Biomolecular Sciences and Biotechnology Institute (GBB), Department of Biophysical Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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In this paper we present the quasi-Gaussian entropy theory in a comprehensive and consistent way, introducing a new derivation of the theory very suited for applications to molecular systems, and addressing its use in the case of multi-phase systems. A general derivation of the possible confinement of the system within a part of phase space is given, and for water it is shown that for this a hard sphere excluded volume model can be used. To obtain the temperature dependence of the pressure, a new differential equation is derived, and besides the previously introduced Gaussian and Gamma states, in this paper we also describe a new statistical state, the Inverse Gaussian state. We discuss the properties of these different statistical states and for water compare their thermodynamics with experimental data, finding that both the Gamma and Inverse Gaussian states are excellent descriptions. © 1997 American Institute of Physics. [S0021-9606(97)50305-9]

I. INTRODUCTION

The key point in statistical mechanics is the evaluation of the (configurational) partition function, which is in general a high-dimensional integral over all coordinates. For a system not at very low density with a realistic Hamiltonian, it is virtually impossible to derive in this way rigorous but handable expressions for the various thermodynamic properties. In recent articles¹⁻⁴ however, we showed that in the canonical ensemble it is possible to switch from the highdimensional partition function to the one-dimensional potential energy distribution function of the system, which is in a way a special projection of the Hamiltonian. The advantage of this approach is the fact that, because of the macroscopic character of usual systems, the potential energy distribution function is almost Gaussian ("quasi-Gaussian"). Hence mathematically already relatively simple distributions can be used to model the real distribution, yielding very compact expressions for the excess thermodynamic properties (i.e., with respect to a proper reference state).

We also showed that, using this approach, in a very natural way a hidden differential equation, the *thermodynamic master equation*, arises. For every type of distribution, which defines a different statistical state of the system, the solution of this master equation yields the temperature dependence of the excess heat capacity C'_V and hence of the excess entropy S', internal energy U' and Helmholtz free energy A'. In the previous articles we derived and tested the temperature dependence of these excess thermodynamic properties at constant volume for a Gaussian and Gamma distribution.

In this article we will introduce a new distribution, the Inverse Gaussian distribution, which is very related to the Gamma distribution, and derive its thermodynamics. We will also derive a new differential equation, the *conjugated pressure equation*, the solution of which yields the temperature dependence of the excess pressure p' and hence, combined with the previous properties, of the excess enthalpy H' and Gibbs free energy G'.

In Ref. 2 we proposed the idea of a phase-space confinement, i.e., a division of phase space into a "stable" and "unstable" part, in a somewhat ad hoc way, based on a general double state model. In this article we will derive the phase-space confinement in a more natural way, and discuss its implications and the behaviour of the confinement for water as a function of the density. Moreover, we will discuss the properties of the statistical states described and we will compare their zero and infinite temperature limits with general statistical mechanical results.

In section II we will present the general theory in a comprehensive and consistent way, introducing a new derivation of the theory very suited for molecular systems, and in section III we summarize the properties of the various statistical states. In "Discussion and results" (section IV) we will address aspects of multiphase systems, the temperature limits of the expressions of the thermodynamic properties as discussed in section III, the phase-space confinement and its relation to hard-sphere excluded volume and present new results of the excess pressure at constant density using the conjugated pressure equation.

II. GENERAL THEORY

A. Definition of the system

The Helmholtz free energy of a system at fixed volume, temperature and number of molecules is

$$A = -kT \ln Q, \tag{1}$$

where Q is the overall partition function. For a system of N identical molecules in the classical limit

$$Q \approx \frac{1}{N!} Q^e Q^{\rm kin} Q^{\rm pot},\tag{2}$$

with Q^e the electronic partition function, a constant for most of the systems, Q^{kin} the kinetic energy partition function and

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^{a)}Author to whom correspondence should be addressed.

 $Q^{\rm pot}$ the configurational partition function involving the potential energy of the system. The most general expression of $Q^{\rm pot}$ is¹

$$Q^{\text{pot}} = \sum_{l} \int' e^{-\beta(\Phi + \psi + \mathscr{E}^{l})} d\mathbf{x}, \qquad (3)$$

where x are the atomic coordinates. Φ is the intermolecular potential energy, ψ is the intramolecular potential energy (excluding bond length and bond angle vibrational energy), \mathcal{E}^{l} is the overall *l*th quantum vibrational bond energy (in general a function of the coordinates), $\beta = 1/kT$ and the sum runs over all accessible vibrational states $\{l\}$ of the system in the temperature range of interest. The prime on the integral means that we integrate only over configurations where all the bond lengths and angles are fixed at their equilibrium values, see the Appendix. In a previous article¹ we derived the quasi-Gaussian entropy theory from the completely general expression given in Eq. 3. However, in many cases such a derivation of the theory is not very suitable for applications. In this paper we will therefore introduce a very general approximation of Q^{pot} , valid for many different types of molecules, from which we will derive a very useful form of the theory for applications to molecular systems.

In fact we can simplify Eq. 3, considering that in general for systems where the vibrational energies have a significant dependence on the coordinates, such a dependence is observed only up to temperatures where the molecules are largely confined in the vibrational ground state (for water, see Refs. 5 and 6). In such systems, as the temperature is increased to values where the first excited states become significantly populated, the vibrational energies converge to the ideal gas ones, i.e., bond vibrational energies of the same molecules in the ideal gas condition which are in general independent of the coordinates. For these kind of systems we can rewrite Eq. 3 as

$$Q^{\text{pot}} = \sum_{l} \int' e^{-\beta(\Phi + \psi + \mathscr{E}^{l})} d\mathbf{x}$$
$$= \sum_{l} e^{-\beta E^{l}} \int' e^{-\beta(\Phi + \psi)} e^{-\beta(\mathscr{E}^{l} - E^{l})} d\mathbf{x}$$
(4)

with E^l the coordinate averaged vibrational energy of the *l*th state. The fact that the vibrational energies E^l converge to the ideal gas ones (E_{id}^l) when the temperature allows a relevant excitation implies, at least for all the terms in Eq. 4 significantly different from zero (i.e., βE^l not too large), that

$$\int' e^{-\beta(\Phi+\psi)} e^{-\beta(\mathscr{E}^{l}-E^{l})} d\mathbf{x}$$
$$\cong \int' e^{-\beta(\Phi+\psi)} e^{-\beta(\mathscr{E}^{0}-E^{0})} d\mathbf{x}.$$
(5)

Hence

$$Q^{\text{pot}} \cong \left(\sum_{l} e^{-\beta(E^{l} - E^{0})}\right) \int e^{-\beta(\Phi + \psi + \mathcal{E}^{0})} d\mathbf{x}$$
(6)

with \mathcal{E}^0 the overall vibrational ground state energy of the system. Since the same argument also implies that

$$\sum_{l} e^{-\beta(E^{l} - E^{0})} \cong \sum_{l} e^{-\beta(E^{l}_{id} - E^{0}_{id})}$$
(7)

we finally obtain

$$Q^{\text{pot}} \cong Q^{v}_{\text{id}} \int' e^{-\beta \mathscr{U}'} d\mathbf{x}$$
(8)

with $\mathscr{U}' = \Phi + \psi + \mathscr{E}^0 - E_{id}^0$ and where $E_{id}^0 Q_{id}^v$ are the overall vibrational ground state energy and partition function of the ideal gas (with $\Phi=0$), respectively. It is easy to see that Eq. 8 is always exact if the system is completely confined in the vibrational ground state, or if no vibrations are present (monatomic molecules) or when the vibrational energies can be considered independent of the coordinates, and therefore from the temperature, hence being identical to the ideal gas ones.

If moreover, at least in the whole temperature range of interest, only a part of the configurational space is energetically accessible (i.e., the system is confined within a part of the configurational space) we can rewrite Eq. 8 as

$$Q^{\text{pot}} \cong Q_{\text{id}}^{v} \int e^{-\beta \mathscr{U}'} d\mathbf{x}, \qquad (9)$$

where now the star denotes an integration over the accessible part of the configurational space only. It should be noted that the unaccessible configurations do not necessarily correspond only to the ones which are forbidden by a simple excluded volume concept, where it is assumed that the pair potential energy has an infinite barrier as in a hard sphere liquid. In fact, according to the *total* intermolecular potential energy, even configurations with non-penetrating molecules might be energetically excluded up to very high temperatures. Clearly in the infinite temperature limit every finite energy configuration will be accessible implying that only the confinement due to the infinite energy configurations can be considered exact, i.e., really temperature independent.

Eq. 9, which reduces to Eq. 8 in case the whole configurational space is available, is a very general expression that can be used for many different types of molecules: for all the cases where we applied the theory $previously^{1,2}$ (water, methanol and methane) Eq. 9 is completely valid.

B. Definition of the reference states and excess properties

For all the systems where Eq. 9 can be used, we can define two reference states (ideal reference and confined ideal reference) at the same temperature and density, but without inter (Φ) and intramolecular potential energy (ψ), see Fig. 1. For the *ideal reference* we have

$$A_{\rm ref} = -kT \ln Q_{\rm ref},\tag{10}$$

$$Q_{\rm ref} = \frac{1}{N!} Q^e Q^{\rm kin} Q_{\rm ref}^{\rm pot},\tag{11}$$

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FIG. 1. Definition of the (reference) states and of the various differences for a property X. The prime and the star on the integral denote restrictions due to fixed bondlengths and angles and a possible confinement of the system within a part of phase space, respectively.

$$Q_{\rm ref}^{\rm pot} = Q_{\rm id}^v \int' d\mathbf{x},\tag{12}$$

and for the *confined ideal reference*

$$A_{*\mathrm{ref}} = -kT \ln Q_{*\mathrm{ref}}, \qquad (13)$$

$$Q_{*\text{ref}} = \frac{1}{N!} Q^e Q^{\text{kin}} Q^{\text{pot}}_{*\text{ref}},$$
(14)

$$Q_{*\mathrm{ref}}^{\mathrm{pot}} = Q_{\mathrm{id}}^{v} \int^{\prime *} dx.$$
(15)

Therefore the excess Helmholtz free energy of the confined ideal reference state with respect to the ideal reference state is

$$A_{\rm ref}' = A_{\rm *ref} - A_{\rm ref} = -kT \ln \epsilon$$
 (16)

with

$$\epsilon = \frac{\int '^* d\mathbf{x}}{\int ' d\mathbf{x}} \tag{17}$$

the fraction of available configurational space (phase-space fraction) previously introduced in a different way.² Hence the corresponding excess entropy, internal energy, heat capacity and pressure are^7

$$S_{\rm ref}' = -\left(\frac{\partial A_{\rm ref}'}{\partial T}\right)_V = k \ln \epsilon, \qquad (18)$$

$$U'_{\rm ref} = A'_{\rm ref} + TS'_{\rm ref} = 0,$$
 (19)

$$C_{Vref}' = \left(\frac{\partial U_{ref}'}{\partial T}\right)_{V} = 0, \qquad (20)$$

$$p_{\rm ref}' = -\left(\frac{\partial A_{\rm ref}'}{\partial V}\right)_T = kT \frac{d \ln \epsilon}{dV} = \xi T, \qquad (21)$$

where ϵ and ξ , at least within the whole temperature range of interest, are by definition independent of the temperature.

We define the confined ideal reduced free energy as

$$A^{*} = A - A_{* \operatorname{ref}} = -kT \ln \frac{Q^{\operatorname{pot}}}{Q_{*\operatorname{ref}}^{\operatorname{pot}}}$$
$$= kT \ln \langle e^{\beta \mathscr{U}'} \rangle = \langle \mathscr{U}' \rangle + kT \ln \langle e^{\beta \Delta \mathscr{U}'} \rangle, \qquad (22)$$

where

$$\Delta \mathscr{U}' = \mathscr{U}' - \langle \mathscr{U}' \rangle, \tag{23}$$

$$\langle e^{\beta \mathscr{U}'} \rangle = \frac{\int'^* d\mathbf{x}}{\int'^* e^{-\beta \mathscr{U}'} d\mathbf{x}} = \frac{\int'^* e^{-\beta \mathscr{U}'} e^{\beta \mathscr{U}'} d\mathbf{x}}{\int'^* e^{-\beta \mathscr{U}'} d\mathbf{x}}.$$
 (24)

Hence the confined ideal reduced internal energy, heat capacity, entropy and pressure are

$$U^* = -\left(\frac{\partial}{\partial\beta} \ln \frac{Q^{\text{pot}}}{Q^{\text{pot}}_{*\text{ref}}}\right)_V = \langle \mathscr{U}' \rangle, \qquad (25)$$

$$C_{V}^{*} = \left(\frac{\partial U^{*}}{\partial T}\right)_{V} = \left(\frac{\partial \langle \mathscr{U}' \rangle}{\partial T}\right)_{V}, \qquad (26)$$

$$S^* = -\frac{(A^* - U^*)}{T} = -k \ln\langle e^{\beta \Delta \mathscr{U}'} \rangle, \qquad (27)$$

$$p^* = -\left(\frac{\partial A^*}{\partial V}\right)_T.$$
(28)

We also define the *ideal reduced* free energy as

$$A' = A - A_{\text{ref}} = A^* + A'_{\text{ref}} = A^* - kT \ln \epsilon$$
⁽²⁹⁾

and so the ideal reduced internal energy, heat capacity, entropy and pressure are

$$U' = -\left(\frac{\partial}{\partial\beta} \ln \frac{Q^{\text{pot}}}{Q^{\text{pot}}_{\text{ref}}}\right)_{V} = \langle \mathscr{U}' \rangle = U^{*}, \qquad (30)$$

$$C_{V}^{\prime} = \left(\frac{\partial U^{\prime}}{\partial T}\right)_{V} = \left(\frac{\partial \langle \mathscr{U}^{\prime} \rangle}{\partial T}\right)_{V} = C_{V}^{*}, \qquad (31)$$

$$S' = -\frac{(A' - U')}{T} = S^* + k \ln \epsilon, \qquad (32)$$

$$p' = -\left(\frac{\partial A'}{\partial V}\right)_T = p^* + T\xi.$$
(33)

Finally, from these equations follow the (confined) ideal reduced⁸ enthalpy and Gibbs free energy

$$H' = U^* + (p^* + T\xi)V = H^* + TV\xi,$$
(34)

$$G' = A^* - kT \ln \epsilon + (p^* + T\xi)V = G^* - kT \ln \epsilon + TV\xi.$$
(35)

It should be noted that the ideal reduced properties of the systems previously investigated^{1,2} can be considered as different cases of Eqs. 29–35 since for those systems the reference conditions chosen can be considered as special conditions of Eq. 12.

C. The potential energy distribution

Eq. 27 can be explicitly expressed as

$$S^* = -k \ln G_{\Delta \mathcal{U}'}(\beta)$$

= $-k \ln \int e^{\beta \Delta \mathcal{U}'} \rho(\Delta \mathcal{U}') d\Delta \mathcal{U}',$ (36)

where $G_{\Delta \mathscr{U}'}(\beta)$ is the moment generating function^{9,10} of the potential energy distribution function $\rho(\Delta \mathscr{U}')$ (note that ρ is in general temperature dependent). From the fact that a macroscopic system can be considered as a very large collection

of identical, independent subsystems (elementary systems), we can conclude that because of the central limit theorem^{9,11} the corresponding potential energy distribution function can be regarded as uninormal. In fact the possible deviations from the uninormal shape in the far tail of the distribution are in general negligible because of the very sharply peaked behaviour of the curve around its mode (maximum of probability), also due to the macroscopic nature of the system,^{12,13} and therefore the integrand in Eq. 36 can be modeled considering ρ an exact uninormal distribution. In general we can express the potential energy distribution as^{12,14}

$$\rho(\Delta \mathscr{U}') = \frac{\Omega(\Delta \mathscr{U}')}{Q^{\text{pot}}} e^{-\beta(\Delta \mathscr{U}' + \mathscr{U}')}$$
(37)

with

$$\Omega(\Delta \mathscr{U}') = \int'^{*} \delta(\Delta \mathscr{U}'(\mathbf{x}) - \Delta \mathscr{U}') d\mathbf{x}$$
(38)

the confined configurational microcanonical partition function, and hence

$$\frac{d\rho}{d\Delta \mathscr{U}'} = -\rho(\Delta \mathscr{U}') \left[\beta - \frac{d \ln \Omega}{d\Delta \mathscr{U}'}\right].$$
(39)

Using a Padé approximant,^{15,16} instead of a usual Taylor series, to expand the function between brackets in Eq. 39 around the mode of the distribution, we finally obtain a general differential equation, equivalent to the one of the generalized Pearson system of curves,^{1,17,18} which can be used to obtain the possible potential energy distribution functions:

$$\frac{d\rho}{d\Delta \mathscr{U}'} = -\left(\Delta \mathscr{U}' - \Delta \mathscr{U}'_m\right)\rho \; \frac{P^m(\Delta \mathscr{U}')}{G^n(\Delta \mathscr{U}')},\tag{40}$$

where $\Delta \mathscr{U}'_m$ is the value of $\Delta \mathscr{U}'$ where ρ has its mode and $P^m(\Delta \mathscr{U}')$ and $G^n(\Delta \mathscr{U}')$ are some arbitrary polynomials of order *m* and *n*:

$$P^{m}(\Delta \mathscr{U}') = \sum_{i=0}^{m} a_{i}(\Delta \mathscr{U}')^{i}, \qquad (41)$$

$$G^{n}(\Delta \mathscr{U}') = \sum_{j=0}^{n} b_{j}(\Delta \mathscr{U}')^{j}, \qquad (42)$$

where without loss of generality $a_m = 1$. The solutions of Eq. 40 are therefore fully defined by the parameters $\Delta \mathscr{U}'_m$, $\{a_i\}$ and $\{b_j\}$ which can be expressed¹ in terms of the central potential energy moments M_n . Hence with the use of physical-mathematical restrictions¹ we can select the physically acceptable distributions, fully defined by a limited set of central moments, and then order them according to their increasing complexity. We also showed that these potential energy moments can be expressed as a function of the isochoric heat capacity and a limited number of its temperature derivatives¹

$$M_2(T) = kT^2 C_V', (43)$$

$$M_3(T) = (kT^2)^2 \left(\frac{\partial C_V'}{\partial T}\right)_V + 2(kT)^2 C_V', \qquad (44)$$

•••

$$M_{k}(T) = M_{k}\left(T, C_{V}', \left(\frac{\partial C_{V}'}{\partial T}\right)_{V}, \left(\frac{\partial^{2} C_{V}'}{\partial T^{2}}\right)_{V}, \cdots, \left(\frac{\partial^{k-2} C_{V}'}{\partial T^{k-2}}\right)_{V}\right),$$
(45)

where $M_k = \langle (\Delta \mathcal{U}')^k \rangle$ is the *k*th central potential energy moment and we used the fact that $C_V^* = C_V'$. If the functional shape of ρ is defined by the first *n* central moments, from Eqs. 36 and 45 it follows that

$$S^* = S^* \left(T, C_V', \left(\frac{\partial C_V'}{\partial T} \right)_V, \left(\frac{\partial^2 C_V'}{\partial T^2} \right)_V, \cdots, \left(\frac{\partial^{n-2} C_V'}{\partial T^{n-2}} \right)_V \right).$$
(46)

D. The thermodynamic master equation

We define the *intrinsic entropy function* as¹

$$\alpha = \frac{S'}{C_V'} = \frac{S^*}{C_V'} + \frac{k \ln \epsilon}{C_V'}$$
$$= \alpha^* \left(T, C_V', \left(\frac{\partial C_V'}{\partial T} \right)_V, \left(\frac{\partial^2 C_V'}{\partial T^2} \right)_V, \cdots, \left(\frac{\partial^{n-2} C_V'}{\partial T^{n-2}} \right)_V \right)$$
$$+ \frac{k \ln \epsilon}{C_V'}$$
(47)

with $\alpha^* = S^*/C'_V$ the *confined* intrinsic entropy function, and using the general thermodynamic relation $(\partial S'/\partial T)_V$ $= (\partial S^*/\partial T)_V = C'_V/T$, we obtain the *thermodynamic master equation*¹ (TME)

$$\frac{C_V'}{T} = C_V' \left(\frac{\partial \alpha^*}{\partial T}\right)_V + \alpha^* \left(\frac{\partial C_V'}{\partial T}\right)_V.$$
(48)

This is a completely defined differential equation where its unique, always existing solution gives the temperature dependence of the ideal reduced isochoric heat capacity C'_V , once the values of $C'_V,...,(\partial^{n-2}C'_V/\partial T^{n-2})_V$ at one arbitrary temperature T_0 are known. Note that in Eqs. 47 and 48 we used a generalized expression of the intrinsic entropy function, treating explicitly the possible confinement of the system, which reduces to the usual one when $\epsilon=1$ and therefore $\alpha=\alpha^*$. From the solution of the master equation we can obtain the confined ideal reduced entropy via Eq. 46, and then the confined ideal reduced internal energy and free energy at fixed density via

$$U^{*}(T) = U'(T) = U'(T_{0}) + \int_{T_{0}}^{T} C'_{V}(T) dT, \qquad (49)$$

$$A^{*}(T) = U'(T) - TS^{*}(T).$$
(50)

It is interesting to note that, since

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$$\alpha^* = \frac{S^*}{C_V'} = -\frac{S^*/\beta}{(\partial S^*/\partial \beta)_V}$$
(51)

the confined intrinsic entropy function is the ratio between the average slope of S^* versus β (remembering that $S^*=0$ when $\beta=0$) and the instantaneous slope $(\partial S^*/\partial \beta)_V$. One can moreover prove that^{1,2}

$$\lim_{T \to \infty} \alpha^*(T) = -\frac{1}{2} \tag{52}$$

which implies that the (confined) ideal reduced thermodynamics of every system in the infinite temperature limit tends to that of a Gaussian state, see section III A.

E. The conjugated pressure equation

From Eq. 46 it is moreover possible to obtain the confined ideal reduced pressure of the system $p^* = p - p_{*ref}$ as a function of the temperature. In fact from the basic thermodynamic relation

$$\left(\frac{\partial S^*}{\partial V}\right)_T = \left(\frac{\partial p^*}{\partial T}\right)_V \tag{53}$$

we obtain

$$\frac{1}{T} \left(\frac{\partial C_V}{\partial V} \right)_T = \left(\frac{\partial^2 p^*}{\partial T^2} \right)_V$$
(54)

and hence in general

$$\left(\frac{\partial f_0}{\partial V}\right)_T = T \left(\frac{\partial^2 p^*}{\partial T^2}\right)_V,\tag{55}$$

$$\left(\frac{\partial f_1}{\partial V}\right)_T = \left(\frac{\partial^2 p^*}{\partial T^2}\right)_V + T\left(\frac{\partial^3 p^*}{\partial T^3}\right)_V,\tag{56}$$

• • •

$$\left(\frac{\partial f_l}{\partial V}\right)_T = l \left(\frac{\partial^{l+1} p^*}{\partial T^{l+1}}\right)_V + T \left(\frac{\partial^{l+2} p^*}{\partial T^{l+2}}\right)_V,\tag{58}$$

where

$$f_0 = C'_V; \quad f_1 = \left(\frac{\partial C'_V}{\partial T}\right)_V; \quad f_l \left(\frac{\partial^l C'_V}{\partial T^l}\right)_V.$$
(59)

Therefore from Eqs. 46, 47 and 53 we finally obtain another closed differential equation at fixed density for the temperature dependence of the confined ideal reduced pressure, the conjugated pressure equation (CPE)

$$\left(\frac{\partial p^*}{\partial T}\right)_V = T\alpha^*(T) \left(\frac{\partial^2 p^*}{\partial T^2}\right)_V + C_V'(T) \left(\frac{\partial \alpha^*}{\partial V}\right)_T$$
(60)

or, equivalently, using Eqs. 46 and 54-59

$$\begin{pmatrix} \frac{\partial p^*}{\partial T} \end{pmatrix}_{V} = \sum_{l} \left[\left(\frac{\partial S^*}{\partial f_l} \right)_{T,f_{l'}} \left(\frac{\partial f_l}{\partial V} \right)_{T} \right]$$

$$= \sum_{l} \left[\left(\frac{\partial S^*}{\partial f_l} \right)_{T,f_{l'}} \left\{ l \left(\frac{\partial^{l+1} p^*}{\partial T^{l+1}} \right)_{V} + T \left(\frac{\partial^{l+2} p^*}{\partial T^{l+2}} \right)_{V} \right\} \right]$$

$$(61)$$

with $l' \neq l$ and l=0,...,(n-2). Eq. 60 or 61 can be solved once the first n-1 temperature derivatives of the confined ideal reduced pressure are known at one arbitrary temperature T_0 . Its solution provides the temperature dependence of $(\partial p^*/\partial T)_V$ for a system at fixed density and, if the confined ideal reduced pressure is known at one temperature as well, also the temperature dependence of the confined ideal reduced pressure, enthalpy and Gibbs free energy via

$$p^{*}(T) = p^{*}(T_{0}) + \int_{T_{0}}^{T} \left(\frac{\partial p^{*}}{\partial T}\right)_{V} dT,$$
(62)

$$H^{*}(T) = U'(T) + p^{*}(T)V,$$
(63)

$$G^{*}(T) = A^{*}(T) + p^{*}(T)V.$$
(64)

Note that it is not necessary to explicitly solve the conjugated pressure differential equation if the temperature dependence of A^* is already known from the thermodynamic master equation, since $p^*(T) = -(\partial A^*(T)/\partial V)_T$. As $A^*(T)$ is an explicit function of T only, with $U'_0, C'_{V0}, (\partial C'_{V0}/\partial T)_V, ...$ as parameters (i.e., the values of U'etc. at the reference temperature T_0) depending only on the volume, the resulting volume derivatives at T_0 can be related to $p_0^*, (\partial p_0^*/\partial T)_V, (\partial^2 p_0^*/\partial T^2)_V, ...,$ according to Eqs. 55–59 (see also the description of the Gamma and Inverse Gaussian states).

Hence the knowledge of the potential energy distribution function at one temperature, as well as the knowledge of ϵ and ξ fully defines the whole (confined) 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 thermodynamical complexity given by the number of the heat capacity temperature derivatives, necessary to define the corresponding type of potential energy distribution function.

F. Reduced thermodynamic properties

The reference states defined by Eqs. 10-15 can be used also to express the (confined) ideal reduced properties of an ideal gas, see Fig. 1. Using Eq. 29 and Eqs. 30-32, considering that in an ideal gas $\Phi=0$, we obtain

$$A_{id}' = A_{id}^* + A_{ref}' = \langle \psi \rangle_{id} + kT \ln \langle e^{\beta \Delta \psi} \rangle_{id} - kT \ln \epsilon_{id}, \quad (65)$$

$$U'_{\rm id} = \langle \psi \rangle_{\rm id}, \tag{66}$$

$$C'_{V \text{ id}} = \left(\frac{\partial \langle \psi \rangle_{\text{id}}}{\partial T}\right)_{V},\tag{67}$$

(57)

$$S'_{id} = S^*_{id} + S'_{ref} = -k \ln \langle e^{\beta \Delta \psi} \rangle_{id} + k \ln \epsilon_{id}, \qquad (68)$$

where the "id" subscript denotes the ideal gas condition. It is important to note that $\epsilon_{id} = \int_{id}^{\prime*} d\mathbf{x} / \int^{\prime} d\mathbf{x}$ is due only to restrictions in the intramolecular configurational space, implying always that $d\epsilon_{id}/dV=0$ and, apart from the case of very large molecules with many intramolecular interactions, $\epsilon_{id}=1$. It should be noted moreover that in Eq. 65, since $\Phi=0$, the two expectation values only depend on the intramolecular coordinates and therefore are also independent of the volume of the system. Hence

$$-\left(\frac{\partial A'_{id}}{\partial V}\right)_{T} = p'_{id} = p_{id} - p_{ref} = 0$$
(69)

which implies that the pressure of the ideal reference condition is identical to the ideal gas one. We can now express the reduced properties of a system, i.e., the thermodynamic properties with respect to the ideal gas condition, using the fact that usually ϵ_{id} =1, as

$$A^{r} = A' - A'_{id} = \langle \mathscr{U}' \rangle - \langle \psi \rangle_{id} + kT \ln \frac{\langle e^{\beta \Delta \mathscr{U}'} \rangle}{\langle e^{\beta \Delta \psi} \rangle_{id}} - kT \ln \epsilon,$$
(70)

$$S^{r} = S' - S'_{id} = -k \ln \langle e^{\beta \Delta \mathcal{U}'} \rangle + k \ln \epsilon + k \ln \langle e^{\beta \Delta \psi} \rangle_{id},$$
(71)

$$U^{r} = U^{\prime} - U^{\prime}_{id} = \langle \mathscr{U}^{\prime} \rangle - \langle \psi \rangle_{id}, \qquad (72)$$

$$C_{V}^{r} = C_{V}^{\prime} - C_{V \text{ id}}^{\prime} = \left(\frac{\partial \langle \mathscr{U}^{\prime} \rangle}{\partial T}\right)_{V} - \left(\frac{\partial \langle \psi \rangle_{\text{id}}}{\partial T}\right)_{V}, \quad (73)$$

$$p' = p' - p'_{id} = p',$$
 (74)

$$H^{r} = H' - H'_{id} = U^{r} + p^{r}V,$$
(75)

$$G^{r} = G' - G'_{id} = A^{r} + p^{r}V.$$
 (76)

It is evident that if we consider small molecules where $\psi=0$, the reduced thermodynamic properties are identical to the ideal reduced ones.

Hence the knowledge of the statistical state of a system and, when $\psi \neq 0$, also of the corresponding ideal gas condition provides the complete reduced thermodynamics at every temperature. We showed^{1,2} that statistical states defined by relatively simple potential energy distribution functions (Gaussian and Gamma states) describe with high accuracy the gas and liquid-state reduced thermodynamics. In the next section we will derive in detail the properties of three different statistical states: the Gaussian, the Gamma and the Inverse Gaussian statistical state. Moreover, we will summarize the properties of the constant alpha approximation, which is valid for strongly confined Gamma or Inverse Gaussian states for a certain temperature interval.

III. DESCRIPTION OF DIFFERENT STATISTICAL STATES

A. Gaussian state

The symmetric Gaussian distribution corresponds to $\{m = 0, n=0\}$ in the generalized Pearson system, Eq. 40. The distribution is given by

$$\rho(\Delta \mathscr{U}') = \frac{1}{\sqrt{2\pi b_0}} \exp\left\{-\frac{\Delta \mathscr{U}'^2}{2b_0}\right\}$$
(77)

with $b_0 = M_2$. Using the fact that the moment generating function of a Gaussian is simply^{1,9,19}

$$G_{\Delta \mathscr{U}'}(\beta) = \exp\left\{\frac{b_0 \beta^2}{2}\right\}$$
(78)

and expressing M_2 in terms of C'_V (Eq. 43), we obtain for the confined intrinsic entropy function

$$\alpha^* = -\frac{1}{2}.\tag{79}$$

The thermodynamic master equation (TME), Eq. 48, therefore reduces to

$$\left(\frac{\partial C_V'}{\partial T}\right)_V = -2\frac{C_V'}{T} \tag{80}$$

the solution of which provides for a confined Gaussian state¹

$$\alpha^*(T) = -\frac{1}{2},$$
(81)

$$C_{V}'(T) = C_{V0}'\left(\frac{T_{0}}{T}\right)^{2},$$
(82)

$$S'(T) = -\frac{1}{2} C'_{V0} \left(\frac{T_0}{T}\right)^2 + k \ln \epsilon,$$
(83)

$$U'(T) = U'_0 + T_0 C'_{V0} \left(1 - \frac{T_0}{T} \right), \tag{84}$$

and

$$A'(T) = U'_0 + T_0 C'_{V0} \left(1 - \frac{T_0}{2T} \right) - kT \ln \epsilon, \qquad (85)$$

where U'_0 and C'_{V0} are the values of U' and C'_V at an arbitrary reference temperature T_0 .

Since $\alpha^* = -1/2$, and hence $(\partial \alpha^*/\partial T)_V = 0$ and $(\partial \alpha^*/\partial V)_T = 0$ it follows that $(\partial (\partial \alpha^*/\partial T)_V/\partial V)_T = (\partial (\partial \alpha^*/\partial V)_T/\partial T)_V = 0$. Therefore we see that if at one density the statistical state of a system is an exact Gaussian one, for all other densities it must be Gaussian too. This result, obvious for a Gaussian state, is true in general for each statistical state, implying that the thermodynamic complexity is conserved at every density.

Since $(\partial \alpha^* / \partial V)_T = 0$, the conjugated pressure equation (CPE), Eq. 60, is in this case a simple first order differential equation

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TABLE I. The $T \rightarrow \infty$ limits of the confined ideal reduced properties for different states. Values between square brackets denote limits of ideal reduced properties.

	Stat. mech. Gaussian		Γ_+/Γ	IG_+/IG	
C'_V	0	0	0	0	
$S^*[S']$	$0 [k \ln \epsilon]$	$0 [k \ln \epsilon]$	$0 [k \ln \epsilon]$	$0 [k \ln \epsilon]$	
U'	$U^{*\mathrm{ref}}$	$U_0'+T_0C_{V0}'$	$U_0'+\frac{T_0C_{V0}'}{1-\delta_0}$	$U_0' + rac{T_0 C_{V0}'}{\gamma_0} \left(rac{1}{\sqrt{1-2\gamma_0}} - 1 \right)$	
$A^*[A']$	$U^{*\mathrm{ref}}[\infty]$	$U_0' + T_0 C_{V0}' \left[\infty\right]$	$U_0' + \frac{T_0 C_{V0}'}{1 - \delta_0} [\infty]$	$U_0' + \frac{T_0 C_{V0}'}{\gamma_0} \left(\frac{1}{\sqrt{1 - 2\gamma_0}} - 1 \right) \ [\infty]$	
<i>p</i> *	$-dU^{*\mathrm{ref}}/dV$	$-d(U'_0+T_0C'_{V0})/dV$	$-d \Biggl(U_0' + \frac{T_0 C_{V0}'}{1-\delta_0} \Biggr) \Bigg/ dV$	$-d\left(U_0'+\frac{T_0C_{V0}'}{\gamma_0}\left(\frac{1}{\sqrt{1-2\gamma_0}}-1\right)\right) / dV$	
$\alpha^*[\alpha]$	$-\frac{1}{2}\left[-\infty\right]$	$-\frac{1}{2}\left[-\infty\right]$	$-\frac{1}{2}\left[-\infty\right]$	$-\frac{1}{2}[-\infty]$	
δ	0	0	0	0	
γ	0	0	0	0	

$$\left(\frac{\partial p^*}{\partial T}\right)_V = -\frac{1}{2} T \left(\frac{\partial^2 p^*}{\partial T^2}\right)_V.$$
(86)

The solution is

$$p^{*}(T) = p_{0}^{*} + T_{0} \left(\frac{\partial p_{0}^{*}}{\partial T} \right)_{V} \left(1 - \frac{T_{0}}{T} \right), \tag{87}$$

where p_0^* and $(\partial p_0^*/\partial T)_V$ are the values at the reference temperature T_0 . The ideal reduced pressure p'(T) follows from Eq. 87, using $p' = p^* + T\xi$ and $(\partial p'/\partial T)_V$ $= (\partial p^*/\partial T)_V + \xi$ (Eq. 33):

$$p'(T) = p'_0 + T_0 \left\{ \left(\frac{\partial p'_0}{\partial T} \right)_V - \xi \right\} \left(1 - \frac{T_0}{T} \right) + \xi (T - T_0).$$
(88)

The $T \rightarrow \infty$ and $T \rightarrow 0$ limits of the various thermodynamic properties are summarized in Tables I and II. It must be noted that only for the confined properties the infinite temperature limits are always physically meaningful, see also section IV B.

B. Gamma state

The Gamma distribution, given by^{1,2,9}

$$\rho(\Delta \mathscr{U}') = \frac{b_1(1/b_1^2)^{b_0/b_1^2}}{\Gamma(b_0/b_1^2)} (b_0 + b_1 \Delta \mathscr{U}')^{b_0/b_1^2 - 1} \\ \times \exp\left\{-\frac{b_0 + b_1 \Delta \mathscr{U}'}{b_1^2}\right\}$$
(89)

TABLE II. The $T \rightarrow 0$ (or $T \rightarrow T_*$) limits of (confined) ideal reduced properties for different states, where $T_*(\Gamma_-)$ and $T_*(IG_-)$ are given by Eqs. 113 and 138. $\alpha^*(\Gamma_-)$ and $A^*(IG_-)$ are obtained by setting $\epsilon = 1$ and the sign of the p^* limits for the Gaussian, Γ_- and IG_- states depends on the sign of $\partial p_0^*/\partial T$ or B_i^* , respectively.

	Class. stat. mech. $T \rightarrow 0$	Gaussian $T \rightarrow 0$	Γ_+ $T \rightarrow 0$	Γ_{-} $T \rightarrow T_{*}$	IG_+ $T \rightarrow 0$	IG_{-} $T \rightarrow T_{*}$
C'_V	(in)finite	∞	$\frac{C_{V0}'}{\delta_0^2}$	∞	∞	ω
S'/S^*	$-\infty$	$-\infty$	$-\infty$	$-\infty$	$-\infty$	—∞
U'	\mathscr{U}'_{\min}	$-\infty$	$U_0'\!-\!\frac{T_0C_{V0}'}{\delta_{\!0}}$	$-\infty$	$U_0^\prime \!=\! rac{T_0 C_{V0}^\prime}{\gamma_0}$	$-\infty$
A'/A^*	\mathscr{U}'_{\min}	$-\infty$	$U_0^\prime \!-\! rac{T_0 C_{V0}^\prime}{\delta_{\!0}}$	$-\infty$	$U_0^\prime\!-\!rac{T_0C_{V0}^\prime}{\gamma_0}$	$U_0' - \frac{T_0 C_{V0}'}{\gamma_0} \left(1 - \frac{T_* \sqrt{1 - 2 \gamma_0}}{T_0 \gamma_0}\right) - k T_* \ln \epsilon$
p'/p^*	$-d \mathscr{U}'_{\min}/dV$	±∞	$-d \left(U_0' - \frac{T_0 C_{V0}'}{\delta_0} \right) \middle/ dV$	±∞	$-d\left(U_0'-rac{T_0C_{V0}'}{\gamma_0} ight) \Bigg/ dV$	$\pm\infty$
$\alpha/lpha^*$	$-\infty$ or ≤ -1	$-\frac{1}{2}$	-∞	$\frac{k\ln\epsilon}{C_{V0}'}\frac{\delta_0^2}{(1-\delta_0)^2}$	-2	0
δ	_	0	1	$-\infty$	$\frac{3}{4}$	—∞
γ	_	0	$\frac{2}{3}$	$-\infty$	$\frac{1}{2}$	-∞

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with $\Gamma(\cdot)$ the Gamma function,²⁰ $b_0 = M_2$ and $b_1 = M_3/(2M_2)$, corresponds to the $\{m=0, n=1\}$ solution of the generalized Pearson system, Eq. 40. The moment generating function of this Gamma distribution is^{1,9,19}

$$G_{\Delta \mathscr{U}'}(\beta) = \exp\left\{-\beta \frac{b_0}{b_1}\right\} (1 - \beta b_1)^{-b_0/b_1^2}$$
(90)

and expressing the central moments M_2 and M_3 , appearing in b_0 and b_1 , in terms of C'_V and $(\partial C'_V / \partial T)_V$ (Eqs. 43–44), the confined intrinsic entropy function is in this case given by¹

$$\alpha^* = \frac{1}{\delta} + \frac{1}{\delta^2} \ln(1 - \delta) \tag{91}$$

with

$$\delta = \frac{M_3}{2kTM_2} = \frac{T(\partial C'_V / \partial T)_V}{2C'_V} + 1.$$
(92)

The expression of α^* , combined with the general thermodynamic master equation (Eq. 48), yields

$$T\left(\frac{\partial\alpha^*}{\partial T}\right)_V + (2\,\delta - 1\,)\,\alpha^* - 1 = 0,\tag{93}$$

where $(\partial \alpha^* / \partial T)_V = (d\alpha^* / d\delta) (\partial \delta / \partial T)_V$ and $(d\alpha^* / d\delta)$ follows from Eq. 91. After straightforward algebra we obtain as a simple form of the TME

$$\left(\frac{\partial\delta}{\partial T}\right)_{V} = -\frac{\delta(1-\delta)}{T}.$$
(94)

The solution provides $\delta(T)$, which can be expressed in terms of C'_V and $(\partial C'_V / \partial T)_V$. Hence this gives rise to a new differential equation in C'_V , the solution of which yields for a confined Gamma state^{1,2}

$$\delta(T) = \frac{T_0 \delta_0}{T(1 - \delta_0) + T_0 \delta_0},\tag{95}$$

$$\alpha^{*}(T) = \frac{1}{\delta(T)} + \frac{1}{\delta^{2}(T)} \ln\{1 - \delta(T)\},$$
(96)

$$C_V'(T) = C_{V0}'\left(\frac{\delta(T)}{\delta_0}\right)^2,\tag{97}$$

$$S'(T) = \frac{C'_{V0}}{\delta_0^2} \left[\delta(T) + \ln\{1 - \delta(T)\} \right] + k \ln \epsilon, \qquad (98)$$

$$U'(T) = U'_0 + (T - T_0)C'_{V0} \frac{\delta(T)}{\delta_0}, \qquad (99)$$

$$A'(T) = U'_0 - \frac{T_0 C'_{V0}}{\delta_0} - \frac{T C'_{V0}}{\delta_0^2} \ln\{1 - \delta(T)\} - kT \ln \epsilon,$$
(100)

with δ_0 the value of δ at T_0 . Note that $(\partial C'_V / \partial T)_V$ is always negative, like in the Gaussian state.

Since for a Gamma state the pressure differential equation (Eq. 60) is very complicated, it is more convenient to obtain the confined ideal reduced pressure via the volume derivative of $A^*(T)$, using Eq. 100. Thus, with the usual notation where $(\partial U'_0/\partial V)_T$ etc. are the derivatives evaluated at T_0

$$p^{*}(T) = -\left[\frac{\partial A^{*}}{\partial U'_{0}}\left(\frac{\partial U'_{0}}{\partial V}\right)_{T} + \frac{\partial A^{*}}{\partial C'_{V0}}\left(\frac{\partial C'_{V0}}{\partial V}\right)_{T} + \frac{\partial A^{*}}{\partial \delta_{0}}\left(\frac{\partial \delta_{0}}{\partial V}\right)_{T}\right],$$
(101)

where from general thermodynamic relations we have

$$\left(\frac{\partial U_0'}{\partial V}\right)_T = T_0 \left(\frac{\partial p_0^*}{\partial T}\right)_V - p_0^*, \qquad (102)$$

$$\left(\frac{\partial C_{V0}'}{\partial V}\right)_{T} = T_{0} \left(\frac{\partial^{2} p_{0}^{*}}{\partial T^{2}}\right)_{V}, \qquad (103)$$

and

$$\left(\frac{\partial \delta_0}{\partial V}\right)_T = \frac{1}{C'_{V0}} \left(\frac{d \alpha_0^*}{d \delta_0}\right)^{-1} \left[\left(\frac{\partial p_0^*}{\partial T}\right)_V - \alpha_0^* T_0 \left(\frac{\partial^2 p_0^*}{\partial T^2}\right)_V \right]$$
(104)

as follows from the CPE at T_0 , with $(d\alpha_0^*/d\delta_0)$ following from Eq. 91. The derivatives $\partial A^*/\partial U'_0$, $\partial A^*/\partial C'_{V0}$ and $\partial A^*/\partial \delta_0$ follow from Eq. 100. After tedious but straightforward algebra we finally obtain

$$p^{*}(T) = p_{0}^{*} + B_{0}^{*} + B_{1}^{*} \frac{T}{T(1 - \delta_{0}) + T_{0}\delta_{0}} + B_{2}^{*}\left(\frac{T}{T_{0}}\right) \ln\left\{\frac{T(1 - \delta_{0})}{T(1 - \delta_{0}) + T_{0}\delta_{0}}\right\},$$
(105)

where

$$B_{i}^{*} = A_{i1}T_{0} \left(\frac{\partial p_{0}^{*}}{\partial T} \right)_{V} + A_{i2}T_{0}^{2} \left(\frac{\partial^{2} p_{0}^{*}}{\partial T^{2}} \right)_{V} \quad i = 0, 1, 2 \quad (106)$$

with

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

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

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

$$A_{21} = \frac{2(1-\delta_0)}{D}, \quad A_{22} = \frac{1}{D},$$
(107)

and

$$D = 2(1 - \delta_0) \ln(1 - \delta_0) + \delta_0(2 - \delta_0).$$
(108)

The ideal reduced pressure p'(T) follows from Eq. 105, using $p' = p^* + T\xi$, $(\partial p'/\partial T)_V = (\partial p^*/\partial T)_V + \xi$ and $(\partial^2 p'/\partial T^2)_V = (\partial^2 p^*/\partial T^2)_V$ (Eq. 33):

$$p'(T) = p'_{0} + B_{0} + B_{1} \frac{T}{T(1 - \delta_{0}) + T_{0} \delta_{0}} + B_{2} \left(\frac{T}{T_{0}}\right) \ln \left\{\frac{T(1 - \delta_{0})}{T(1 - \delta_{0}) + T_{0} \delta_{0}}\right\} + \xi T, \quad (109)$$

where

$$B_{0} = A_{01}T_{0} \left(\frac{\partial p_{0}'}{\partial T}\right)_{V} + A_{02}T_{0}^{2} \left(\frac{\partial^{2} p_{0}'}{\partial T^{2}}\right)_{V} + A_{03}T_{0}\xi, \qquad (110)$$

$$B_{i} = A_{i1}T_{0} \left\{ \left(\frac{\partial p_{0}'}{\partial T} \right)_{V} - \xi \right\} + A_{i2}T_{0}^{2} \left(\frac{\partial^{2} p_{0}'}{\partial T^{2}} \right)_{V} \quad i = 1,2$$

$$(111)$$

and

$$A_{03} = -\frac{\delta_0(1-\delta_0)}{D}.$$
 (112)

In this way the temperature behavior of the (confined) ideal reduced pressure, enthalpy and Gibbs free energy is obtained.

As pointed out previously,² since the Gamma distribution has a limited domain, it can be defined either from $-\infty$ to some upper limit or from some under limit to $+\infty$. The first case corresponds to a distribution with an asymmetric tail on the left (defining the negative Gamma state Γ_{-} , with $\delta < 0$ and $-\frac{1}{2} < \alpha^* < 0$, the second case corresponds to an asymmetric tail on the right (defining the positive Gamma state Γ_+ , with $0 < \delta < 1$ and $\alpha^* < -\frac{1}{2}$). Note that for $\delta = 0$ the distribution is a Gaussian. In Ref. 2 we describe the properties of and differences between the two Gamma states in detail. Basically, the Γ_+ state is physically acceptable in the whole semi-classical temperature range, whereas the Γ_{-} state must be considered as an approximation to a more complicated statistical state within some temperature interval. One relevant difference is the low temperature limit: while a Γ_+ state may be extrapolated to $T \rightarrow 0$ (although of course in that limit the semi-classical description is not valid any more, see section IV B), for a Γ_{-} state there exist a temperature

$$T_* = -T_0 \delta_0 / (1 - \delta_0) > 0 \tag{113}$$

at which the solution encounters a singularity. For both states the different temperature limits for various thermodynamic properties are given in Tables I and II and discussed in section IV B.

C. Inverse Gaussian state

The Inverse Gaussian (IG) distribution, given by 21,22

$$\rho(\Delta \mathscr{U}') = \sqrt{\frac{c_1}{2\pi} (c_0 + \Delta \mathscr{U}')^{-3/2}} \\ \times \exp\left\{-\frac{c_1}{2c_0^2} \frac{\Delta \mathscr{U}'^2}{(c_0 + \Delta \mathscr{U}')}\right\}$$
(114)

with $c_0 = 3M_2^2/M_3$ and $c_1 = c_0^3/M_2$ corresponds to a degenerated $\{m=1, n=2\}$ solution of the generalized Pearson system. The full $\{m=1, n=2\}$ solution is characterized by the

first five central moments, but with a relation between the parameters the actual number of necessary moments reduces to three and the distribution reduces to Eq. 114.

Using the fact that the moment generating function of this distribution is given $by^{21,23}$

$$G_{\Delta \mathscr{U}'}(\beta) = \exp\left\{-\beta c_0 + \frac{c_1}{c_0} \left(1 - \sqrt{1 - \frac{2c_0^2}{c_1}\beta}\right)\right\}$$
(115)

and using the expressions for M_2 and M_3 (Eqs. 43–44), we obtain for the confined intrinsic entropy function

$$\alpha^{*} = \frac{1}{\gamma} - \frac{1}{\gamma^{2}} \left(1 - \sqrt{1 - 2\gamma} \right), \tag{116}$$

where

$$\gamma = \frac{M_3}{3kTM_2} = \frac{2}{3} \left(\frac{T(\partial C'_V / \partial T)V}{2C'_V} + 1 \right) = \frac{2}{3} \delta$$
(117)

with δ the characteristic quantity of the Gamma state (see Eq. 92). The similarity between the expressions of α^* for the IG distribution (Eq. 116) and the Gamma distribution (Eq. 91) can be seen by expanding both expressions in a Taylor series around δ =0, obtaining

$$\alpha^{*IG} = -\frac{1}{2} - \frac{\delta}{3} - \frac{5}{18} \,\delta^2 - \cdots , \qquad (118)$$

$$\alpha^{*\Gamma} = -\frac{1}{2} - \frac{\delta}{3} - \frac{\delta^2}{4} - \cdots$$
 (119)

Hence for small δ (i.e., for not too asymmetric distributions) both IG and Gamma distributions will give almost identical results.

The temperature dependence of the various thermodynamic properties can be obtained from the TME, Eq. 48, written in the form

$$T\left(\frac{\partial \alpha^*}{\partial T}\right)_V + (3\gamma - 2)\alpha^* - 1 = 0, \qquad (120)$$

where $(\partial \alpha^* / \partial T)_V = (d\alpha^* / d\gamma)(\partial \gamma / \partial T)_V$ and $(d\alpha^* / d\gamma)$ follows from Eq. 116. After straightforward algebra we finally obtain as a simple form of the TME

$$\left(\frac{\partial\gamma}{\partial T}\right)_{V} = -\frac{\gamma(1-2\gamma)}{T}$$
(121)

which provides $\gamma(T)$. Since γ is a function of C'_V and $(\partial C'_V / \partial T)_V$ and, Eq. 117, we have a new differential equation in C'_V , yielding for a confined IG state

$$\gamma(T) = \frac{T_0 \gamma_0}{T(1 - 2 \gamma_0) + 2T_0 \gamma_0},$$
(122)

$$\alpha^{*}(T) = \frac{1}{\gamma(T)} - \frac{1}{\gamma^{2}(T)} \left(1 - \sqrt{1 - 2\gamma(T)}\right), \quad (123)$$

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$$C_{V}'(T) = C_{V0}'\left(\frac{T_{0}}{T}\right)^{1/2} \left(\frac{\gamma}{\gamma_{0}}\right)^{3/2},$$
(124)

$$S'(T) = C'_{V}(T) \left\{ \frac{1}{\gamma(T)} - \frac{1}{\gamma^{2}(T)} \left(1 - \sqrt{1 - 2\gamma(T)} \right) \right\}$$
$$+ k \ln \epsilon, \qquad (125)$$

$$U'(T) = U'_{0} + \frac{T_{0}C'_{V0}}{\gamma_{0}} \left(\sqrt{\frac{T}{T_{0}}}\frac{\gamma}{\gamma_{0}} - 1\right),$$
(126)

and

$$A'(T) = U'_{0} - \frac{T_{0}C'_{V0}}{\gamma_{0}} + \frac{TC'_{V0}}{\gamma_{0}^{2}} \left(\sqrt{\frac{T_{0}}{T}} \frac{\gamma_{0}}{\gamma} - \sqrt{1 - 2\gamma_{0}} \right)$$
$$-kT \ln \epsilon.$$
(127)

Note that, similar to the Gaussian and Gamma states, $(\partial C'_V / \partial T)_V$ is always negative.

Since, just as for a Gamma state, the pressure differential equation is very complicated, also in this case it is more convenient to obtain the ideal reduced pressure directly via the volume derivative of $A^*(T)$, using Eq. 127. Thus with Eqs. 102 and 103, and $(\partial \gamma_0 / \partial V)_T$ via the CPE at T_0 , we obtain in a similar way

$$p^{*}(T) = p_{0}^{*} + B_{0}^{*} + B_{1}^{*} \left(\frac{T}{T_{0}}\right) \left(\sqrt{1 - 2\gamma_{0}(1 - T_{0}/T)} - \sqrt{1 - 2\gamma_{0}}\right) + B_{2}^{*} \left(\frac{T}{T_{0}}\right) \left(\frac{1 - T_{0}/T}{\sqrt{1 - 2\gamma_{0}(1 - T_{0}/T)}} - \frac{1}{\sqrt{1 - 2\gamma_{0}}}\right), \qquad (128)$$

where

$$B_{i}^{*} = A_{i1}T_{0} \left(\frac{\partial p_{0}^{*}}{\partial T}\right)_{V} + A_{i2}T_{0}^{2} \left(\frac{\partial^{2} p_{0}^{*}}{\partial T^{2}}\right)_{V} \quad i = 0, 1, 2, \quad (129)$$

with

$$A_{01} = \frac{2\sqrt{1-2\gamma_0}+3\gamma_0-2}{D},$$

$$A_{02} = -\frac{1}{\gamma_0}\frac{\sqrt{1-2\gamma_0}+\gamma_0-1}{D},$$
(130)

$$A_{11} = -\frac{2\sqrt{1-2\gamma_0}}{D}, \ A_{12} = \frac{1}{\gamma_0}\frac{\sqrt{1-2\gamma_0}-1}{D},$$
 (131)

$$A_{21} = -\frac{\gamma_0 \sqrt{1 - 2\gamma_0}}{D},$$

$$A_{22} = -\frac{1}{2} \frac{(1 - \gamma_0) \sqrt{1 - 2\gamma_0} + 2\gamma_0 - 1}{D},$$
 (132)

$$A_{22} = -\frac{1}{\gamma_0} \frac{(1 - \gamma_0)\sqrt{1 - 2\gamma_0 + 2\gamma_0 - 1}}{D},$$
 (132)

and

$$D = (\gamma_0 - 2)\sqrt{1 - 2\gamma_0} - 3\gamma_0 + 2.$$
(133)

The ideal reduced pressure p'(T) follows from Eq. 128, using $p' = p^* + T\xi$, $(\partial p'/\partial T)_V = (\partial p^*/\partial T)_V + \xi$ and $(\partial^2 p'/\partial T^2)_V = (\partial^2 p^*/\partial T^2)_V$ (Eq. 33):

$$p'(T) = p'_{0} + B_{0} + B_{1} \left(\frac{T}{T_{0}}\right) \left(\sqrt{1 - 2\gamma_{0}(1 - T_{0}/T)} - \sqrt{1 - 2\gamma_{0}}\right) + B_{2} \left(\frac{T}{T_{0}}\right) \left(\frac{1 - T_{0}/T}{\sqrt{1 - 2\gamma_{0}(1 - T_{0}/T)}} - \frac{1}{\sqrt{1 - 2\gamma_{0}}}\right) + \xi T, \qquad (134)$$

where

$$B_{0} = A_{01}T_{0} \left(\frac{\partial p_{0}'}{\partial T}\right)_{V} + A_{02}T_{0}^{2} \left(\frac{\partial^{2} p_{0}'}{\partial T^{2}}\right)_{V} + A_{03}T_{0}\xi, \qquad (135)$$

$$B_{i} = A_{i1}T_{0} \left\{ \left(\frac{\partial p_{0}'}{\partial T} \right)_{V} - \xi \right\} + A_{i2}T_{0}^{2} \left(\frac{\partial^{2} p_{0}'}{\partial T^{2}} \right)_{V} \quad i = 1,2$$
(136)

and

$$A_{03} = -\frac{\gamma_0 \sqrt{1 - 2\gamma_0}}{D}.$$
 (137)

In this way the temperature behavior of the (confined) ideal reduced pressure, enthalpy and Gibbs free energy is obtained.

Moreover, there exist also negative and positive IG states (IG₋ and IG₊). The IG₋ state is characterized by a finite energy upper limit of the distribution with $-\frac{1}{2} < \alpha^* < 0$ and $\gamma < 0$. The IG₊ state is characterized by a finite energy lower limit of the distribution and $\alpha^* < -\frac{1}{2}$, $0 < \gamma < 3/4$. Clearly, for $\gamma = 0$ the distribution is a Gaussian. In the IG₋ state there is a temperature

$$T_* = -2\gamma_0 T_0 / (1 - 2\gamma_0) > 0, \qquad (138)$$

where the solution in the temperature encounters a singularity. Hence also the IG_ state must be regarded as an approximation to a more complex statistical state, valid within some temperature range. For both states the different temperature limits for the various thermodynamic properties are given in Tables I and II and discussed in section IV B.

D. Constant alpha approximation

In the case of a strongly confined Gamma (or Inverse Gaussian) state, it turns out that $\alpha(T)$ is almost constant over a large temperature interval.^{1,2} These strongly confined states correspond to typical liquid densities. In that case

$$\left(\frac{\partial\alpha}{\partial T}\right)_{V} = \left(\frac{\partial\alpha^{*}}{\partial T}\right)_{V} - \frac{k\ln\epsilon}{C_{V}^{2}(T)} \left(\frac{\partial C_{V}'}{\partial T}\right)_{V},$$
(139)

where the first term on the right-hand side is positive for a Γ_+ (or IG₊) state and the second term negative (since

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 $(\partial C'_V / \partial T)_V < 0$ and $\epsilon < 1$). For these strongly confined states both terms approximately cancel and hence $(\partial \alpha / \partial T)_V \cong 0$, so $\alpha(T) \cong \alpha(T_0) = \alpha_0$, reducing the TME to

$$\left(\frac{\partial C_V'}{\partial T}\right)_V = \frac{1}{\alpha_0} \frac{C_V'}{T}$$
(140)

yielding the constant alpha equations^{1,2}

$$C_V'(T) = C_{V0}' \left(\frac{T}{T_0}\right)^{\lambda_0},$$
 (141)

$$S'(T) = \frac{C'_{V0}}{\lambda_0} \left(\frac{T}{T_0}\right)^{\lambda_0},\tag{142}$$

$$U'(T) = U'_0 - \frac{T_0 C'_{V0}}{\lambda_0 + 1} \left\{ 1 - \left(\frac{T}{T_0}\right)^{\lambda_0 + 1} \right\},$$
(143)

$$A'(T) = U'_0 - \frac{T_0 C'_{V0}}{\lambda_0 + 1} \left\{ \frac{1}{\lambda_0} \left(\frac{T}{T_0} \right)^{\lambda_0 + 1} + 1 \right\},$$
 (144)

with

$$\lambda_0 = 1/\alpha_0 < 0. \tag{145}$$

Furthermore, since in the range of typical liquid densities $(\partial \alpha / \partial T)_V \cong 0$, it follows that also $(\partial (\partial \alpha / \partial T)_V / \partial V)_T = (\partial (\partial \alpha / \partial V)_T / \partial T)_V \cong 0$. Hence the first derivative of α in V is approximately temperature independent, and we obtain as conjugated pressure equation (Eq. 60), using Eq. 141 for $C'_V(T)$:

$$\left(\frac{\partial p'}{\partial T}\right)_{V} = \frac{T}{\lambda_{0}} \left(\frac{\partial^{2} p'}{\partial T^{2}}\right)_{V} + C_{V0}' \left(\frac{\partial \alpha_{0}}{\partial V}\right)_{T} \left(\frac{T}{T_{0}}\right)^{\lambda_{0}}$$
(146)

yielding

$$p'(T) = p'_{0} + B_{0} \left\{ \left(\frac{T}{T_{0}} \right)^{\lambda_{0}+1} - 1 \right\} - B_{1} \left(\frac{T}{T_{0}} \right)^{\lambda_{0}+1} \ln \left(\frac{T}{T_{0}} \right),$$
(147)

where

$$B_0 = \frac{T_0}{\lambda_0 + 1} \left(\frac{\partial p'_0}{\partial T}\right)_V + \frac{T_0 C'_{V0} \lambda_0}{(\lambda_0 + 1)^2} \left(\frac{\partial \alpha_0}{\partial V}\right)_T,$$
(148)

$$B_1 = \frac{T_0 C'_{V0} \lambda_0}{\lambda_0 + 1} \left(\frac{\partial \alpha_0}{\partial V}\right)_T.$$
(149)

On the other hand, using the CPE at T_0 , we can express $(\partial \alpha_0 / \partial V)_T$ in terms of $(\partial p'_0 / \partial T)_V$ and $(\partial^2 p'_0 / \partial T^2)_V$, giving

$$B_0 = \frac{2\lambda_0 + 1}{(\lambda_0 + 1)^2} T_0 \left(\frac{\partial p'_0}{\partial T}\right)_V - \frac{T_0^2}{(\lambda_0 + 1)^2} \left(\frac{\partial^2 p'_0}{\partial T^2}\right)_V, \quad (150)$$

$$B_1 = \frac{\lambda_0 T_0}{\lambda_0 + 1} \left(\frac{\partial p'_0}{\partial T} \right)_V - \frac{T_0^2}{\lambda_0 + 1} \left(\frac{\partial^2 p'_0}{\partial T^2} \right)_V.$$
(151)

Both sets of expressions of B_0 and B_1 are completely equivalent. However, it seems from a practical point of view, that the latter are more useful, since the experimental values of $(\partial^2 p'_0 / \partial T^2)_V$ appear to be more accurate than the values of $(\partial \alpha_0 / \partial V)_T$, see also section IV D.

Note that the approximation is valid for the phase space as a whole. Since the constant alpha approximation is a local approximation only (although for liquids applicable over a large temperature range, especially for the entropy and Helmholtz free energy^{1,2}), the $T \rightarrow 0$ and $T \rightarrow \infty$ limits are not given, as they are in principle irrelevant (for every confined system the infinite temperature limit of $\alpha = -\infty$, see section IV B).

IV. DISCUSSION AND RESULTS

A. Multiphase systems

The basic derivation of the theory (section II) does not have any assumption on the phase condition of the system, being then valid even for macroscopic multi-phase systems at fixed overall density. In fact, such systems can also be considered as a very large collection of identical independent subsystems (multi-phase elementary systems), each containing all the phases present in the overall system. It is evident hence that we can still apply the central limit theorem on macroscopic multi-phase systems just as for single-phase ones. However, it must be noted that the potential energy distribution required to model a multi-phase system, although uninormal, is likely to be much more complex than the one needed for a single phase condition. This implies that only very sophisticated solutions of the generalized Pearson system can be used as good descriptions of a multi-phase statistical state. We can investigate this point, considering a biphasic system (the generalization to more phases is straightforward).

In general in a macroscopic system consisting of two macroscopic phases we can express the total Helmholtz free energy as the sum of the free energies of the two phases,

$$A = -kT \ln Q = -kT \ln Q_{\rm I} - kT \ln Q_{\rm II} = A_{\rm I} + A_{\rm II},$$
(152)

where $A_{\rm I}$ and $A_{\rm II}$ are the free energies of phase I and II and $Q_{\rm I}$ and $Q_{\rm II}$ the corresponding partition functions. We can express in the usual way also the ideal reduced free energy as

$$A' = A - A_{\rm ref} = kT \ln \langle e^{\beta \mathscr{U}'} \rangle - kT \ln \epsilon$$
(153)

or, equivalently, using Eq. 152 and the definition of the ideal reference state partition function, Eq. 11, as

$$A' = A_{\rm I} - A_{\rm I \, ref} + A_{\rm II} - A_{\rm II \, ref} + A_{\rm I \, ref} + A_{\rm II \, ref} - A_{\rm ref}$$
$$= A_{\rm I}' + A_{\rm II}' + kT \, \ln \frac{(V/N)^{N}}{(V_{\rm I}/N_{\rm I})^{N_{\rm I}} (V_{\rm II}/N_{\rm II})^{N_{\rm II}}},$$
(154)

where $A_{J \text{ ref}}$, A'_{J} , V_{J} and N_{J} are the ideal reference state free energy, ideal reduced free energy, volume and number of molecules of phase J. $V = V_{\text{I}} + V_{\text{II}}$ and $N = N_{\text{I}} + N_{\text{II}}$ are the volume and number of molecules of the total system. Expressing the ideal reduced free energy of each phase via Eqs. 22 and 29 we have

$$A' = kT \ln \langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{I}} - kT \ln \epsilon_{\mathrm{I}} + kT \ln \langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{II}} - kT \ln \epsilon_{\mathrm{II}}$$
$$+ kT \ln \frac{(V/N)^{N}}{(V_{\mathrm{I}}/N_{\mathrm{I}})^{N_{\mathrm{I}}} (V_{\mathrm{II}}/N_{\mathrm{II}})^{N_{\mathrm{II}}}}$$
(155)

and hence combining with Eq. 153 we finally obtain

$$\langle \boldsymbol{\epsilon}^{\beta \mathscr{U}'} \rangle = \langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{I}} \langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{II}} \left(\frac{\overline{\boldsymbol{\epsilon}}(V/N)}{\overline{\boldsymbol{\epsilon}}_{\mathrm{I}}(V_{\mathrm{I}}/N_{\mathrm{I}})} \right)^{N_{\mathrm{I}}} \left(\frac{\overline{\boldsymbol{\epsilon}}(V/N)}{\overline{\boldsymbol{\epsilon}}_{\mathrm{II}}(V_{\mathrm{II}}/N_{\mathrm{II}})} \right)^{N_{\mathrm{II}}},$$
(156)

where

$$\overline{\boldsymbol{\epsilon}} = \boldsymbol{\epsilon}^{1/N}, \tag{157}$$

the positive real *N*th root of ϵ , is the overall *molecular* phase-space fraction, and

$$\overline{\epsilon}_{\rm I} = \epsilon_{\rm I}^{1/N_{\rm I}},\tag{158}$$

$$\overline{\boldsymbol{\epsilon}}_{\mathrm{II}} = \boldsymbol{\epsilon}_{\mathrm{II}}^{1/N_{\mathrm{II}}},\tag{159}$$

are the molecular phase-space fractions of the two phases. From Eq. 156 it is evident that the moment generating function of a biphasic system has a complexity, which is in general (much) higher than the complexity of the moment generating functions of its single phases, being even more complex than the product of the two.

The fact that the moment generating function of a macroscopic biphasic system is not identical to the product of its single-phase moment generating functions, although the overall partition function can be factorized (Eq. 152), means that the potential energy distributions of the two phases are not completely statistically independent of each other. This residual correlation between the two subparts is due to the fact that we have considered two subsystems with different density, while this correlation would disappear if we subdivide the whole system into parts of identical density and composition.

In fact in the latter case, now denoting with Q_{I} and Q_{II} the partition functions of two identical macroscopic halves of the whole system, each being multiphasic if the whole system is multiphasic, since in this case

$$\overline{\epsilon}_{\mathrm{I}} = \overline{\epsilon}_{\mathrm{II}} = \overline{\epsilon}, \tag{160}$$

$$V_{\rm I} = V_{\rm II} = \frac{1}{2} V,$$
 (161)

$$N_{\rm I} = N_{\rm II} = \frac{1}{2} N, \tag{162}$$

and

$$\langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{I}} = \langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{II}} = G(\beta).$$
 (163)

Eq. 156 reduces to

$$\langle e^{\beta \mathscr{U}'} \rangle = \langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{I}} \langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{II}} = G(\beta)^2.$$
(164)

The last equation shows that if we subdivide the whole system in this way, the moment generating function is given exactly by the product of the ones of its subparts, implying that the potential energy distributions of the subparts are now completely statistically independent. Hence, subdividing further each subpart into two identical halves and so forth until we reach the size of a single (multiphase) elementary system (the smallest thermodynamic subsystem that can be considered fully independent from the rest), from Eqs. 163 and 164 we finally obtain

$$\langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{I}} = \langle e^{\beta \mathscr{U}'} \rangle_{\mathrm{II}} = g(\beta)^{n/2},$$
(165)

$$\langle e^{\beta \mathscr{U}'} \rangle = g(\beta)^{n/2} g(\beta)^{n/2} = g(\beta)^n, \qquad (166)$$

where $g(\beta)$ and *n* are the moment generating function and the number of the elementary systems contained within the whole system and $n \rightarrow \infty$ in a macroscopic condition. Eqs. 165 and 166 show that the moment generating function of every macroscopic system is always fully defined by the moment generating function of the corresponding (multi-phase) elementary system.

B. Temperature limits

In this section we will derive from general statistical mechanical considerations the zero and infinite temperature limits of various thermodynamic properties. We will than show that in the infinite temperature limit the statistical states described in section III are always consistent with these general results, and in the zero temperature limit the statistical states which can be considered completely physically possible even close to T=0 (the Γ_+ and IG₊ states, where the potential energy has a lower limit) are consistent with classical statistical mechanics.

1. Infinite temperature limit

We can define in general from Eq. 22 the confined ideal reduced free energy as

$$A^{*} = kT \ln \langle e^{\beta \mathscr{U}'} \rangle = -kT \ln \frac{\int '^{*} e^{-\beta \mathscr{U}'} d\mathbf{x}}{\int '^{*} d\mathbf{x}}$$
$$= -kT \ln \langle e^{-\beta \mathscr{U}'} \rangle_{*\text{ref}}$$
(167)

which also implies

$$A^* = U^{*\text{ref}} - kT \ln \left\{ 1 + M_2^{*\text{ref}} \frac{\beta^2}{2} - M_3^{*\text{ref}} \frac{\beta^3}{3!} + \cdots \right\},$$
(168)

where M_n^{ref} is the *n*th central potential energy moment evaluated in the confined ideal reference ensemble and $U^{\text{ref}} = \langle \mathscr{U}' \rangle_{\text{ref}}$ is the corresponding average potential energy, which are clearly temperature independent. Since for every temperature A^* is finite, it follows that all the moments in Eq. 168, which are identical to the infinite temperature ones of the system, are finite as well. Therefore

$$\lim_{T \to \infty} U' = U^{*\text{ref}},\tag{169}$$

$$\lim_{T \to \infty} C_V' = \lim_{T \to \infty} \frac{M_2^{*\text{ret}}}{kT^2} = 0,$$
(170)

and by expanding the logarithm in Eq. 168

$$\lim_{T \to \infty} A^* = U^{*\text{ref}},\tag{171}$$

and hence

$$\lim_{T \to \infty} TS^* = \lim_{T \to \infty} S^* = 0.$$
(172)

So, considering that $(\partial S^*/\partial T)_V = C'_V/T$ and $C'_V \ge 0$ it follows that $S^* \le 0$. Moreover,^{1,2}

$$\lim_{T \to \infty} \alpha^* = -\frac{1}{2} \tag{173}$$

and then

$$\lim_{T \to \infty} \alpha = \lim_{T \to \infty} \alpha^* + \lim_{T \to \infty} \frac{k \ln \epsilon}{C'_V(T)} = -\infty.$$
(174)

From the definition of δ we also have

$$\lim_{T \to \infty} \delta = \lim_{T \to \infty} \frac{M_3^{*\text{ref}}}{2M_2^{*\text{ref}}kT} = 0, \qquad (175)$$

and hence, using $\gamma = (2/3)\delta$, we find $\lim_{T\to\infty} \gamma = 0$. Finally, the infinite temperature limit of the confined ideal reduced pressure $p^* = -(\partial A^*/\partial V)_T$ is

$$\lim_{T \to \infty} p^* = -\frac{dU^{*\text{ref}}}{dV},\tag{176}$$

which is in general finite, so $\lim_{T\to\infty} p' = \infty$ for $\xi > 0$ (see Eq. 33).

From Table I it is evident that all the statistical states described in section III are consistent with these general infinite temperature limits. If moreover the confinement is exact (i.e., really temperature independent) even the full ideal reduced temperature limits (given between square brackets in Table I) are completely correct.

2. Zero temperature limit

For a pure classical system even for temperatures very close to zero, we can express the confined ideal reduced free energy as

$$A^* = -\frac{1}{\beta} \ln \frac{\int'^* e^{-\beta \mathscr{U}'} d\mathbf{x}}{\int'^* d\mathbf{x}}.$$
(177)

Therefore, since²⁴ $\lim_{\beta\to\infty} \int \frac{x}{2} \exp\{-\beta \mathcal{U}'\} dx / \int \frac{dx}{dx} = 0$, we can use L'Hospital's rule²⁰ to obtain

$$\lim_{\beta \to \infty} A^* = \lim_{\beta \to \infty} U' = \mathscr{U}'_{\min}, \qquad (178)$$

with \mathscr{U}'_{\min} the minimum possible potential energy, which must be finite, and hence

$$\lim_{T \to 0} S^* = \lim_{T \to 0} \frac{U' - A^*}{T}$$
$$= \lim_{T \to 0} \left[\frac{\langle \mathscr{U}' \rangle - \mathscr{U}'_{\min}}{T} + k \ln \frac{\int'^* e^{-\beta(\mathscr{U}' - \mathscr{U}'_{\min})} d\mathbf{x}}{\int'^* d\mathbf{x}} \right]$$
$$= \lim_{T \to \infty} \left[C'_V + k \ln \frac{\int'^* e^{-\beta(\mathscr{U}' - \mathscr{U}'_{\min})} d\mathbf{x}}{\int'^* d\mathbf{x}} \right].$$
(179)

In the last expression the last term clearly tends to $-\infty$, and therefore if C'_V tends to a finite value S^* (and hence S') will

tend to $-\infty$. If C'_V tends to $+\infty$, the entropy will tend to $-\infty$ as well, since applying L'Hospital's rule again to the first line of Eq. 179 we have

$$\lim_{T \to 0} S^* = \lim_{T \to 0} [C'_V + S^*].$$
(180)

Remembering that $S^* \leq 0$ this last equation implies that if $C'_V \rightarrow +\infty$, both S^* and S' must tend to $-\infty$. Hence

$$\lim_{T \to 0} \alpha^* = \lim_{T \to 0} \alpha \leq -1.$$
(181)

Note that if the limit if C'_V is finite, α^* and α must tend to $-\infty$. Finally, from Eq. 178 it follows that

$$\lim_{T \to 0} p^* = \lim_{T \to 0} p' = -\frac{d\mathcal{U}_{\min}}{dV} = 0,$$
(182)

where in the last equation the volume derivative would not be zero in the very unusual case where the overall volume is smaller than the volume of the classical crystal where all the atoms are at the positions of their overall lower energy limit.

The requirement that \mathscr{U}'_{\min} is finite, implies that at very low temperature only the Γ_+ and IG₊ states can be used as a proper description of the system. These states are consistent with classical statistical mechanics, even in the zero temperature limit, see Table II. The Gaussian state, for example, does not fulfill Eq. 181. For the Γ_- and IG₋ states, the zero temperature limits are even impossible, because of the occurance of a singularity at T_* , given by Eqs. 113 and 138. If in the low temperature regime the system is still within an exact Γ_+ or IG₊ state, Eq. 182 yields an extra relation between δ_0 (or γ_0), p_0^* , $(\partial p_0^*/\partial T)_V$ and $(\partial^2 p_0^*/\partial T^2)_V$ of the form

$$p_0^* + A_{01} T_0 \left(\frac{\partial p_0^*}{\partial T} \right)_V + A_{02} T_0^2 \left(\frac{\partial^2 p_0^*}{\partial T^2} \right)_V = 0.$$
(183)

However, for real systems this relation cannot be used, because of the emerging quantum character at low temperature.

It is also important to note that in the zero temperature limit a classical system does not have to converge to a harmonic one. In fact, this harmonic condition is obtained when both the overall energy lower limit is really an energy minimum (with continuous and zero forces) and the potential energy close to the minimum can be described by a second order expansion (with non-zero continuous force derivatives). It is obvious that these conditions are not fulfilled by every type of potential energy function, implying that there is no general rule for the zero temperature limit of the heat capacity, which can be even infinite, as for the IG_+ state.

C. Phase-space confinement

A very simple model for the phase-space confinement as introduced in Eq. 17 is excluded volume due to "hard body" interactions. If, because of the strong Pauli repulsions at close contact, it is possible to define for (almost) spherical molecules like water an interparticle distance $\sigma_{\rm HS}=2r_{\rm HS}$ at which the two-particle interaction energy is virtually infinite

in the temperature range of interest, the confined ideal reference state can be described as a hard sphere (HS) system.^{13,25} Using the Carnahan-Starling equation of state (EOS),²⁶

$$p_{\rm HS} = \rho_N k T \left[\frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \right]$$
(184)

with $p_{\rm HS}$ the pressure, $\eta = v \rho_N$, ρ_N the number density, $v = \pi \sigma_{\rm HS}^3/6$ the hard-sphere volume per molecule and $\sigma_{\rm HS}$ the hard-sphere diameter, we obtain²⁵ for the excess Helmholtz free energy, Eq. 16

$$A'_{\rm ref} = -NkT \left[\frac{3 \eta^2 - 4 \eta}{(1 - \eta)^2} \right] = -NkT \ln \overline{\epsilon}_{\rm HS}, \qquad (185)$$

where $\overline{\epsilon}_{\text{HS}} = \epsilon_{\text{HS}}^{1/N}$ is the hard sphere phase-space fraction *per molecule*. Hence

$$\overline{\epsilon}_{\rm HS} = \exp\left\{\frac{3\,\eta^2 - 4\,\eta}{(1-\eta)^2}\right\} \tag{186}$$

and

$$\xi_{\rm HS} = Nk \, \frac{d \, \ln \,\overline{\epsilon}_{\rm HS}}{dV} = -\frac{Nk}{V} \left[\frac{2\,\eta^2 - 4\,\eta}{(1-\eta)^3} \right] \tag{187}$$

which is always positive since $\eta < 1$. Within this model, p^* is the pressure of the system with respect to a HS fluid at the same temperature and density. We will show that for water Eq. 186 provides a good description of the experimentally observed phase-space fractions. Note that since water does not have any intramolecular interactions ($\psi=0$), the reduced properties are identical to the ideal reduced ones.

In Ref. 2 we presented for water values of $\overline{\epsilon}$ and δ for a confined Gamma state at various liquid densities, calculated from experimental values of S^r , C_V^r and $\partial C_V^r / \partial T$ (i.e., δ was calculated from C_V^r and $\partial C_V^r / \partial T$, Eq. 92, yielding S^* , Eq. 98, and hence $\overline{\epsilon} = \exp\{(S_{\exp}^r - S^*)/Nk\})$. Values of $\overline{\epsilon}$ were evaluated at two different temperatures (T_0 and 653 K) and were consistent within the accuracy, indicating that a confined Gamma state is a very good description of the real physical state at those liquid conditions. We now extended these calculations at T_0 to the low-density region as well, see Fig. 2 (open diamonds). Clearly, apart from some noise, we see a gradual decrease of $\overline{\epsilon}$ with the density, i.e., an increasing confinement.

FIG. 2. Molecular phase-space fraction $\overline{\epsilon}$ of water as a function of density. Legend: from entropy fit (\blacklozenge), from values of $\partial C_{V0}^r/\partial T$ at T_0 , partly from Ref. 2 (\diamondsuit), other values from Ref. 2 at T_0 (+) and 653 K (×) and HS confinement, Eq. 186, using $\sigma_{\rm HS}$ =2.70 Å (—).

In order to reduce the noise, we calculated values of $\overline{\epsilon}$ and δ_0 for all the densities by least-square fitting Eq. 98 on the experimental reduced entropy data, denoted by $\overline{\epsilon}_{\rm fit}$ and $\delta_{0 \text{ fit}}$. We feel that this procedure is allowed, since the temperature at which $\overline{\epsilon}$ is evaluated does not seem to affect the value. Results are given in Fig. 2 (filled diamonds) and Table III. From the figure and the table it is clear that the values of $\overline{\epsilon}$ and δ_0 obtained from the entropy fit are in good agreement with the previous values ($\overline{\epsilon}_{T_0}$ and $\overline{\epsilon}_{653}$), based on $\partial C_V^r / \partial T$. We then fitted a HS confinement curve (Eq. 186) through the data, yielding $\sigma_{\rm HS}$ =2.70 Å, see Fig. 2. In the table we also give these $\overline{\epsilon}_{\rm HS}$ values and the corresponding $\delta_{0\,\rm HS}$ values, obtained by solving $\delta_{0 \text{ HS}}$ from $S_{0 \text{ exp}}^r$ – $Nk \ln \overline{\epsilon}_{\text{HS}}$ $= C_{V0}^{r} [1/\delta_{0 \text{ HS}} + 1/\delta_{0 \text{ HS}}^{2} \ln(1 - \delta_{0 \text{ HS}})].$ All the data are consistent within the experimental accuracy, implying among others that the $\delta_{0 \text{ HS}}$ values in fact can be considered as "exact" values. Especially from the values of $\delta_{0 \text{ fit}}$ and $\delta_{0 \text{ HS}}$ in the liquid regime, it is clear that, increasing the density, the energy distribution gradually changes from a left-handed (Gamma) distribution, via a Gaussian (37 mol/dm³) into a right-handed (Gamma) distribution, as already stated in Ref.

TABLE III. $\overline{\epsilon}$ and δ_0 parameters for liquid water.

$\frac{\rho_N}{(\text{mol/dm}^3)}$	Т ₀ (К)	$\overline{oldsymbol{\epsilon}}_{T_0}{}^{\mathrm{a}}$	$\overline{\epsilon}_{653}{}^{\mathrm{b}}$	$\overline{\epsilon}_{\rm fit}^{\ \rm c}$	$\overline{\epsilon}_{\mathrm{HS}}^{\mathrm{d}}$	${\delta_0}^{ m a}$	$\delta_{0\ { m fit}}{}^{ m c}$	$\delta_{0~{ m HS}}{}^{ m e}$
30.38	653.0	0.42(0.37)	0.37	0.33	0.37	-0.13(-0.23)	-0.49	-0.27
37.24	613.0	0.21(0.35)	0.32	0.28	0.28	-0.26(0.22)	0.05	0.02
42.69	563.0	0.24(0.33)	0.26	0.26	0.21	0.30(0.44)	0.35	0.22
49.00	513.0	0.15(0.24)	0.20	0.22	0.15	0.34(0.49)	0.49	0.31
55.32	313.0	0.09(0.14)	~ 0.22	0.11	0.09	0.49(0.57)	0.49	0.49

^aFrom Ref. 2, evaluated at T_0 with two different methods to obtain $\partial C_{V0}^r / \partial T$.

^bFrom Ref. 2, evaluated at T=653 K.

^cFrom least-square fitting Eq. 98 to experimental entropy data.

^dFrom least-square fitting Eq. 186 to $\overline{\epsilon}_{fit}$ values.

^eUsing $\overline{\epsilon}_{HS}$ values, see text.

TABLE IV. Molecular (hard sphere) radii of water.

Method	r (Å)
HS confinement fit on $\overline{\epsilon}^{a}$	1.35
HS $g_{OO}(r)^{b}$	1.27
1	1.32
$\overline{2} \sigma_{\rm LJ}^{\rm c}$	
b parameter van der Waals EOs ^d	1.44
b parameter Redlich-Kwong/Soave EOS ^e	1.28
b parameter Peng-Robinson EOS ^f	1.24
van der Waals radius oxygen ^g	1.40

^aFit of Eq. 186 on experimental $\overline{\epsilon}$ values, see text and Fig. 2.

^bBy fitting the height of the first peak of the oxygen-oxygen radial distribution function (RDF) at 300 K and 1.0 g/ml (Ref. 5) to the HS RDF (Ref. 39).

^cFrom the Lennard-Jones σ parameter, based on viscosity data (Ref. 27). ^dFrom the *b* parameter of the van der Waals EOS (Ref. 27), where $b = (1/8)RT_c/p_c$ and using the relation $b = 2\pi\sigma_{\text{HS}}^3/3$ (Ref. 13); the critical parameters T_c and p_c were taken from Ref. 36.

^eIdem via the Redlich-Kwong or Soave EOS, where $b = 0.08664RT_c/p_c$ (Ref. 27).

^fIdem via the Peng-Robinson EOS, where $b = 0.07780RT_c/p_c$ (Ref. 27). ^gReference 40.

2. Another implication is the fact that at least for water the $\Gamma_{-} \rightarrow \Gamma_{+}$ transition of the effective Gamma states (i.e., approximate Gamma state descriptions without confinement)² at low density is for the greater part due to the HS confinement; using the confinement the energy distribution is left-handed over the whole temperature range, see also section IV D.

In Table IV we present some radii which are an indication of the possible HS radius of water. All values are very close to our value of $r_{\rm HS}$ =1.35 Å, implying that our value is physically meaningful. Also Pierotti⁴¹ points out that various methods, including the Scaled Particle Theory, yield an average radius of ~1.35 Å. The results based on the *b* parameter of the different cubic equations of state (basically modified van der Waals equations^{13,27}), like the Redlich-Kwong,²⁸ Soave²⁹ and Peng-Robinson³⁰ EOS, are perhaps somewhat fortuitous, since it is known that they are not very suited for polar molecules.²⁷ However, the *b* parameters are calculated via critical properties (the critical temperature T_c and pressure p_c) and the relation between *b* and the HS volume is valid in the low density limit, where these EOS still might be reasonable.

At this point it must be stressed that there is in fact a (rather narrow) window of $\overline{\epsilon}$ and δ_0 values, which are consistent with the experimental data. However, within the accuracy of the experimental data, it is very difficult to distinguish between these values. Moreover, the values of for example $\partial C_V^r / \partial T$ are (probably) much affected by the specific choice of the EOS used to collect and present all the real (often inconsistent) experimental data in consistent thermodynamic tables. So from a pragmatic point of view, it is much better to use a HS model for the $\overline{\epsilon}$ and ξ values, and then to calculate $\delta_{0 \text{ HS}}$ or $\gamma_{0 \text{ HS}}$ values, based on the heat capacity and entropy at one temperature T_0 only.

For larger molecules lacking an almost spherical shape a simple HS description may not be sufficient. For non-

spherical molecules several equations of state have been proposed.^{31–35} For hard ellipsoid-of-revolution (HER) fluids with length to breath ratio κ , Maeso and Solana³² for example proposed a generalized Carnahan-Starling EOS, with κ -dependent coefficients $a_i(\kappa)$:

$$p_{\rm HER} = \rho_N kT \bigg[\frac{1 + a_1(\kappa) \,\eta + a_2(\kappa) \,\eta^2 + a_3(\kappa) \,\eta^3}{(1 - \eta)^3} \bigg], \quad (188)$$

where

$$a_1(\kappa) = -1.18 + 1.09/\kappa + 1.09\kappa,$$

$$a_2(\kappa) = -1.92 + 1.59/\kappa + 1.33\kappa$$

and

$$a_3(\kappa) = 5.23 - 2.91/\kappa - 2.96\kappa$$

for $1/3 < \kappa < 3$, yielding

$$\overline{\epsilon}_{\text{HER}} = (1 - \eta)^{(1 + a_3)} \\ \times \exp\left\{\frac{\frac{1}{2}(3 + a_1 - a_2 - 3a_3)\eta^2 - (2 + a_1 - a_3)\eta}{(1 - \eta)^2}\right\}$$
(189)

and

$$\xi_{\text{HER}} = -\frac{Nk}{V} \left[\frac{-(1+a_3)\eta^3 + (3-a_2)\eta^2 - (3+a_1)\eta}{(1-\eta)^3} \right].$$
(190)

These equations reduce to the HS ones (Eqs. 184, 186 and 187) for $a_1 = a_2 = 1$ and $a_3 = -1$, and may be used for more complex molecules.

D. Entropy, heat capacity and pressure results

For three different densities (9.038, 37.24 and 55.32 mol/dm³) we will compare the results of the confined Gaussian, Gamma and Inverse Gaussian states and the constant alpha approximation with the experimental data, 36,37 see also Ref. 2 for further details. It should be noted that there is substantial noise especially in the experimental heat capacity data at higher density, although already calculated from a 6th order polynomial fit on the reduced entropy data, probably due³⁸ to the shape of the EOS, used to produce the steam tables of Burnham et al.³⁷ We use the HS confinement values $\overline{\epsilon}_{\text{HS}}$, ξ_{HS} and $\delta_{0 \text{ HS}}$ from the previous section, with $\sigma_{\rm HS}$ =2.70 Å (based on a Gamma state analysis), and $\gamma_{0 \rm HS}$ for the IG state, obtained in a similar way as $\delta_{0 \text{ HS}}$, i.e., by solving $\gamma_{0 \text{ HS}}$ from $S_{0 \text{ exp}}^r - Nk \ln \overline{\epsilon}_{\text{HS}} = C_{V0}^r [1/\gamma_{0 \text{ HS}} + 1/\gamma_{0 \text{ HS}}^2(1 - \sqrt{1 - 2\gamma_{0 \text{ HS}}})]$. We will compare the reduced entropy, heat capacity and pressure, since with these properties all other properties can be reconstructed. Within the constant alpha approximation, the pressure is calculated using Eqs. 150 and 151, since for the equivalent Eqs. 148 and 149 the accuracy on the experimental values of $\partial \alpha_0 / \partial V$ is not enough. It should be mentioned once more, that since water has no intramolecular interactions, the reduced properties are in this case identical to the ideal reduced ones.

At 9 mol/dm³ (dense gas condition) the potential energy distribution is left-handed, since $\delta_{0 \text{ HS}} = -1.99$



FIG. 3. Results for water at ρ_N =9.038 mol/dm³: reduced entropy *S^r*. Legend: experimental (\blacklozenge), confined Gaussian (---), confined Gamma (—) and confined IG (···), using a HS confinement with $\sigma_{\rm HS}$ =2.70 Å, and constant alpha (-···-).

 $(\gamma_{0 \text{ HS}} = -1.45)$ at $T_0 = 661$ K. The confined Gamma and IG results are almost identical, and agree very well with the experimental data over a temperature range of at least 500 K, see Figs. 3, 4 and 5. Obviously the Gaussian state gives worse results, since the energy distribution is quite asymmetric (note especially the shift in the entropy, because $\alpha_0^* =$ - 0.226, instead of $-\frac{1}{2}$). Since for lower density systems with a small confinement ($\overline{\epsilon}_{HS}$ =0.79 in this case) the intrinsic entropy function is not all temperature independent² (see Eq. 139), also the constant alpha approximation, being a local approximation, is much worse than the Gamma and IG states: the entropy for example is reproduced only within a temperature range of \sim 75 K. As already mentioned in the previous section, at least for water the $\Gamma_- \rightarrow \Gamma_+$ transition of the effective Gamma states (i.e., approximate Gamma state descriptions without confinement)^{1,2} at low density is for the



FIG. 5. Results for water at ρ_N =9.038 mol/dm³: reduced pressure p^r . Legend: experimental (\blacklozenge), confined Gaussian (---), confined Gamma (—) and confined IG (···), using a HS confinement with $\sigma_{\rm HS}$ =2.70 Å, and constant alpha (-···-).

greater part due to the HS confinement. At least within the range of 500 K the energy distribution remains left-handed.

From Table III it is clear that at 37 mol/dm³ (low density liquid) the statistical state is almost Gaussian, since $\delta_{0 \text{ HS}} = 0.02 (\gamma_{0 \text{ HS}} = 0.015)$ at $T_0 = 613$ K. This is also evident from Figs. 6, 7 and 8, where the Gaussian state predictions are very close to the Gamma and IG ones and all agree very well with the experimental data over a range of at least 500 K. The Gamma and IG results obviously are identical, since both states converge to the Gaussian state for δ_0 or γ_0 tending to zero. Clearly, at this not too high density with $\overline{\epsilon}_{\text{HS}} = 0.32$, the constant alpha approximation, being a local approximation, breaks down after ~200 K for the entropy and heat capacity. The pressure results, however, are very good, although this may be a little bit fortuitous.



-12.0 -14.0-16.0 Reduced entropy S^r (J/mol K) -18.0 -20.0-22.0 -24.0 -26.0600 700 800 900 1000 1100 Temperature (K)

FIG. 4. Results for water at ρ_N =9.038 mol/dm³: reduced heat capacity C'_V . Legend: experimental (\blacklozenge), confined Gaussian (---), confined Gamma (—) and confined IG (···), using a HS confinement with $\sigma_{\rm HS}$ =2.70 Å, and constant alpha (-···-).

FIG. 6. Results for water at ρ_N =37.24 mol/dm³: reduced entropy *S^r*. Legend: experimental (\blacklozenge), confined Gaussian (---), confined Gamma (—) and confined IG (…), using a HS confinement with $\sigma_{\rm HS}$ =2.70 Å, and constant alpha (----).



FIG. 7. Results for water at ρ_N =37.24 mol/dm³: reduced heat capacity C'_V . Legend: experimental (\blacklozenge), confined Gaussian (---), confined Gamma (—) and confined IG (···), using a HS confinement with $\sigma_{\rm HS}$ =2.70 Å, and constant alpha (-···-).

Turning to the highest density (55 mol/dm³), where we have a right-handed potential energy distribution $(\delta_{0 \text{ HS}}=0.49, \gamma_{0 \text{ HS}}=0.31 \text{ at } T_0=313 \text{ K})$, we see that the Gamma and IG results are virtually identical for all properties, even for this value of $\delta_{0 \text{ HS}}$, and again agree very well with the experimental data over a range of at least 500 K, see Figs. 9, 10 and 11. Since $\delta_{0 \text{ HS}}=0.49$, the Gaussian state is clearly not sufficient in this case (note especially the shift in the entropy, as $\alpha_0^* = -0.771$). The constant alpha approximation, however, although less accurate than the Gamma and IG states, gives satisfactory results at this high density with a strong confinement ($\overline{\epsilon}_{\text{HS}}=0.09$), which seems to be the case for many different liquids at high density.^{1,2}



FIG. 8. Results for water at ρ_N =37.24 mol/dm³: reduced pressure p^r . Legend: experimental (\blacklozenge), confined Gaussian (---), confined (—) and confined IG (···), using a HS confinement with $\sigma_{\rm HS}$ =2.70 Å, and constant alpha (----).



FIG. 9. Results for water at ρ_N =55.32 mol/dm³: reduced entropy S^r. Legend: experimental (\blacklozenge), confined Gaussian (---), confined Gamma (—) and confined IG (···), using a HS confinement with $\sigma_{\rm HS}$ =2.70 Å, and constant alpha (-···-).

V. CONCLUSIONS

The basis of the quasi-Gaussian entropy theory is the fact that the *excess* Helmholtz free energy (or entropy), i.e., with respect to a proper reference state, can be expressed in terms of the moment generating function of the potential energy distribution (Eqs. 22 and 36), therefore reducing the statistical mechanical description, which is usually based on the high-dimensional configurational partition function, to a one-dimensional problem. Furthermore, because of the macroscopic character of usual systems, the central limit theorem can be used to show that this potential energy distribution can be described by a uninormal distribution function, close to a Gaussian ("quasi-Gaussian").

In this article we derived the quasi-Gaussian entropy theory, using slightly different, but more convenient refer-

60.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 40.0 50.0 50.0 40.0 50.0 50.0 40.0 50.0

FIG. 10. Results for water at ρ_N =55.32 mol/dm³: reduced heat capacity C'_V . Legend: experimental (\blacklozenge), confined Gaussian (---), confined Gamma (—) and confined IG (···), using a HS confinement with $\sigma_{\rm HS}$ =2.70 Å, and constant alpha (-···-).

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FIG. 11. Results for water at ρ_N =55.32 mol/dm³: reduced pressure p^r . Legend: experimental (\blacklozenge), confined Gaussian (---), confined Gamma (—) and confined IG (···), using a HS confinement with $\sigma_{\rm HS}$ =2.70 Å, and constant alpha (-···-).

ence states than the ones used previously to derive the basic theory.^{1,2} Moreover, we now included a general description of the possible confinement of the system within a part of phase space (configurational space). Although the theory is in principle valid for single-phase, as well as multi-phase systems, specific attention is paid to the conditions in the latter case, concerning the use of the central limit theorem and the moment generating function. We also showed that the generalized Pearson system of distributions, which we used to generate and classify different uninormal distributions of increasing complexity, follows directly from the statistical mechanical definition of the energy distribution.

The excess Helmholtz free energy, internal energy, entropy and heat capacity are defined by the potential energy distribution, the parameters of which can be always expressed in terms of the excess heat capacity and a limited set of its temperature derivatives, and their temperature dependence follows from the solution of the thermodynamic master equation (Eq. 48). In this article we derived a new differential equation, the conjugated pressure equation (Eq. 60 or 61), the solution of which yields the temperature dependence of the excess pressure and hence of the enthalpy and Gibbs free energy. Therefore each type of potential energy distribution provides the complete excess thermodynamics of the system at constant density, and hence defines a different statistical state.

For the Gaussian, Gamma and Inverse Gaussian (IG) distribution we derived the corresponding thermodynamics and showed that in the infinite temperature limit all the statistical states are consistent with statistical mechanics, and in the zero temperature limit the statistical states with a finite energy lower limit (the Γ_+ and IG₊ states, defined by the right-handed Gamma and IG distributions) are still completely consistent with classical statistical mechanics.

For water we showed that the confinement of the system within a part of phase space can be modeled very well by the

excluded volume of a hard sphere (HS) fluid, yielding a HS diameter $\sigma_{\rm HS}$ =2.70 Å, which is in agreement with values obtained from other methods. Using this HS confinement, for three different densities (dense gas, low and high-density liquid) we compared the results of the different statistical states with experimental entropy, heat capacity and pressure data, indicating that both the Gamma and IG states give excellent results within a temperature range of at least 500 K. If the quantities δ or γ (Eq. 92 and 117), which are a measure of the asymmetry of the distribution, are approximately zero within the accuracy, also the Gaussian state can be used successfully.

Finally, we also compared the experimental data with the constant alpha approximation, merely a local approximation, which is valid for high density liquids within a certain temperature range, especially for the prediction of the Helmholtz free energy. Because of its simplicity, though, it is very suited for approximate applications, like for example the calculation of the liquid-vapour equilibrium pressure along the coexistence line, where the accuracy of this approximation is comparable to that of the Gamma state previously used.⁴

It is interesting to note that a similar derivation of this theory in the isothermal-isobaric ensemble (NpT), expressing the excess Gibbs free energy in terms of the moment generating function of the instantaneous enthalpy distribution, and hence expressing the entropy in terms of (a limited set of temperature derivatives of) the isobaric heat capacity, although very appealing from a practical point of view, is not possible in a rigorous way. The reason is the fact that the ideal reference state in that case would be a system with no inter and intramolecular interactions ($\Phi = \psi = 0$) at exactly zero pressure. The latter implies that the excess Gibbs free energy of the system is infinite and therefore we cannot use this "exact" reference condition. However, we showed that it is still possible for gases to use this theory for the potential energy distribution in the NpT ensemble, although in an approximate way, by chosing a proper reference state, see Ref. 3.

The fact that already relatively simple statistical states reproduce with high accuracy, both for liquids and gases, the temperature dependence of all thermodynamic properties at fixed density (in the liquid regime much better than usual equations of state, like the van der Waals, Peng-Robinson, Soave or Redlich-Kwong equations), implies that this theory could provide the basis for a general, fully physically consistent fluid equation of state. In a forthcoming article, we will describe the use of the quasi-Gaussian entropy theory in different ensembles, and derive in this way the density dependence of the thermodynamic properties, which might be used to construct a complete equation of state, combining temperature and density dependence.

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APPENDIX

J

In general for a molecular system in the classical limit the atomic motions, not involving changes in bond lengths and bond angles, can be described in a pure classical way, while the bond vibrations require a real quantum mechanical treatment. These quantum bond vibrations, however, virtually do not alter the bond lengths and angles from their equilibrium (ground state) values, implying that the other (classical) atomic motions are equivalent to the ones of a completely classical system in the presence of ideal holonomic constraint forces, which keep the bond lengths and angles fixed. Hence defining η as a set of generalized coordinates on the constraint surface (coordinates which define positions only on the surface) and π_{η} as their conjugated momenta, we can express the partition function for a system of N identical molecules in the electronic ground state as

$$Q = \frac{G^0 h^{-d}}{N!} \sum_{l} \int e^{-\beta(\mathscr{V}_c(\boldsymbol{\eta}, l) + \mathscr{K}_c(\boldsymbol{\eta}, \boldsymbol{\pi}_\eta))} d\boldsymbol{\eta} d\boldsymbol{\pi}_\eta, \quad (A1)$$

where \mathscr{V}_c and \mathscr{K}_c are the total potential (including vibrational) and kinetic energy functions, evaluated on the *d*-dimensional constraint surface. G^0 is the overall electronic ground state degeneracy factor (the electronic ground state energy has been included in \mathscr{V}_c), *h* Planck's constant and the summation runs over all accessible vibrational states $\{l\}$.

If we define **b** as the bond lengths and angles, b^0 as their equilibrium values and π_b as the corresponding conjugated momenta, we can rewrite the integral in Eq. A1 as

$$\int e^{-\beta(\mathscr{V}_{c}(\boldsymbol{\eta},l)+\mathscr{K}_{c}(\boldsymbol{\eta},\boldsymbol{\pi}_{\eta}))} d\boldsymbol{\eta} d\boldsymbol{\pi}_{\eta}$$

$$= \int e^{-\beta(\mathscr{V}(\boldsymbol{\eta},\boldsymbol{b},l)+\mathscr{K}(\boldsymbol{\eta},\boldsymbol{b},\boldsymbol{\pi}_{\eta},\boldsymbol{\pi}_{b}))} \delta(\boldsymbol{b}-\boldsymbol{b}^{0})$$

$$\times \delta(\boldsymbol{\pi}_{\boldsymbol{b}}-\boldsymbol{\pi}_{\boldsymbol{b}}^{0}) d\boldsymbol{\eta} d\boldsymbol{b} d\boldsymbol{\pi}_{\eta} d\boldsymbol{\pi}_{\boldsymbol{b}}, \qquad (A2)$$

where now the energy is evaluated in the whole phase space and $\pi_b^0(\eta, \pi_\eta)$ are the values of π_b on the constraint surface in such a way that $\dot{b}=0$.

For macroscopic systems Eq. A2 can be factorized as it follows from the fact that the integral on the momenta is virtually independent of the coordinates although the integrand generally is not. Hence

$$\int e^{-\beta(\mathscr{F}(\boldsymbol{\eta},\boldsymbol{b},l)+\mathscr{K}(\boldsymbol{\eta},\boldsymbol{b},\boldsymbol{\pi}_{\eta},\boldsymbol{\pi}_{b}))} \delta(\boldsymbol{b}-\boldsymbol{b}^{0})$$

$$\times \delta(\boldsymbol{\pi}_{b}-\boldsymbol{\pi}_{b}^{0}) d\boldsymbol{\eta} d\boldsymbol{b} d\boldsymbol{\pi}_{\eta} d\boldsymbol{\pi}_{b}$$

$$= \int e^{-\beta\mathscr{F}(\boldsymbol{\eta},\boldsymbol{b},l)} \delta(\boldsymbol{b}-\boldsymbol{b}^{0}) d\boldsymbol{\eta} d\boldsymbol{b} \int e^{-\beta\mathscr{K}(\boldsymbol{\eta}^{*},\boldsymbol{b}^{0},\boldsymbol{\pi}_{\eta},\boldsymbol{\pi}_{b})}$$

$$\times \delta(\boldsymbol{\pi}_{b}-\boldsymbol{\pi}_{b}^{0}(\boldsymbol{\eta}^{*},\boldsymbol{\pi}_{\eta})) d\boldsymbol{\pi}_{\eta} d\boldsymbol{\pi}_{b}, \qquad (A3)$$

where η^* , b^0 is an arbitrary configuration on the constraint surface. Now considering that when $\pi_b = \pi_b^0$ we have $\dot{b} = 0$, we can express the second integral on the right-hand side of Eq. A3 as

$$\int e^{-\beta \mathscr{H}(\boldsymbol{\eta}^*, \boldsymbol{b}^0, \boldsymbol{\pi}_{\eta}, \boldsymbol{\pi}_b)} \delta(\boldsymbol{\pi}_b - \boldsymbol{\pi}_b^0(\boldsymbol{\eta}^*, \boldsymbol{\pi}_{\eta})) d\boldsymbol{\pi}_{\eta} d\boldsymbol{\pi}_b$$
$$= \int e^{-\beta \mathscr{H}(\boldsymbol{\eta}^*, \boldsymbol{b}^0, \boldsymbol{\pi}_{\eta}, \dot{\boldsymbol{b}})} \frac{\delta(\dot{\boldsymbol{b}})}{J(\boldsymbol{\eta}^*, \boldsymbol{b}^0)} d\boldsymbol{\pi}_{\eta} d\boldsymbol{\pi}_b, \qquad (A4)$$

where $J(\boldsymbol{\eta}^*, \boldsymbol{b}^0)$ is the Jacobian for the transformation $\boldsymbol{\pi}_{\eta}$, $\boldsymbol{\pi}_b \rightarrow \boldsymbol{\pi}_{\eta}$, \boldsymbol{b} , evaluated at $(\boldsymbol{\eta}^*, \boldsymbol{b}^0)$, which is a function of the coordinates only and hence a constant for a given configuration. Using Eq. A4 in Eq. A3 and transforming $\boldsymbol{\eta}, \boldsymbol{b}, \boldsymbol{\pi}_{\eta},$ $\boldsymbol{\pi}_b \rightarrow \boldsymbol{x}. \boldsymbol{p}$, remembering that the Jacobian of the transformation from one set of generalized coordinates and conjugated momenta to any other is unity, we finally obtain

$$Q = \frac{G^0 h^{-d}}{N!} \sum_{l} \int e^{-\beta \mathcal{H}(\mathbf{x},l)} \delta(\mathbf{b} - \mathbf{b}^0) d\mathbf{x}$$
$$\times \int e^{-\beta \mathcal{H}(\mathbf{p})} \frac{\delta(\dot{\mathbf{b}})}{J(\mathbf{x}^0)} d\mathbf{p}$$
(A5)

with $x^0 = \eta^*, b^0$. Eq. A5 is therefore Eq. A1 expressed in terms of the usual coordinates and momenta x, p and describing the constraints in terms of the bonds properties and their time derivatives instead of using these properties and their conjugated momenta which are in general complicated functions involving the mass tensor. Hence with the notation previously¹ used to introduce the theory we have

$$Q = \frac{1}{N!} Q^e Q^{\rm kin} Q^{\rm pot} \tag{A6}$$

with

$$Q^e = \frac{G^0}{J(\mathbf{x}^0)},\tag{A7}$$

$$Q^{\text{pot}} = \sum_{l} \int e^{-\beta \mathscr{V}} \delta(\boldsymbol{b} - \boldsymbol{b}^{0}) d\boldsymbol{x} = \sum_{l} \int' e^{-\beta \mathscr{V}} d\boldsymbol{x}, \quad (A8)$$

$$Q^{\rm kin} = h^{-d} \int e^{-\beta \mathscr{K}} \delta(\dot{\boldsymbol{b}}) d\boldsymbol{p}, \qquad (A9)$$

where in the last equation we must calculate \dot{b} at the arbitrary position on the constraint surface x^0 .

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