Chapter 3

Description of different statistical states

In this Chapter we will describe the temperature dependence of thermodynamic properties for different statistical states. We subsequently discuss the states defined by the simplest solutions of the generalized Pearson system (Eq. 2.41), i.e., the Gaussian, Gamma and Inverse Gaussian state and compare the zero and infinite temperature limits of the corresponding thermodynamic properties with general statistical mechanical results. Also two approximate states, the effective Gamma and Inverse Gaussian state, are addressed.

Moreover we will describe the constant alpha approximation, which is not a real statistical state, but merely a local approximated solution of the thermodynamic master equation, Eq. 2.50. For this approximation no specific knowledge about the energy distribution is required.
### 3.1 Gaussian state

The symmetric Gaussian distribution corresponds to \( \{ m = 0, n = 0 \} \) in the generalized Pearson system, Eq. 2.41. The distribution is given by

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

with \( b_0 = M_2 \). Using the fact that the moment generating function of a Gaussian is simply

\[
G_{\Delta U'}(\beta) = \exp \left\{ \frac{b_0\beta^2}{2} \right\}
\]

and expressing \( M_2 \) in terms of \( C_V \) (Eq. 2.45), we obtain for the confined intrinsic entropy function

\[
\alpha^* = -\frac{1}{2}
\]

The thermodynamic master equation (TME), Eq. 2.50, therefore reduces to

\[
\left( \frac{\partial C_V'}{\partial T} \right)_V = -2 \frac{C_V'}{T}
\]

the solution of which provides for a confined Gaussian state

\[
\alpha^*(T) = -\frac{1}{2}
\]

\[
C_V'(T) = C_{V_0} \left( \frac{T_0}{T} \right)^2
\]

\[
S'(T) = -\frac{1}{2} C_{V_0} \left( \frac{T_0}{T} \right)^2 + k \ln \epsilon
\]

\[
U'(T) = U_0' + T_0 C_{V_0} \left( 1 - \frac{T_0}{T} \right)
\]

and

\[
A'(T) = U_0' + T_0 C_{V_0} \left( 1 - \frac{T_0}{2T} \right) - kT \ln \epsilon
\]

where \( U_0' \) and \( C_{V_0} \) 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. Note that we used the fact that the expression for $A'(T)$ is the complete and most general solution of the TME for a Gaussian state. Assuming this for each statistical state implies that at every density the statistical state (i.e., the thermodynamic complexity) is conserved, since there exists also a TME for the density dependence.\footnote{106}

Since $(\partial \alpha^*/\partial V)_T = 0$, the conjugated pressure equation (CPE), Eq. 2.62, is in this case a simple first order differential equation

$$\left( \frac{\partial p^*}{\partial T} \right)_V = -\frac{1}{2} T \left( \frac{\partial^2 p^*}{\partial T^2} \right)_V \quad (3.10)$$

The solution is

$$p^*(T) = p_0^* + T_0 \left( \frac{\partial p_0^*}{\partial T} \right)_V \left( 1 - \frac{T_0}{T} \right) \quad (3.11)$$

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. 3.11, using $p' = p^* + T \xi$ and $(\partial p'/\partial T)_V = (\partial p^*/\partial T)_V + \xi$ (Eq. 2.34):

$$p'(T) = p_0^* + T_0 \left\{ \left( \frac{\partial p_0^*}{\partial T} \right)_V - \xi \right\} \left( 1 - \frac{T_0}{T} \right) + \xi(T - T_0) \quad (3.12)$$

The $T \to \infty$ and $T \to 0$ limits of the various thermodynamic properties are summarized in Tables 3.1 and 3.2. It must be noted that only for the confined properties the infinite temperature limits are always physically meaningful, see also section 3.6.

### 3.2 Gamma state

The Gamma distribution, given by\textsuperscript{5, 78, 81}

$$\rho(\Delta U') = \frac{b_1 \left( b_1^2 / b_0^2 \right)^{b_0 / b_1^2} \Gamma \left( b_0 / b_1^2 \right)}{\Gamma \left( b_0 / b_1^2 \right)} \left( b_0 + b_1 \Delta U' \right)^{b_0 / b_1^2 - 1} \exp \left\{ -\frac{b_0 + b_1 \Delta U'}{b_1^2} \right\} \quad (3.13)$$

with $\Gamma(\cdot)$ the Gamma function,\textsuperscript{97} $b_0 = M_2$ and $b_1 = M_3/(2 M_2)$, corresponds to the $\{m = 0, n = 1\}$ solution of the generalized Pearson system, Eq. 2.41. The moment generating function of this Gamma distribution is\textsuperscript{5, 23, 24, 81}

$$G_{\Delta U}(\beta) = e^{-\beta b_0 / b_1^2} (1 - \beta b_1)^{-b_0 / b_1^2} \quad (3.14)$$

where, since $m + 1 = n$, we have $b_1 < kT$, see also Appendix D. 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. 2.45-2.46), the confined intrinsic entropy function is in this case given by\(^5\)

\[
\alpha^s = \frac{1}{\delta} + \frac{1}{\delta^2} \ln(1 - \delta) \tag{3.15}
\]

with

\[
\delta = \frac{M_3}{2kT M_2} = \frac{T (\partial C_V/\partial T)_V}{2C_V} + 1 \tag{3.16}
\]

The expression of \(\alpha^s\), combined with the general thermodynamic master equation (Eq. 2.50), yields

\[
T \left( \frac{\partial \alpha^s}{\partial T} \right)_V + (2\delta - 1) \alpha^s - 1 = 0 \tag{3.17}
\]

where \((\partial \alpha^s/\partial T)_V &= (d\alpha^s/d\delta)(\partial \delta/\partial T)_V\) and \((d\alpha^s/d\delta)\) follows from Eq. 3.15. After straightforward algebra we obtain as a simple form of the TME

\[
\left( \frac{\partial \delta}{\partial T} \right)_V = -\frac{\delta(1 - \delta)}{T} \tag{3.18}
\]

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\(^5,78\)

\[
\delta(T) = \frac{T_0 \delta_0}{T(1 - \delta_0) + T_0 \delta_0} \tag{3.19}
\]

\[
\alpha^s(T) = \frac{1}{\delta(T)} + \frac{1}{\delta^2(T)} \ln \{1 - \delta(T)\} \tag{3.20}
\]

\[
C_V(T) = C_{V0} \left( \frac{\delta(T)}{\delta_0} \right)^2 \tag{3.21}
\]

\[
S'(T) = \frac{C_{V0}}{\delta_0^2} [\delta(T) + \ln \{1 - \delta(T)\}] + k \ln \epsilon \tag{3.22}
\]

\[
U'(T) = U'_0 + (T - T_0) C_{V0} \frac{\delta(T)}{\delta_0} \tag{3.23}
\]

\[
A'(T) = U'_0 - \frac{T_0 C_{V0}}{\delta_0} - \frac{TC_{V0}}{\delta_0^2} \ln \{1 - \delta(T)\} - kT \ln \epsilon \tag{3.24}
\]

with \(\delta_0\) the value of \(\delta\) at \(T_0\). Note that \((\partial C_V/\partial T)_V\) is always negative,\(^38\) like in the Gaussian state.

Since for a Gamma state the pressure differential equation (Eq. 2.62) is very complicated, it is more convenient to obtain the confined ideal reduced pressure
Gamma state

via the volume derivative of \( A^*(T) \), using Eq. 3.24. Thus, with the usual notation where \((\partial U'_0/\partial V)\)_T etc. are the derivatives evaluated at \( T_0 \)

\[
p^*(T) = -\left[ \frac{\partial A^*}{\partial U'_0}(\frac{\partial U'_0}{\partial V})_T + \frac{\partial A^*}{\partial C'_V}(\frac{\partial C'_V}{\partial V})_T + \frac{\partial A^*}{\partial \delta_0}(\frac{\partial \delta_0}{\partial V})_T \right]
\]

where from general thermodynamic relations we have

\[
\left( \frac{\partial U'_0}{\partial V} \right)_T = T_0 \left( \frac{\partial p'}{\partial T} \right)_V - p'_0 
\]

\[
\left( \frac{\partial C'_V}{\partial V} \right)_T = T_0 \left( \frac{\partial^2 p'}{\partial T^2} \right)_V 
\]

and

\[
\left( \frac{\partial \delta_0}{\partial V} \right)_T = \frac{1}{C'_V} \left( \frac{\partial \alpha'_0}{\partial \delta_0} \right)^{-1} \left[ \left( \frac{\partial \alpha'_0}{\partial T} \right)_V - \alpha'_0 T_0 \left( \frac{\partial^2 \alpha'_0}{\partial T^2} \right)_V \right] 
\]

as follows from the CPE at \( T_0 \), with \((\partial \alpha'_0/\partial \delta_0)\) following from Eq. 3.15. The derivatives \( \partial A^*/\partial U'_0, \partial A^*/\partial C'_V \) and \( \partial A^*/\partial \delta_0 \) follow from Eq. 3.24. After tedious but straightforward algebra we finally obtain

\[
p^*(T) = p'_0 + B_0 + B^*_1 \frac{T}{T(1-\delta_0) + T_0 \delta_0} + B^*_2 \left( \frac{T}{T_0} \right) \ln \left\{ \frac{T(1-\delta_0)}{T(1-\delta_0) + T_0 \delta_0} \right\} 
\]

where

\[
B^*_i = A_{i1} T_0 \left( \frac{\partial p'_0}{\partial T} \right)_V + A_{i2} T_0^2 \left( \frac{\partial^2 p'_0}{\partial T^2} \right)_V \quad i = 0, 1, 2 
\]

with

\[
A_{01} = -\frac{2(1-\delta_0) \ln(1-\delta_0) + \delta_0}{D} \quad A_{02} = \frac{1}{\delta_0} \frac{(1-\delta_0) \ln(1-\delta_0) + \delta_0}{D} 
\]

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

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

and

\[
D = 2(1-\delta_0) \ln(1-\delta_0) + \delta_0(2-\delta_0) 
\]

The ideal reduced pressure \( p'(T) \) follows from Eq. 3.29, using \( p' = p^* + T \xi \), \( (\partial \xi/\partial T)_V = (\partial p'/\partial T)_V + \xi \) and \( (\partial^2 \xi/\partial T^2)_V = (\partial^2 p'/\partial T^2)_V \) (Eq. 2.34):

\[
p'(T) = p'_0 + B_0 + B_1 \frac{T}{T(1-\delta_0) + T_0 \delta_0} + B_2 \left( \frac{T}{T_0} \right) \ln \left\{ \frac{T(1-\delta_0)}{T(1-\delta_0) + T_0 \delta_0} \right\} + \xi T 
\]
where
\[ B_0 = A_0 T_0 \left( \frac{\partial \rho_0}{\partial T} \right)_V + A_\alpha T_0^2 \left( \frac{\partial^2 \rho_0}{\partial T^2} \right)_V + A_\alpha T_0 \xi \] (3.34)
\[ B_i = A_i T_0 \left\{ \left( \frac{\partial \rho_0}{\partial T} \right)_V - \xi \right\} + A_\alpha T_0^2 \left( \frac{\partial^2 \rho_0}{\partial T^2} \right)_V \quad i = 1, 2 \] (3.35)
and
\[ A_\alpha = -\frac{\delta_0(1 - \delta_0)}{D} \] (3.36)

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

\[ \Gamma_{-} \quad \Gamma_{+} \]

(a) Left-handed  (b) Right-handed

Figure 3.1: Left-handed and right-handed Gamma distributions, defining the \( \Gamma_{-} \) and \( \Gamma_{+} \) states.

As pointed out elsewhere,\(^{78}\) 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 \( \Gamma_{-} \), 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 \( \Gamma_{+} \), with \( 0 < \delta < 1 \) and \( \alpha^* < -\frac{1}{2} \)), see Fig. 3.1. Note that for \( \delta = 0 \) the distribution is a Gaussian. In Ref. 78 we describe the properties of and differences between the two Gamma states in detail. Basically, the \( \Gamma_{+} \) state is physically acceptable in the whole semi-classical temperature range, whereas the \( \Gamma_{-} \) state must be considered as an approximation to a more complicated statistical state within some temperature interval. Because of the finite upper energy limit in a \( \Gamma_{-} \) distribution, the approximation will be worse for very high temperature, since in that case the distribution is “squeezed” against the upper limit. However, in the same limit all states converge to a Gaussian state, so the effect will be very small. One other difference is the low temperature limit: while a \( \Gamma_{+} \) state may be extrapolated to \( T \to 0 \) (although of course in that limit the
semi-classical description is not valid any more, see section 3.6), for a $\Gamma_-$ state there exist a temperature

$$T_s = -T_0 \delta_0/(1 - \delta_0) > 0$$  \hspace{1cm} (3.37)$$

at which the solution encounters a singularity. For both states the different temperature limits for various thermodynamic properties are given in Tables 3.1 and 3.2 and discussed in section 3.6.

### 3.3 Effective Gamma state

For a Gamma state the knowledge of $U'_0$, $C'_{V_0}$, $\partial C'_{V_0}/\partial T$, $p'_0$, $\partial p'_0/\partial T$, $\partial^2 p'_0/\partial T^2$, $\epsilon$ and $\xi$ is required for a complete thermodynamic description. We can however obtain a simplified description, the effective Gamma state, as a local approximate Gamma state around the reference temperature $T_0$ by setting $\epsilon = 1$, $\xi = 0$ and using an effective $\delta'^{eff}_0$ in such a way that the entropy $S'_0$ at $T_0$ is exactly reproduced. Hence $\delta'^{eff}_0$ follows from solving

$$\alpha_0 = \frac{S'_0}{C'_{V_0}} = \frac{1}{\delta'^{eff}_0} + \frac{1}{\delta'^{eff}_0^2} \ln \left(1 - \delta'^{eff}_0\right)$$  \hspace{1cm} (3.38)$$

Since $\xi = 0$, it follows that $p' = p^*$, $\partial p'/\partial T = \partial p^*/\partial T$ etc. Hence for this effective Gamma state we obtain from Eqs. 3.19-3.24, 3.29 and 3.30

$$\delta'^{eff}(T) = \frac{T_0 \delta'^{eff}_0}{T(1 - \delta'^{eff}_0) + T_0 \delta'^{eff}_0}$$  \hspace{1cm} (3.39)$$

$$\alpha'^{eff}(T) = \frac{1}{\delta'^{eff}_0(T)} + \frac{1}{\delta'^{eff}_0(T)^2} \ln \left\{1 - \delta'^{eff}_0(T)\right\}$$  \hspace{1cm} (3.40)$$

$$C'_V(T) = C'_{V_0} \left(\frac{\delta'^{eff}(T)}{\delta'^{eff}_0}\right)^2$$  \hspace{1cm} (3.41)$$

$$S'(T) = \frac{C'_{V_0}}{\delta'^{eff}_0} \left[\delta'^{eff}(T) + \ln \left\{1 - \delta'^{eff}(T)\right\}\right]$$  \hspace{1cm} (3.42)$$

$$U'(T) = U'_0 + (T - T_0) C'_{V_0} \frac{\delta'^{eff}(T)}{\delta'^{eff}_0}$$  \hspace{1cm} (3.43)$$

$$A'(T) = U'_0 - \frac{T_0 C'_{V_0}}{\delta'^{eff}_0} - \frac{T C'_{V_0}}{\delta'^{eff}_0} \ln \left\{1 - \delta'^{eff}_0(T)\right\}$$  \hspace{1cm} (3.44)$$

and

$$p'(T) = p'_0 + B'^{eff}_0 + B'^{eff}_1 \frac{T}{T(1 - \delta'^{eff}_0) + T_0 \delta'^{eff}_0}$$

$$+ B'^{eff}_2 \left(\frac{T}{T_0}\right) \ln \left\{\frac{T(1 - \delta'^{eff}_0)}{T(1 - \delta'^{eff}_0) + T_0 \delta'^{eff}_0}\right\}$$  \hspace{1cm} (3.45)$$
with

\[ B_{i}^{11} = A_{i1} T_{0} \left( \frac{\partial \mu_{0}}{\partial T} \right)_{V} + A_{i2} T_{0}^{2} \left( \frac{\partial^{2} \mu_{0}}{\partial T^{2}} \right)_{V} \quad i = 0, 1, 2 \]  

(3.46)

For this approximate state we therefore need for a complete thermodynamic description \( U_{0}, C_{V0}, S_{0}, \mu_{0}, \partial \mu_{0}/\partial T \) and \( \partial^{2} \mu_{0}/\partial T^{2} \) at one temperature \( T_{0} \). The zero and infinite temperature limits of these equations are of course identical to those of the confined ideal properties of the usual Gamma state, see Tables 3.1 and 3.2. Clearly, the Gamma state and effective Gamma state become identical in the low density limit. For high density systems the effective Gamma state might still be a good local approximation for e.g. the entropy or the Helmholtz free energy; the description of the heat capacity \( C_{V} \) obviously will be worse, since in effect the value of \( \partial C_{V}/\partial T \) is adapted to compensate the effect of the phase-space confinement.

3.4 Inverse Gaussian state

The Inverse Gaussian (IG) distribution, given by\(^{99,100}\)

\[ \rho(\Delta \mu') = \sqrt{\frac{c_{1}}{2\pi}} (c_{0} + \Delta \mu')^{-3/2} \exp \left\{ -\frac{c_{1}}{2c_{0}^{2}} (c_{0} + \Delta \mu')^{2} \right\} \]  

(3.47)

with \( c_{0} = 3M_{3}^{2}/M_{2} \) 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. 3.47.

Using the fact that the moment generating function of this distribution is given by\(^{99,101}\)

\[ G_{\Delta \mu}(\beta) = \exp \left\{ -\beta c_{0} + \frac{c_{1}}{c_{0}} \left( 1 - \sqrt{1 - \frac{2\beta^{2}}{c_{1}}} \right) \right\} \]  

(3.48)

and using the expressions for \( M_{2} \) and \( M_{3} \) (Eqs. 2.45-2.46), we obtain for the confined intrinsic entropy function

\[ \alpha^{*} = \frac{1}{\gamma} - \frac{1}{\gamma^{2}} \left( 1 - \sqrt{1 - 2\gamma} \right) \]  

(3.49)

where

\[ \gamma = \frac{M_{3}}{3kT M_{2}} = \frac{2}{3} \left( \frac{T(\partial C'_{V}/\partial T)_{V} + 1}{2C'_{V}} \right) = \frac{2}{3} \delta \]  

(3.50)
with $\delta$ the characteristic quantity of the Gamma state (see Eq. 3.16). The similarity between the expressions of $\alpha^*$ for the IG distribution (Eq. 3.49) and the Gamma distribution (Eq. 3.15) can be seen by expanding both expressions in a Taylor series around $\delta = 0$, obtaining

$$\alpha^*_{IG} = -\frac{1}{2} - \frac{\delta}{3} - \frac{5\delta^2}{18} - \cdots$$  \hspace{1cm} (3.51)

$$\alpha^*_\Gamma = -\frac{1}{2} - \frac{\delta}{3} - \frac{\delta^2}{4} - \cdots$$  \hspace{1cm} (3.52)

Hence for small $\delta$ (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. 2.50, written in the form

$$T \left( \frac{\partial \alpha^*}{\partial T} \right)_V + (3\gamma - 2)\alpha^* - 1 = 0$$  \hspace{1cm} (3.53)

where $(\partial \alpha^*/\partial T)_V = (d\alpha^*/d\gamma)(\partial \gamma/\partial T)_V$ and $(d\alpha^*/d\gamma)$ follows from Eq. 3.49. After straightforward algebra we finally obtain as a simple form of the TME

$$\left( \frac{\partial \gamma}{\partial T} \right)_V = -\frac{\gamma(1 - 2\gamma)}{T}$$  \hspace{1cm} (3.54)

which provides $\gamma(T)$. Since $\gamma$ is a function of $C'_V$ and $(\partial C'_V/\partial T)_V$, Eq. 3.50, we have a new differential equation in $C'_V$, yielding for a confined IG state

$$\gamma(T) = \frac{T_0\gamma_0}{T(1 - 2\gamma_0) + 2T_0\gamma_0}$$  \hspace{1cm} (3.55)

$$\alpha^*(T) = \frac{1}{\gamma(T)} - \frac{1}{\gamma^2(T)} \left( 1 - \sqrt{1 - 2\gamma(T)} \right)$$  \hspace{1cm} (3.56)

$$C'_V(T) = C'_V_0 \left( \frac{T_0}{T} \right)^{1/2} \left( \frac{\gamma}{\gamma_0} \right)^{3/2}$$  \hspace{1cm} (3.57)

$$S'(T) = C'_V(T) \left\{ \frac{1}{\gamma(T)} - \frac{1}{\gamma^2(T)} \left( 1 - \sqrt{1 - 2\gamma(T)} \right) \right\} + k\ln \epsilon$$  \hspace{1cm} (3.58)

$$U'(T) = U'_0 + \frac{T_0C'_V_0}{\gamma_0} \left( \sqrt{\frac{T}{T_0}} \frac{\gamma}{\gamma_0} - 1 \right)$$  \hspace{1cm} (3.59)

and

$$A'(T) = U'_0 - \frac{T_0C'_V_0}{\gamma_0} + \frac{TC'_V_0}{\gamma_0^2} \left( \sqrt{\frac{T_0}{T}} \frac{\gamma}{\gamma_0} - \sqrt{1 - 2\gamma_0} \right) - kT\ln \epsilon$$  \hspace{1cm} (3.60)
Note that, similar to the Gaussian and Gamma states, \( \langle \partial C'_V / \partial T \rangle_V \) 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. 3.60. Thus with Eqs. 3.26 and 3.27, and \( (\partial \gamma_0 / \partial V)_T \) via the CPE at \( T_0 \), we obtain in a similar way

\[
p^*(T) = p_0^* + B_0^* + B_1^* \left( \frac{T}{T_0} \right) \left( \sqrt{1 - 2\gamma_0(1 - T_0/T)} - \sqrt{1 - 2\gamma_0} \right) + B_2^* \left( \frac{T}{T_0} \right) \left( \frac{1 - T_0/T}{\sqrt{1 - 2\gamma_0(1 - T_0/T)}} - \frac{1}{\sqrt{1 - 2\gamma_0}} \right)
\]

where

\[
B_i^* = A_{ii} T_0 \left( \frac{\partial p_0^*}{\partial T} \right)_V + A_{i2} T_0^2 \left( \frac{\partial^2 p_0^*}{\partial T^2} \right)_V \quad i = 0, 1, 2
\]

with

\[
A_{01} = \frac{2\sqrt{1 - 2\gamma_0} + 3\gamma_0 - 2}{D} \quad A_{02} = -\frac{1}{\gamma_0} \frac{\sqrt{1 - 2\gamma_0} + \gamma_0 - 1}{D}
\]

\[
A_{11} = -\frac{2\sqrt{1 - 2\gamma_0}}{D} \quad A_{12} = \frac{1}{\gamma_0} \frac{\sqrt{1 - 2\gamma_0} - 1}{D}
\]

\[
A_{21} = -\frac{\gamma_0 \sqrt{1 - 2\gamma_0}}{D} \quad A_{22} = -\frac{1}{\gamma_0} \frac{(1 - \gamma_0) \sqrt{1 - 2\gamma_0} + 2\gamma_0 - 1}{D}
\]

and

\[
D = (\gamma_0 - 2) \sqrt{1 - 2\gamma_0} - 3\gamma_0 + 2
\]

The ideal reduced pressure \( p'(T) \) follows from Eq. 3.61, 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. 2.34):

\[
p'(T) = p_0' + B_0 + B_1 \left( \frac{T}{T_0} \right) \left( \sqrt{1 - 2\gamma_0(1 - T_0/T)} - \sqrt{1 - 2\gamma_0} \right) + B_2 \left( \frac{T}{T_0} \right) \left( \frac{1 - T_0/T}{\sqrt{1 - 2\gamma_0(1 - T_0/T)}} - \frac{1}{\sqrt{1 - 2\gamma_0}} \right) + \xi T
\]

where

\[
B_0 = A_{01} T_0 \left( \frac{\partial p_0'}{\partial T} \right)_V + A_{02} T_0^2 \left( \frac{\partial^2 p_0'}{\partial T^2} \right)_V + A_{03} T_0 \xi
\]

\[
B_i = A_{ii} T_0 \left\{ \left( \frac{\partial p_0'}{\partial T} \right)_V - \xi \right\} + A_{i2} T_0^2 \left( \frac{\partial^2 p_0'}{\partial T^2} \right)_V \quad i = 1, 2
\]
and

\[ A_{\alpha} = -\frac{\gamma_0 \sqrt{1 - 2\gamma_0}}{D} \]  

(3.68)

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

\[ T_s = -2\gamma_0 T_0 / (1 - 2\gamma_0) > 0 \]  

(3.69)

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 3.1 and 3.2 and discussed in section 3.6.

Note that we can also define an effective Inverse Gaussian state as a local approximate state around \(T_0\) by setting \(\epsilon = 1, \xi = 0\) and using an effective \(\gamma^{eff}_0\), calculated from

\[ \alpha_0 = \frac{S'_0}{C'_V} = \frac{1}{\gamma^{eff}_0} + \frac{1}{\gamma^{eff}_0} \left( 1 - \sqrt{1 - 2\gamma^{eff}_0} \right) \]  

(3.70)

i.e., by adapting the value of \(\partial C'_V / \partial T\) to reproduce the value of \(S'\) at \(T_0\).

### 3.5 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. These strongly confined states correspond to typical liquid densities. In that case

\[ \left( \frac{\partial \alpha}{\partial T} \right)_V = \left( \frac{\partial \alpha^*}{\partial T} \right)_V - k \ln \frac{e}{C'_V(T)} \left( \frac{\partial C'_V}{\partial T} \right)_V \]  

(3.71)

where the first term on the right-hand side is positive for a \(\Gamma_+\) (or IG₊) state and the second term negative (since \(\partial C'_V / \partial T\)_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

\[ \left( \frac{\partial C'_V}{\partial T} \right)_V = \frac{1}{\alpha_0} \frac{C'_V}{T} \]  

(3.72)
yields the constant alpha equations\(^5,^7,^8\)

\[
C'_V(T) = C'_{V0} \left( \frac{T}{T_0} \right)^{\lambda_0} \tag{3.73}
\]

\[
S'(T) = \frac{C'_{V0}}{\lambda_0} \left( \frac{T}{T_0} \right)^{\lambda_0} \tag{3.74}
\]

\[
U'(T) = U'_0 - \frac{T_0 C'_{V0}}{\lambda_0 + 1} \left\{ 1 - \left( \frac{T}{T_0} \right)^{\lambda_0 + 1} \right\} \tag{3.75}
\]

\[
A'(T) = U'_0 - \frac{T_0 C'_{V0}}{\lambda_0 + 1} \left\{ \frac{1}{\lambda_0} \left( \frac{T}{T_0} \right)^{\lambda_0 + 1} + 1 \right\} \tag{3.76}
\]

with

\[
\lambda_0 = 1/\alpha_0 < 0 \tag{3.77}
\]

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 \(\alpha\) in \(V\) is approximately temperature independent, and we obtain as conjugated pressure equation (Eq. 2.62), using Eq. 3.73 for \(C'_V(T)\):

\[
\left( \frac{\partial p'}{\partial T} \right)_V = \frac{T}{\lambda_0} \left( \frac{\partial^2 p'}{\partial T^2} \right)_V + C'_{V0} \left( \frac{\partial \alpha_0}{\partial V} \right)_T \left( \frac{T}{T_0} \right)^{\lambda_0} \tag{3.78}
\]

yielding

\[
p'(T) = p'_0 + B_0 \left\{ \left( \frac{T}{T_0} \right)^{\lambda_0 + 1} - 1 \right\} - B_1 \left( \frac{T}{T_0} \right)^{\lambda_0 + 1} \ln \left( \frac{T}{T_0} \right) \tag{3.79}
\]

where

\[
B_0 = \frac{T_0}{\lambda_0 + 1} \left( \frac{\partial p'_0}{\partial T} \right)_V + \frac{T_0 C'_{V0}}{\lambda_0 + 1} \left( \frac{\partial \alpha_0}{\partial V} \right)_T \tag{3.80}
\]

\[
B_1 = \frac{T_0 C'_{V0}}{\lambda_0 + 1} \left( \frac{\partial \alpha_0}{\partial V} \right)_T \tag{3.81}
\]

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

\[
B_0 = \frac{2\lambda_0 + 1}{(\lambda_0 + 1)^2} T_0 \left( \frac{\partial p'_0}{\partial T} \right)_V - \frac{1}{(\lambda_0 + 1)^2} T_0^2 \left( \frac{\partial^2 p'_0}{\partial T^2} \right)_V \tag{3.82}
\]

\[
B_1 = \frac{\lambda_0}{\lambda_0 + 1} T_0 \left( \frac{\partial p'_0}{\partial T} \right)_V - \frac{1}{\lambda_0 + 1} T_0^2 \left( \frac{\partial^2 p'_0}{\partial T^2} \right)_V \tag{3.83}
\]
Both sets of expressions of $B_0$ and $B_1$ are completely equivalent. However, from a practical point of view it seems that the latter are more useful, since the experimental values of $(\partial^2p_0/\partial T^2)_V$ appear to be more accurate than the values of $(\partial\alpha_0/\partial V)_T$, see also Chapter 4.

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), the $T \to 0$ and $T \to \infty$ limits are not given, as they are in principle irrelevant (for every confined system the infinite temperature limit of $\alpha = -\infty$, see section 3.6).

### 3.6 Temperature limits

In this section we will present the zero and infinite temperature limits of various thermodynamic properties based on general statistical mechanical considerations. The general temperature limits of various properties are derived in Appendix F and summarized in Tables 3.1 and 3.2.

From Table 3.1 it is evident that all statistical states described in this Chapter are consistent with the 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 3.1) are completely correct.

The requirement that $W_{\text{min}}$ is finite, implies that at very low temperature only the $\Gamma_+$ 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 3.2. The Gaussian state, for example, does not fulfill Eq. F.18. For the $\Gamma_-$ and IG$_-$ states, the zero temperature limits are even impossible, because of the occurrence of a singularity at $T_s > 0$, given by Eqs. 3.37 and 3.69. If in the low temperature regime the system is still within an exact $\Gamma_+$ or IG$_+$ state, Eq. F.19 yields an extra relation between $\delta_0$ (or $\gamma_0$), $p_0^i$, $(\partial p_0^i/\partial T)_V$ and $(\partial^2 p_0^i/\partial T^2)_V$ of the form

$$p_0^i + A_0 T_0 \left( \frac{\partial p_0^i}{\partial T} \right)_V + A_2 T_0^2 \left( \frac{\partial^2 p_0^i}{\partial T^2} \right)_V = 0 \quad (3.84)$$

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 with a second order expansion (with non-zero continuous force derivatives). It is obvious that these conditions are not fulfilled.
Table 2: The \( T \rightarrow \infty \) limits of the confined ideal reduced properties for different states. Values between square brackets denote the \( T \rightarrow \infty \) limits of the ideal reduced properties. The limits of the ideal reduced properties of the effective Gamma/IG states are identical to the limits of the confined ideal reduced properties of the effective Gamma/IG states.

\[
\begin{array}{cccccc}
0 & 0 & 0 & 0 & 0 & \infty \\
0 & 0 & \left[ \infty - \right] \frac{\eta}{\eta} & \left[ \infty - \right] \frac{\eta}{\eta} & \left[ \infty - \right] \frac{\eta}{\eta} & \left[ \infty - \right] \frac{\eta}{\eta} \\
\frac{\Delta p}{\left( 1 - \frac{\eta}{\eta} \right) \frac{\eta}{\eta}} + \frac{\eta}{\eta} & \frac{\Delta p}{\left( 1 - \frac{\eta}{\eta} \right) \frac{\eta}{\eta}} + \frac{\eta}{\eta} & \frac{\Delta p}{\left( 1 - \frac{\eta}{\eta} \right) \frac{\eta}{\eta}} + \frac{\eta}{\eta} & \frac{\Delta p}{\left( 1 - \frac{\eta}{\eta} \right) \frac{\eta}{\eta}} + \frac{\eta}{\eta} & \frac{\Delta p}{\left( 1 - \frac{\eta}{\eta} \right) \frac{\eta}{\eta}} + \frac{\eta}{\eta} & \frac{\Delta p}{\left( 1 - \frac{\eta}{\eta} \right) \frac{\eta}{\eta}} + \frac{\eta}{\eta} \\
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0 & 0 & 0 & 0 & 0 & \frac{\eta}{\eta} \\
\end{array}
\]

- IC/IG
- +

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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.

\[ \lim_{T \to 0} \delta_+(T) = 1 \]
\[ \lim_{T \to T_-} \delta_-(T) = -\infty \]
\[ \lim_{T \to \infty} \delta(T) = 0 \]  

with $\delta_+(T)$ and $\delta_-(T)$ the function $\delta(T)$ for a $\Gamma_+$ and $\Gamma_-$ state, respectively, indicating that the behavior of the statistical $\Gamma_+$ and $\Gamma_-$ states for $T \to 0$ ($T \to \infty$).
Description of different statistical states.

Gaussian/IG states are identical to the continuous ideal reduced properties of the LC states.

\( T_{\text{IG}} \) and IG states depend on the sign of \( \Delta p \), which is determined by setting \( e = 1 \). The limits for the Gaussian, IG, and IG states are given by Eqs. 3.68 and 3.69. The limits for the Gaussian, IG, and IG states are identical to the continuous ideal reduced properties of the LC states.

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\( \Delta p / (\sigma_{\text{IG}}^2) = 0 \)

Class. stat. mech. Gaussian

\( \Delta p / (\sigma_{\text{IG}}^2) = 0 \)
Temperature limits

Temperature limits

$T_*$ are the most “asymmetric” (deviating most from the Gaussian state behavior) and for $T \to \infty$ correctly tend to a Gaussian state. The shape of the Gamma distribution, however, is determined by $b_i(T) = kT \delta(T)$, rather than $\delta(T)$, for which we find

$$\lim_{T \to 0} b_{1+}(T) = 0$$
$$\lim_{T \to T_*} b_{1-}(T) = -\infty$$
$$\lim_{T \to \infty} b_i(T) = \frac{kT_0 \delta_0}{1 - \delta_0}$$

(3.86)

The positive Gamma distribution for $T \to 0$ is thus the most symmetric (tending to a Dirac $\delta$-function!) and for $T \to \infty$ becomes the most asymmetric, see also Fig. 3.2. This opposite behavior of distribution and statistical state for temperature lines is not present for density lines, since in that case the limits of $b_i(\rho_N)$ and $\theta = b_i(\rho_N)/kT$ show the same trend as the temperature is fixed.

A final remark concerns the general relation

$$\Omega(\mathcal{U}') = Q_{\text{pol}}^\text{e}(\beta)e^{\beta U} \rho(\mathcal{U}', \beta) = \frac{Q_{\text{pol}}^\text{e} e^{\beta U} \rho(\mathcal{U}', \beta)}{G_{\mathcal{U}'}^\beta(\beta)}$$

(3.87)

where $G_{\mathcal{U}'}^\beta(\beta)$ is the moment generating function of $\rho(\mathcal{U}', \beta)$ at $\beta$ evaluated in the $\beta$ ensemble. Clearly, the configurational volume $\Omega(\mathcal{U}')$ is temperature independent. On first sight, however, it is not obvious that also the right-hand side of this equation is temperature independent for the statistical states we investigated.

For a Gaussian state it is rather easy to show that the right-hand side of Eq. 3.87 is temperature independent. For other states it is more difficult to show this algebraically, but rewriting Eq. 3.87 as

$$\frac{\Omega(\mathcal{U}')}{{Q_{\text{pol}}^\text{e} e^{\beta U} \rho(\mathcal{U}', \beta)} G_{\mathcal{U}'}^\beta(\beta)} = \frac{e^{\beta U} \rho(\mathcal{U}', \beta)}{G_{\mathcal{U}'}^\beta(\beta)}$$

(3.88)

where the left-hand side is temperature independent, it is for a certain value of $\beta$ always possible to find a function $\Omega(\mathcal{U}')$ that fulfills Eq. 3.88. Since the temperature dependence of this equation is governed by an ordinary differential equation, once the equality is fulfilled at one value of $\beta$, it must hold at every temperature.
Description of different statistical states