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On the Joule–Kelvin Coefficient of a Simple Fluid.†

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A model soft-core equation of state is used to account qualitatively for the behaviour of the Joule–Kelvin coefficient μ and its (initial) partial derivatives at high temperatures. The two sign changes which occur in $(\partial\mu/\partial P)_{T_0}$ are present in a hard-core model, but the minimum in $(\partial\mu/\partial T)_{P_0}$, at T_D , is a soft-core effect. A hard-core model is adequate in the low temperature and density region around the inversion curve, but contours of μ at high temperatures and pressures are modified qualitatively when a soft-core is introduced.

1 INTRODUCTION

Our aim in this paper is to examine the behaviour of the Joule–Kelvin coefficient μ , defined by¹

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right], \quad (1)$$

for a simple fluid over a wide range of temperature and pressure. The importance of this coefficient in describing the temperature change which occurs during an isenthalpic throttling process is well-known. We shall note briefly the low temperature and low density features such as the Joule–Kelvin inversion curve, $\mu \equiv 0$, which are adequately accounted for by a hard-core equation of state. We investigate in more detail those properties for which it is necessary to take into account the effective softening of the molecular hard core at high temperatures. In particular we shall examine the

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derivatives $(\partial\mu/\partial T)_{P_0}$ and $(\partial\mu/\partial P)_{T_0}$ along the temperature axis. It is well-known that $(\partial\mu/\partial T)_{P_0}$ exhibits a minimum at the temperature T_D at which the second virial coefficient has a point of inflexion, provided the constant pressure specific heat C_{P_0} is independent of temperature along the axis. However, the properties of $(\partial\mu/\partial P)_{T_0}$ seem to have been less well documented:¹ it changes sign *twice* as a function of temperature, being positive at low and high temperatures and negative in an intermediate range extending roughly from $0.5 \times T_B$ to $6.4 \times T_B$ for a hardcore model with Boyle temperature T_B . Our overall results are presented in the form of contours of μ in the density vs. temperature diagram. As the core is softened, a saddle point region drifts from high to low density and eventually disappears at the temperature axis. Consequently there is considerable variation in the contour patterns between hard and soft-core cases.

2 JOULE-KELVIN INVERSION POINT

The equation of state employed here has been discussed in detail in the preceding paper² and elsewhere.³ As before we shall adopt a simple temperature dependent form for the van der Waals volume parameter b :

$$b = \frac{b_0 \alpha}{t^N} \quad (2)$$

with $0 \leq N < \frac{1}{2}$. In the hard-core limit $N = 0$ and $b = b_0$. Here

$$\alpha = \frac{t_{c0}}{t^{1-N}} \quad (3)$$

and $t = b_0 RT/a$, as in the preceding paper. For the soft-core model (2) the second virial coefficient is given by the expression

$$B = b_0 \left[\frac{\alpha}{t^N} - \frac{1}{t} \right]. \quad (4)$$

The inversion line $\mu \equiv 0$ meets the temperature axis at the Joule-Kelvin inversion point, or Charles temperature T_C , which is located in terms of the second virial coefficient by the condition

$$B - T\dot{B} = 0, \quad \text{at } T_C \quad (5)$$

where $\dot{}$ denotes temperature differentiation. So the Charles temperature is at

$$\frac{T_C}{T_c} \equiv \frac{t_C}{t_c} = \left[\frac{2}{t_{c0}(1+N)} \right]^{1/(1-N)}. \quad (6)$$

[In our calculation of the Joule-Kelvin coefficient in Section 3 we shall require a volume scaling factor, which we shall choose to be the value of the second virial coefficient at the Charles point: B_C . For a hard-core model with $N = 0$, $t_c = 2$ and $B_C = \frac{1}{2}b_0$. In general

$$B_C = \frac{b_0}{t_c} \left(\frac{1 - N}{1 + N} \right), \quad (7)$$

where t_c is given by (6) above. In order to scale the temperature and density, we use either the critical point values, or the inversion point values. The relations between these scales are given for the temperature by (6), and for the density d ($\equiv b_0\rho$) by

$$\frac{d_C}{d_c} = \frac{b_0}{B_C} \cdot \frac{t_{c0}}{x_c t_c} = \frac{t_C}{t_c} \cdot \frac{t_{c0}}{x_c} \left(\frac{1 + N}{1 - N} \right) \quad (8)$$

where again t_C/t_c is given by (6), and t_{c0} and x_c are the corresponding hard-core model critical temperature and density parameters. For the Frisch model $t_{c0} = 0.375312\dots$ and $x_c = 0.514668\dots$. In deriving (8) we have used the fact that $(d_c/x_c) = (t_c/t_{c0})$ for the present model.³ Numerical data for this scale change is included in Table I.]

TABLE I

N	T_1/T_B	T_2/T_B	T_B/T_c	T_C/T_c	d_C/d_c
0	0.497	6.436	2.664	5.329	3.886
1/9	0.453	7.830	3.012	5.834	5.318
1/6	0.429	8.918	3.241	6.198	6.319
1/5	0.414	9.770	3.404	6.446	7.051
1/4	0.390	11.455	3.694	6.912	8.401
3/10	0.364	13.875	4.055	7.504	10.162
1/3	0.346	16.118	4.349	7.990	11.653

For selected values of the exponent N ($=3/n$), the table contains the values of the temperatures T_1 and T_2 , relative to the Boyle point T_B , at which $(\partial\mu/\partial P)_{T_0}$ is zero, and the ratios of the Boyle temperature, the Charles temperature and the density d_C to the critical values for the Frisch model. Here $d_C \equiv b_0/B_C$ (see text section 2).

3 JOULE-KELVIN COEFFICIENT

The calculation of μ via (1) is straightforward, with the result

$$\mu = \frac{b}{C_P} \left\{ \frac{\phi'(u_1 - 1) + 2u_0}{\phi + x\phi' - 2u_0x} \right\}. \quad (9)$$

It is convenient to scale μ in a dimensionless form

$$\mu^* = \frac{\mu R}{B_C} \quad (10)$$

so effectively the specific heat C_p is scaled by the molar gas constant, and the remaining volume dimensions are removed on division by a suitable volume scaling factor B_C , which we have chosen to be the value of the second virial coefficient at the Charles point (7).

Contours of μ^* in the density vs. temperature diagram are presented in Figure 1-7 for the Frisch model, for selected values of the exponent N . The low temperature and pressure region containing the inversion curve $\mu \equiv 0$ changes little in structure as N is increased and the core is softened. However the behaviour of μ elsewhere in the phase diagram undergoes considerable variation. The saddle point feature mentioned in the introduction descends to intersect the temperature axis when the conditions

$$\left(\frac{\partial\mu}{\partial T}\right)_{P_0} = 0 \quad \text{and} \quad \left(\frac{\partial\mu}{\partial P}\right)_{T_0} = 0 \quad (11)$$

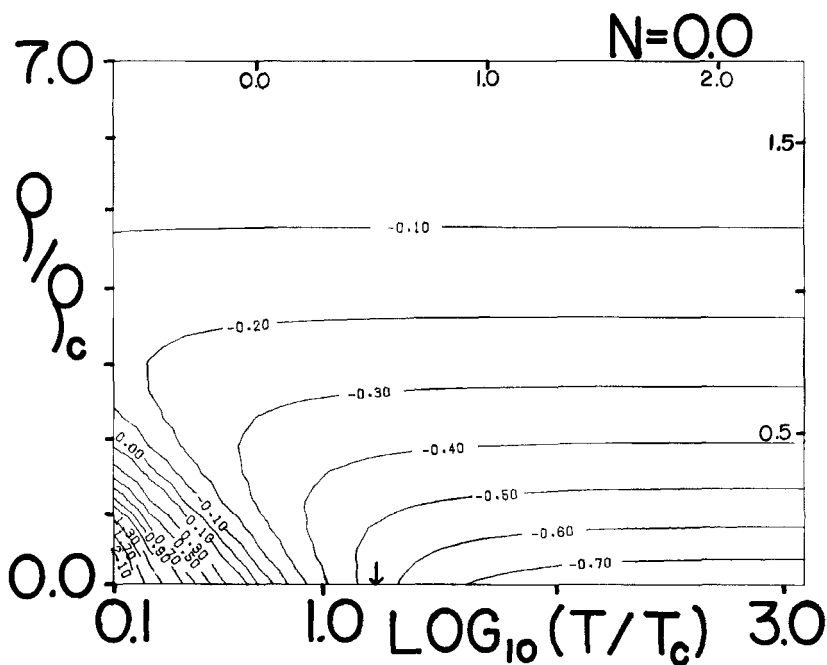


FIGURE 1 Contours of the Joule Kelvin coefficient, labelled with values of μ^* , for the Frisch model with $N = 0$ on a scaled diagram of density vs. logarithm of temperature. On the main axes ρ_c and T_c are the critical density and temperature respectively. The alternative scaling of ρ and T with respect to the Charles point 'volume' B_C and the inversion temperature T_C is indicated at the top and at the right-hand side of the figure. The arrow on the temperature axis indicates the upper temperature where $(\partial\mu/\partial P)_{T_0}$ changes sign, and the contours of μ are vertical.

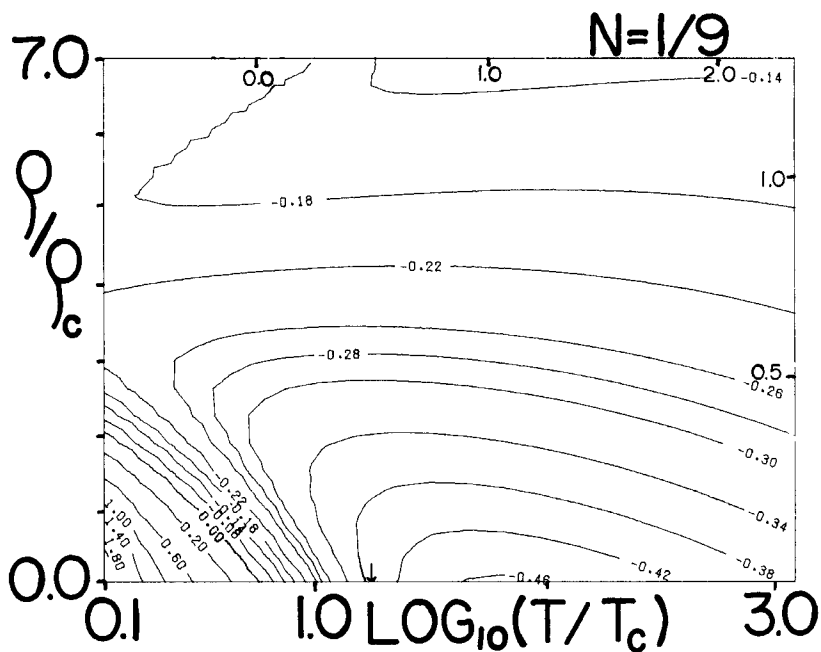


FIGURE 2 Contours of μ as Figure 1, with $N = 1/9$.

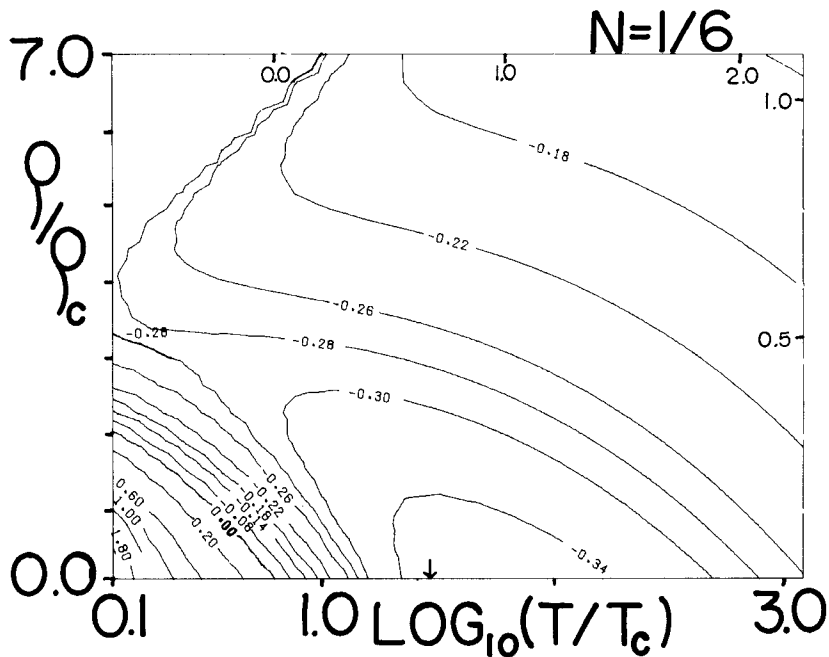


FIGURE 3 Contours of μ as Figure 1, with $N = 1/6$.

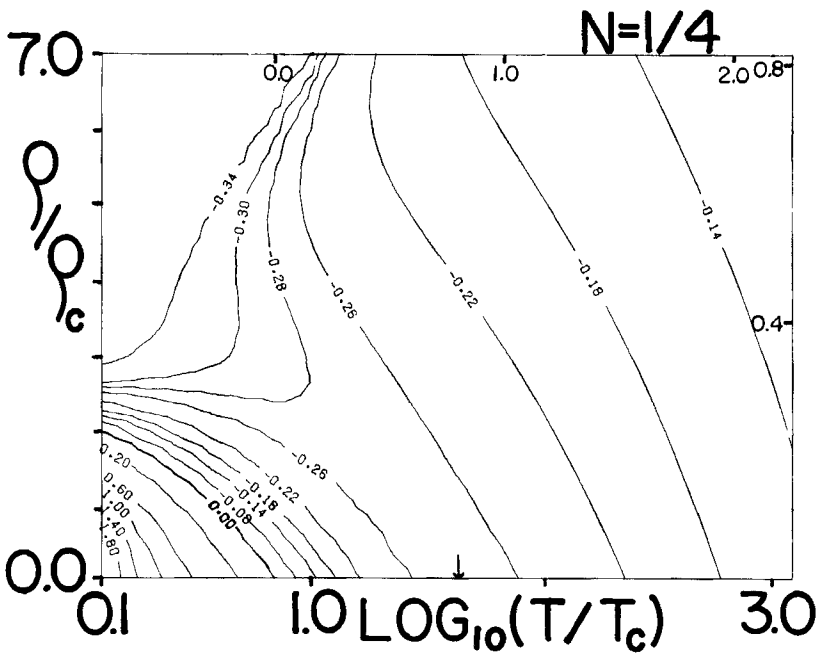


FIGURE 4 Contours of μ as Figure 1, with $N = 1/4$.

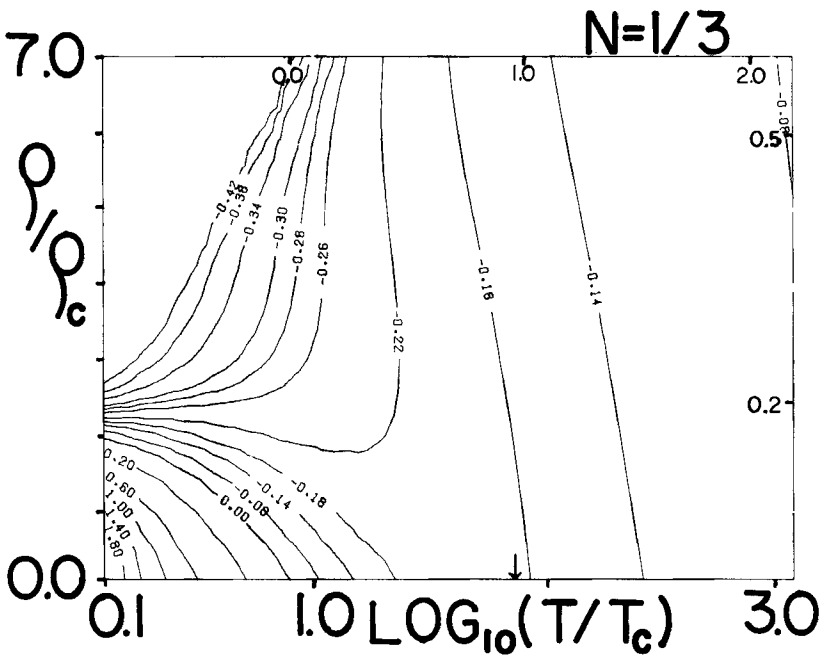


FIGURE 5 Contours of μ as Figure 1, with $N = 1/3$.

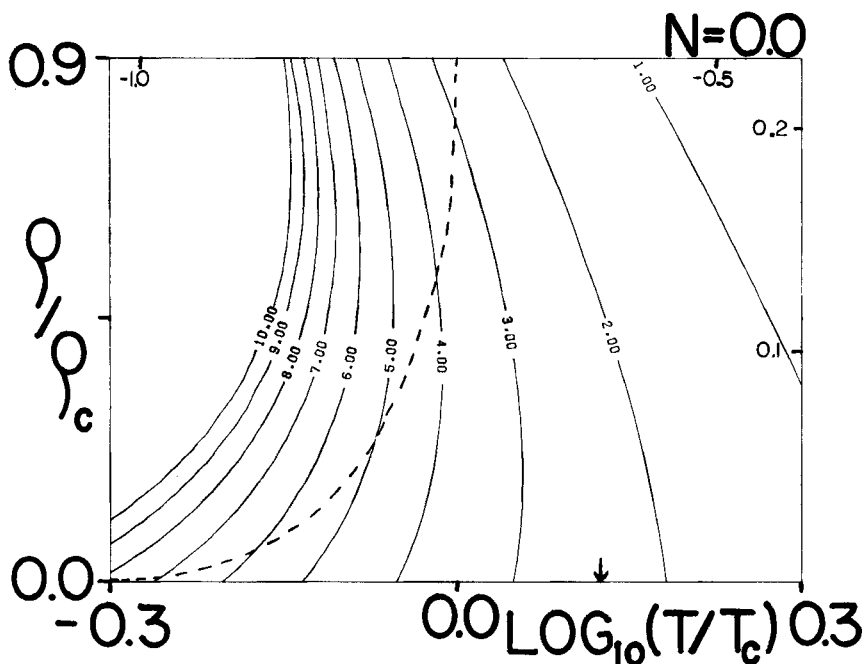


FIGURE 6 Contours of μ as Figure 1, with $N = 0$, showing the low temperature region in the vicinity of the coexistence curve (dashed line). The arrow on the temperature axis indicates the lower temperature where $(\partial\mu/\partial P)_{T_0}$ changes sign.

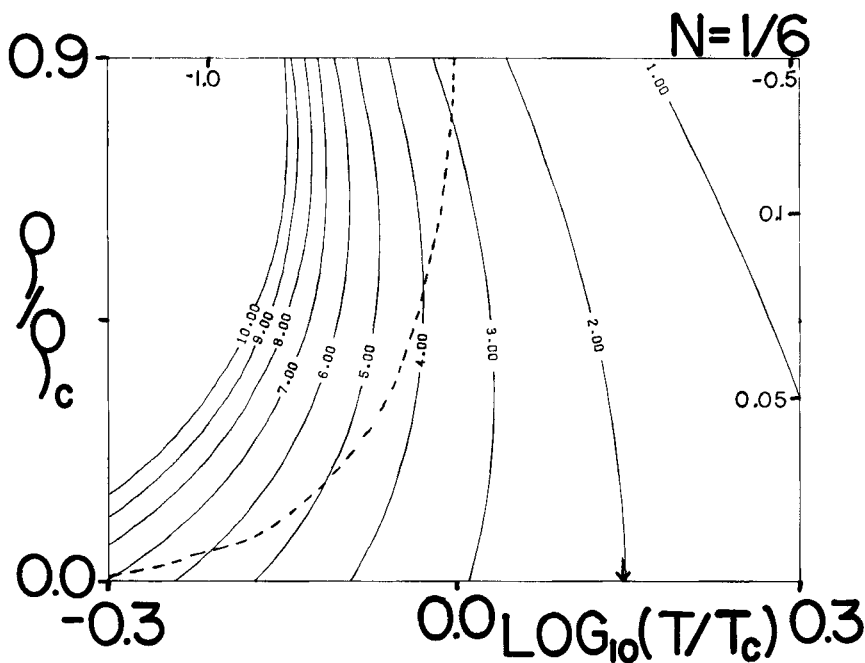


FIGURE 7 Contours of μ as Figure 6, with $N = 1/6$.

are satisfied simultaneously. For a generalized model with second and third virial coefficients of the form

$$B = \left(\frac{b'}{T^N}\right) - \left(\frac{a'}{TM}\right), \quad C = \lambda\left(\frac{b'}{T^N}\right)^2, \quad (12)$$

one finds that (11) is satisfied when N is a solution of the cubic equation

$$\lambda - \left[1 + \frac{N}{M+1}\right] \left[1 - \frac{N}{M}\right]^2 = 0. \quad (13)$$

For our current model $M = 1$, with $\lambda = \frac{5}{8}$, so the cubic reduces to

$$N^3 - 3N + \frac{3}{4} = 0 \quad (14)$$

which has three real roots. The relevant value of N is 0.255564... so $n \equiv 3/N = 11.7387...$, the other unphysical roots being at 1.590... and $-1.845...$

4 PARTIAL DERIVATIVES OF μ

Along the temperature axis μ is determined by the second virial coefficient B :

$$\mu_0 = (T\dot{B} - B)/C_{P_0}. \quad (15)$$

For a hard-core model the variation of the second virial coefficient and of μ_0 along the temperature axis is especially simple, but does not accord with experiment at high temperatures.^{4,1} Substituting for B from (4) with $N = 0$ one obtains

$$\mu_0^* = \frac{2R}{C_{P_0}} \left(\frac{T_C}{T} - 1\right) \quad (16)$$

so at high temperatures μ_0^* approaches a constant negative value. However, in general from (15), assuming C_{P_0} is independent of temperature, one finds that

$$\left(\frac{\partial\mu_0}{\partial T}\right)_{P_0} = \frac{T\ddot{B}}{C_{P_0}}, \quad (17)$$

which vanishes at the temperature T_D where B has a point of inflexion. Consequently for realistic intermolecular potentials μ_0 passes through a minimum at T_D , as is observed experimentally.⁴

The initial pressure dependence of μ is given by

$$\left(\frac{\partial\mu}{\partial P}\right)_{T_0} = \frac{1}{C_{P_0}} \left[(T\dot{C} - C') + (T\dot{B} - B) \frac{T\ddot{B}}{C_{P_0}} \right], \quad (18)$$

again assuming C_{P_0} is constant.¹ Here $C' = (C - B^2)/RT$ is the third "pressure" virial coefficient.² For our model (4), or (12), we find that the derivative in (18) changes sign *twice* as a function of temperature, being positive at low and high temperature and negative in an intermediate range. Table I displays values of T/T_B at which $(\partial\mu/\partial P)_{T_0}$ vanishes, for selected values of the exponent N . In the hard-core case $N = 0$, with $C_{P_0} = \frac{5}{2}R$, the expression in (18) simplifies to

$$\left(\frac{\partial\mu}{\partial P}\right)_{T_0} = \frac{b_0^2}{C_{P_0}RT_B} \cdot \frac{1}{20} \left[\frac{15}{t'} - \frac{104}{t'^2} + \frac{48}{t'^3} \right],$$

where $t' = T/T_B$, whence it is clear that the sign changes in $(\partial\mu/\partial P)_{T_0}$ already occur in the hard-core case, and are not altered qualitatively by any softening of the molecular core. Note that as N varies the upper temperature at which $(\partial\mu/\partial P)_{T_0}$ vanishes "crosses" the point T_D at which $(\partial\mu/\partial T)_{P_0}$ vanishes when N satisfies (14).

CONCLUDING REMARKS

In this paper and the preceding one we have discussed features of two thermodynamic quantities which exhibit qualitative changes when soft-core effects are taken into account. In our simple model equation of state we can adjust only the single exponent parameter N , which is related to the repulsive potential exponent $n \equiv 3/N$. Clearly quantitative correctness is not to be expected, but it is anticipated that the features noticed here recur in more realistic models. We emphasize that the main purpose of constructing a soft-core equation of state as a simple extension of a hard-core equation of state is to permit a qualitative investigation of the range of possible behaviour of various thermodynamic functions of a simple monatomic fluid in the high temperature and pressure region where the repulsive part of the intermolecular potential plays an important role. Moreover, this investigation can be performed by elementary calculations at a thermodynamic level. We thus avoid having to adopt a specific form for the intermolecular potential, and having to carry out the heavy computations required by statistical mechanics, or molecular dynamics.⁵ Furthermore, it would be of interest to examine the experimental thermodynamic quantities, such as C_P and μ , for actual monatomic systems. The high relative temperatures and pressures required are most easily attained for Helium. With an appropriate choice of the parameter N , the model does exhibit qualitative agreement with the observed properties of the monatomic gas Helium⁶ at high temperatures relative to the Boyle point, over a wide range of pressure.⁷

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