A microscopic study of neon and argon gases within the static fluctuation approximation (SFA)


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The thermodynamic properties of neon and argon gases are studied within the static fluctuation approximation (SFA). These properties include the total internal energy, pressure, entropy, compressibility and specific heat. The results are compared with those recently obtained within the Galitskii–Migdal–Feynman (GMF) formalism. The overall agreement is very good. An exception, however, is the specific-heat results for neon. While SFA gives results rather similar to those of the ideal gas, the corresponding GMF results are quite different. It is argued that the discrepancy seems to have arisen from quantum effects in conformity with very recent Monte Carlo computations. Whenever possible, our SFA results are compared to experimental data.

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1. Introduction

In this work, the thermodynamic properties of neon ($^{20}\text{Ne}$) and argon ($^{40}\text{Ar}$) gases are studied at different temperatures and densities within the static fluctuation approximation (SFA). As in all other many-body theories, the sole input in this approximation is the interatomic potential. Here, the “Hartree–Fock” dispersion HFD-B $^{5}\text{Ne}$–$^{5}\text{Ne}$ potential and HFD–B$^{6}\text{Ar}$–$^{6}\text{Ar}$ potential are used. The lower-temperature limit is chosen to be just above the boiling point of the gas, whereas the higher limit can, in principle, be extended to any temperature.

In SFA, the square of the local-field (energy) operator is replaced with its mean value. A closed set of nonlinear integral equations for the system is readily derived. These equations correspond to (i) the distribution of the particles over the energy states; (ii) the mean value of the energy spectrum; (iii) the particle correlations in different states; and (iv) the fluctuations in the local-field operator itself. Ne, Ar and indeed other gases provide a fertile ground for applying many-body formalisms of the type used here — i.e., those formalisms which operate best for relatively low-dense, weakly-interacting systems. Such formalisms have had only limited success in highly-dense and strongly-interacting systems.

One of the motivations for this study is to compare SFA to the Galitskii–Migdal–Feynman (GMF) formalism. This is an independent-pair model — in contrast to SFA which is essentially an independent-particle model of the mean-field variety. The GMF formalism is used to calculate the medium phase shifts of neon gas in the temperature range 27–36 K, and argon gas in the temperature range 87.3–120 K, with the HFD-B binary potential as the main input. This formalism is a “generalized” scattering theory — generalized from free space to a many-body medium. From these shifts, the quantum second virial coefficient $B_q$ is determined by invoking the Beth-Uhlenbeck formula. This coefficient is then used to compute the thermodynamic properties of the gases according to standard recipes. At the critical point, gas–liquid condensation is observed. This arises mainly from the long-range weakly-attractive component of the interatomic potential. In this phenomenon, quantum statistics plays an important role.

Ne gas is widely used in vacuum tubes, high-voltage indicators, lightening resistors, television tubes and helium–neon lasers. Likewise, Ar gas is extensively used in commercial and industrial applications, including as a “reference fluid” to establish and test molecular approaches for predicting thermodynamic properties and for calibrating thermodynamic measurements.

Several theoretical methods have been developed to investigate the properties of Ne and Ar gases. Monte Carlo simulations have been used to predict the
thermophysical properties of pure Ne, pure Ar and the binary mixture Ne–Ar. For Ne, quantum corrections turn out to be necessary for a quantitative description of its vapor pressure curve and the coexisting phase densities.\textsuperscript{16} For Ar, it is necessary to take into account three-body effects.\textsuperscript{16} Such effects have been studied for the thermodynamic properties of the fluid phase of Ar.\textsuperscript{17} The properties of this gas were computed over a wide range of densities and temperatures. These investigations have concluded that the thermodynamic properties of Ar can be reproduced reasonably well if an accurate \textit{ab initio} or empirical two-body potential plus three-body interactions are applied in simulation computations.\textsuperscript{17}

An analytic equation of state, derived from a statistical-mechanical perturbation theory, was applied to calculate the thermodynamic properties of Ar: its internal energy, enthalpy, entropy and heat capacity,\textsuperscript{18} using the Lennard-Jones (LJ) 12–6 potential. These were obtained for both liquid and gaseous argon in the temperature range 83.8–300 K and pressure-range 0.01–1000 atmospheres.\textsuperscript{19} Quantum statistical mechanics was invoked to calculate the thermodynamic properties of Ne gas in the broad temperature range of 25–10,000 K using an \textit{ab initio} potential.\textsuperscript{20} Likewise, quantum path-integral simulations have been applied to investigate the phase diagram and isotopic effects of Ne in the temperature range 17–50 K and for pressures between $10^{-2}$ bar and $2 \times 10^3$ bar with emphasis on the phase coexistence between solid, liquid, and gas phases.\textsuperscript{21} The influence of quantum effects on the phase diagram is quantified by comparing the phase diagrams calculated with and without atomic quantum effects. It is found that these effects are significant enough at pressures below $2 \times 10^3$ bar as to modify the critical pressure, volume and temperature. Similar simulations have been performed more recently.\textsuperscript{22} The phase diagram for a quantum LJ liquid in equilibrium with its gas, as a function of the de Boer quantum parameter $\Lambda$, in the range $0.065 \leq \Lambda \leq 0.11$, is mapped using Gibbs ensemble simulations.\textsuperscript{22} The parameters of the LJ pair potential, resulting from comparing to experimental data, represent liquid Ne in coexistence with its gas phase for a range of physically relevant temperatures.

A semi-classical method was formulated to calculate the thermodynamic properties of several quantum fluids including neon. Vapor–liquid equilibria, liquid and vapor densities, as well as isochoric and isobaric heat capacities, were investigated.\textsuperscript{23} It is found that quantum corrections are important not only for the global behavior of the properties of these fluids but also for the low-temperature regime.

Molecular simulation has recently been used to predict the thermodynamic and vapor-liquid properties of both Ne\textsuperscript{24} and Ar,\textsuperscript{25} using accurate \textit{ab initio} potentials. A common feature of these works is that the potentials can be augmented with additional theoretical terms to improve the agreement with experiment. For Ne, the augmentation involves a quantum term, whereas for Ar, three-body terms are necessary. Vlasiuk \textit{et al.}\textsuperscript{24} have established the important contribution that quantum effects have on the thermodynamic properties of Ne from the triple point to the critical point. The relative contributions of two-body and three-body interactions to the thermodynamic properties of Ar have been determined.\textsuperscript{25} It is concluded that
three-body interactions are of particular importance for liquid-phase properties, but their influence on vapor properties should be minimal at very low densities.

The rest of this work is organized as follows. Section 2 addresses the basic principles of SFA, which is used here to derive and compute the thermodynamic properties of our two systems. In Sec. 3, the results are presented and discussed. The paper closes with some brief remarks in Sec. 4.

2. Theoretical Framework

2.1. SFA: Basic principles

The basic physical idea in this approximation is the replacement of the square of the local-field (energy) operator with its mean value. The implication is that the true quantum-mechanical spectrum of this operator is replaced with a distribution around its expectation value. In this sense, SFA is an improvement on the mean-field theory where the operator is replaced with its expectation value.

The total Hamiltonian \( \hat{H} \) describing a neutral many-particle system can be written as the sum of two terms:

\[
\hat{H} = \hat{H}_0 + \hat{H}_1.
\]

Here, \( \hat{H}_0 \) is the kinetic-energy term:

\[
\hat{H}_0 = \int dr \hat{\psi}^+(r) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \hat{\psi}(r),
\]

\( \hat{\psi}(r) \) and \( \hat{\psi}^+(r) \) being the annihilation and creation field operators, respectively. \( \hat{H}_1 \) is the interaction term:

\[
\hat{H}_1 = \frac{1}{2} \int \int dr_1 dr_2 \hat{\psi}^+(r_1) \hat{\psi}^+(r_2) V(r_1 - r_2) \hat{\psi}(r_2) \hat{\psi}(r_1).
\]

\( V(r_1 - r_2) \) is a central potential, depending only on the magnitude of the interparticle separation, \( |r_1 - r_2| \).

As usual in second quantization, the field operators are written as linear combinations of the creation and annihilation operators, \( \hat{b}_k \) and \( \hat{b}_k^+ \):

\[
\hat{\psi}(r) = \sum_k \psi_k(r) \hat{b}_k;
\]

\[
\hat{\psi}^+(r) = \sum_k \psi_k^*(r) \hat{b}_k^+.
\]

where the coefficient \( \psi_k(r) \) is the single-particle wavefunction and \( \psi_k^*(r) \) is its complex conjugate; the sum is over the complete set of compatible single-particle quantum numbers describing a specific state, \( k \) being the linear momentum of the particle. In homogeneous (infinite) systems, all physical properties must be invariant under spatial translations. This suggests periodic boundary conditions and
single-particle wavefunctions that are plane waves:

$$\psi_k(r) = \frac{1}{\sqrt{\Omega}} \exp(ik \cdot r),$$

(6)

\(\Omega\) being the (normalization) volume of the system.

Thus,

$$\hat{H} = \int dr \hat{\Psi}^+ (r) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \hat{\Psi}(r)$$

$$+ \frac{1}{2} \int dr_1 dr_2 \hat{\Psi}^+ (r_1) \hat{\Psi}^+ (r_2) V(r_1 - r_2) \hat{\Psi}(r_1) \hat{\Psi}(r_2).$$

(7)

Integration over the spatial coordinates gives

$$\hat{H} = \sum_k \left( \frac{\hbar^2 k^2}{2m} - \mu \right) \hat{b}_k^+ \hat{b}_k + \frac{1}{2} \sum_k V(k) \hat{\rho}_k \hat{\rho}_k,$$

(8)

\(V(k)\) being the Fourier transform of \(V(r)\) and \(\hat{\rho}_k\) the number-density operator:

$$V(k) \equiv \int V(r) \exp(ik \cdot r) dr; \quad \hat{\rho}_k \equiv \frac{1}{\Omega} \sum_q \hat{b}_k^+ \hat{b}_q.$$

(9)

The single-particle energy, incorporating the chemical potential \(\mu\), is

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m} - \mu.$$

(10)

This is equivalent to the particle being in a potential well with depth \(-\mu\). It follows that

$$\hat{H} = \sum_k \left( \frac{\hbar^2 k^2}{2m} - \mu \right) \hat{b}_k^+ \hat{b}_k + \frac{1}{2} \sum_k V(k) \hat{\rho}_k \hat{\rho}_k.$$

(11)

The Heisenberg representation of a creation operator \(\hat{b}_k^+ (\tau)\), for a Hamiltonian \(\hat{H}\), is given by

$$\hat{b}_k^+ (\tau) = \exp(\tau \hat{H}) \hat{b}_k^+ (0) \exp(-\tau \hat{H});$$

(12)

\(\tau = it\). The equation of motion for \(\hat{b}_k^+ (\tau)\) in this representation can be written as

$$\frac{d\hat{b}_k^+}{d\tau} = [\hat{H}, \hat{b}_k^+ (\tau)].$$

(13)

In SFA, it is assumed that the Hamiltonian can be expressed as a linear combination of the operator \(\hat{E}_k\) and the number-of-particles operator \(\hat{n}_k = \hat{b}_k^+ \hat{b}_k\):

$$\hat{H} = \sum_k \hat{E}_k \hat{n}_k,$$

(14)

where \(\hat{E}_k\) is hermitian and is assumed to commute with \(\hat{b}_k\) and \(\hat{b}_k^+\), which obey the well-known relations for a Bose system:

$$[\hat{b}_k, \hat{b}_q^+] = \delta_{kq}; \quad [\hat{b}_k^+, \hat{b}_q^+] = 0.$$

(15)
From Eqs. (14) and (15):
\[
\frac{db_k^+}{d\tau} = [\hat{H}, \hat{b}_k^+ (\tau)] = \hat{E}_k \hat{b}_k^+.
\] (16)

The operator \(\hat{E}_k\) describing an infinite homogeneous Bose system is obtained as follows\(^1,2\):
\[
\hat{E}_k = \varepsilon (k) + \frac{1}{\Omega} \sum_q W(k, q) \hat{n}_q,
\] (17)

where
\[
W(k, q) = V(0) + V(|k - q|).
\]

In the mean-field approximation, \(\hat{E}_k\) is replaced with its mean value:
\[
\hat{E}_k \approx \langle \hat{E}_k \rangle.
\] (18)

The implicit assumption is that the fluctuations in the operator are negligible. In SFA, it is the square of this operator that is replaced with its mean value:
\[
\hat{E}_k^2 \approx \langle \hat{E}_k^2 \rangle = \varphi_k^2.
\] (19)

The desired long-range (generating) equation is given by\(^1\)
\[
\langle \hat{n}_k \hat{A} \rangle = \eta_0 (k) \langle \hat{A} \rangle + \eta_1 (k) \langle \Delta \hat{E}_k \hat{A} \rangle,
\] (20)

where
\[
\eta_0 (k) = \frac{1}{2} \left( \frac{1}{\exp(\beta(\langle E_k \rangle + \varphi_k)) - 1} + \frac{1}{\exp(\beta(\langle E_k \rangle - \varphi_k)) - 1} \right); \quad (21)
\]
\[
\eta_1 (k) = \frac{1}{2\varphi_k} \left( \frac{1}{\exp(\beta(\langle E_k \rangle + \varphi_k)) - 1} - \frac{1}{\exp(\beta(\langle E_k \rangle - \varphi_k)) - 1} \right). \quad (22)
\]

Putting \(\hat{A} = \hat{1}\) in Eq. (20) and noting that \(\langle \Delta \hat{E}_k \rangle = 0\), thanks to the symmetry involved, we have
\[
\langle \hat{n}_k \rangle = \eta_0 (k). \quad (23)
\]

The long-range equation can be rewritten in terms of the fluctuations of \(\hat{n}_k\), defined as
\[
\Delta \hat{n}_k \equiv \hat{n}_k - \langle \hat{n}_k \rangle. \quad (24)
\]

Equation (20) becomes
\[
\langle \hat{n}_k \hat{A} \rangle = \eta_1 (k) \langle \Delta \hat{E}_k \hat{A} \rangle. \quad (25)
\]

Putting \(\hat{A} = \Delta \hat{n}_q\) in this equation, one has
\[
\langle \Delta \hat{n}_k \Delta \hat{n}_q \rangle_c = \frac{\eta_1 (k)}{\Omega} \sum_{p \neq k} V(k - p) \langle \Delta \hat{n}_p \Delta \hat{n}_q \rangle_c
\]
\[
= \frac{\eta_1 (k)}{\Omega} (V(k - q) \langle (\Delta \hat{n}_q)^2 \rangle) + \frac{\eta_1 (k)}{\Omega} \sum_{p \neq k} V(k - p) \langle \Delta \hat{n}_p \Delta \hat{n}_q \rangle_c, \quad (26)
\]
the subscript \(c\) denoting \(k \neq q\) “correlation”.
The unknown value \( \langle (\Delta \hat{n}_q)^2 \rangle \) appearing in Eq. (26) is given by

\[
\langle (\Delta \hat{n}_q)^2 \rangle = \langle \hat{n}_q \rangle (1 + \langle \hat{n}_q \rangle) + \frac{2\eta_1(q)}{\Omega} \sum_{p \neq k} V(p - q) \langle \Delta \hat{n}_p \Delta \hat{n}_q \rangle_c. \tag{27}
\]

Substituting \( \hat{A} = \Delta \hat{E}_k \) in Eq. (25), we have

\[
\eta_1(k) \varphi_k^2 = \frac{1}{\Omega} \sum_{p} V(k - p) \langle \Delta \hat{n}_k \Delta \hat{n}_p \rangle_c. \tag{28}
\]

To calculate the thermodynamic properties of the system, one should first determine the grand partition function \( Q \):

\[
Q = \text{Tr}(\exp(-\beta \hat{H})) = \sum_{n_p} \exp \left[ -\beta \sum_{p} \hat{E}_P \hat{n}_p \right] = \Pi_p \sum_{n_p} \exp(-\beta \hat{E}_P \hat{n}_p). \tag{29}
\]

Using the SFA assumptions,\(^1\) one has

\[
\ln Q = -\sum_{P} q_0(p), \tag{30}
\]

where

\[
q_0(p) = \frac{1}{2} \ln[(1 - \exp(-\beta(\langle \hat{E}_P \rangle + \varphi_P)))(1 - \exp(-\beta(\langle \hat{E}_P \rangle - \varphi_P))]. \tag{31}
\]

The mean internal energy is

\[
U = -\left( \frac{\partial \ln Q}{\partial \beta} \right); \tag{32}
\]

so that

\[
U = \sum_{p} \langle \hat{n}_p \hat{E}_p \rangle = \sum_{p} (\langle \hat{E}_p \rangle \langle \hat{n}_p \rangle + \varphi_p^2 \eta_1(p)). \tag{33}
\]

The other thermodynamic properties can now be readily calculated: First, the pressure \( P \) is given by

\[
P = k_B T \frac{\ln Q}{\Omega}. \tag{34}
\]

Second, the entropy \( S \) can be evaluated from the first law of thermodynamics:

\[
S = \frac{U}{T} + k_B \ln Q. \tag{35}
\]

Third, the heat capacity at constant volume \( C_v \) is

\[
C_v = \left( \frac{\partial U}{\partial T} \right)_{\Omega}. \tag{36}
\]

The closed set of coupled nonlinear integral equations (17), (23), (26), (27) and (28) was solved numerically by the Gaussian-quadrature-point method.\(^28\)

### 2.2. Interatomic potential

The input two-body potential is taken as the HFD-B for Ne–Ne\(^29\) and HFD-B3 for Ar–Ar.\(^30\) The corresponding parameters are given in Table 1, and the general form
Table 1. The potential parameters: HFD-B for Ne–Ne and HFD-B3 for Ar–Ar.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ne–Ne</th>
<th>Ar–Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A \times 10^6$</td>
<td>0.89571795</td>
<td>0.113211845</td>
</tr>
<tr>
<td>$r_m$</td>
<td>3.091 Å</td>
<td>3.761 Å</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>42.25 K</td>
<td>143.25 K</td>
</tr>
<tr>
<td>$D$</td>
<td>1.36</td>
<td>1.04</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>13.86434671</td>
<td>9.00053441</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$-0.12993822$</td>
<td>$-2.60270226$</td>
</tr>
<tr>
<td>$C_6$</td>
<td>1.21317545</td>
<td>1.09971113</td>
</tr>
<tr>
<td>$C_8$</td>
<td>0.53222749</td>
<td>0.54511632</td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>0.24570703</td>
<td>0.39278653</td>
</tr>
</tbody>
</table>

is given by

$$V(r) = \varepsilon V^*(x) (x \equiv r/r_m; V(r_m) = -\varepsilon);$$

$$V^*(x) = Ax^\gamma \exp(-\alpha x + \beta x^2) - \left\{ \frac{C_6}{x^6} + \frac{C_8}{x^8} + \frac{C_{10}}{x^{10}} \right\} F(x);$$

$$F(x) = \begin{cases} 
\exp\left[-\left(\frac{D}{x} - 1\right)^2\right], & x < D, \\
1, & x \geq D.
\end{cases} \tag{37}$$

3. Results and Discussion

3.1. Ne system

Our results are displayed in Figs. 1–4. Figure 1 shows the energy $U$ as a function of $T$ at $n = 1 \times 10^{27}$ atoms/m$^3$ ($\rho = 33.20$ kg/m$^3$). As is expected from elementary classical considerations, $U$ is linearly-dependent on $T$. In Fig. 2, $P$ is plotted as a function of $T$, $n$ again being fixed. It is observed that $P$ is linearly-dependent on $T$. This is because, as $T$ increases, the kinetic energy of the system increases linearly, which in turn causes a linear increase in $P$. On the other hand, the plot of $S$ versus $T$ in Fig. 3 shows that $S$ is nearly independent of $T$ in the present (admittedly short) $T$-range. The heat capacity $C_v$ is displayed as a function of $T$ in Fig. 4. From this figure, it is noted that SFA results for $C_v$ ($\sim 14$ J mol$^{-1}$ K$^{-1}$) are almost independent of $T$. These are compared to experimental results in Table 2. The behavior of $C_v$ is consistent with experimental data, although there is a discrepancy of 3–4 mol$^{-1}$ K$^{-1}$. The deviations are within 25%. On the other hand, using accurate ab initio potentials and Monte Carlo techniques, Vlasiuk et al. have found that at temperatures slightly above the triple point, $C_v$ is $(20–22$ mol$^{-1}$ K$^{-1})$. As $T$ increases, $C_v$ gradually decreases until it reaches a minimum of 16.5 J mol$^{-1}$ K$^{-1}$. The discrepancy between theory and experiment is typically within 4–8 mol$^{-1}$ K$^{-1}$. It turns out that these results can be improved when quantum corrections are taken...
Ne; Ar gases in SFA

![Graph of total internal energy vs. temperature for Ne gas](image1)

**Fig. 1.** The total internal energy $U$ [J] of $^{20}\text{Ne}$ gas as a function of temperature $T$ [K] for GMF and SFA methods; the number density $n = 1 \times 10^{27}$ atoms/m$^3$ ($\rho = 33.20$ kg/m$^3$).

![Graph of pressure vs. temperature for Ne gas](image2)

**Fig. 2.** The pressure $P$ [Pa] of $^{20}\text{Ne}$ gas as a function of temperature $T$ [K] for GMF and SFA methods; the number density $n = 1 \times 10^{27}$ atoms/m$^3$ ($\rho = 33.20$ kg/m$^3$).

into account. With these corrections, the deviations of the isochoric heat capacity from experimental results are reduced considerably; they now lie within 1.4%.

For comparison purposes, the results obtained by GMF$^{10}$ are also shown in Figs. 1–4. Clearly, the behavior of the thermodynamic quantities in both methods is
Fig. 3. The entropy $S[J/K]$ of $^{20}\text{Ne}$ gas as a function of temperature $T[K]$ for GMF and SFA methods; the number density $n = 1 \times 10^{27}$ atoms/m$^3$ ($\rho = 33.20$ kg/m$^3$).

Fig. 4. The specific heat $C_v$ of $^{20}\text{Ne}$ gas as a function of temperatures $T[K]$ for GMF and SFA methods; the number density $n = 1 \times 10^{27}$ atoms/m$^3$ ($\rho = 33.20$ kg/m$^3$). The comparison of SFA results with experimental data is shown in Table 2.

almost identical, except that SFA results are consistently greater than GMF results by a constant shift. On the other hand, Fig. 4 exhibits a difference in behavior for $\frac{C_v}{Nk_B}$ between the two methods. While in SFA $\frac{C_v}{Nk_B}$ is nearly independent of $T$, as is the case for the ideal gas, in GMF this quantity is strongly-dependent...
Table 2. Comparison of SFA results for the heat capacity $C_v$ of $^{20}\text{Ne}$ (this work) with experimental data.$^{30}$

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$C_v$ (This work)</th>
<th>$C_v$ (Ref. 30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>13.94</td>
<td>17.87</td>
</tr>
<tr>
<td>28</td>
<td>13.88</td>
<td>17.65</td>
</tr>
<tr>
<td>29</td>
<td>13.84</td>
<td>17.45</td>
</tr>
<tr>
<td>30</td>
<td>13.79</td>
<td>17.27</td>
</tr>
<tr>
<td>31</td>
<td>13.74</td>
<td>17.11</td>
</tr>
<tr>
<td>32</td>
<td>13.69</td>
<td>16.96</td>
</tr>
<tr>
<td>33</td>
<td>13.67</td>
<td>16.85</td>
</tr>
<tr>
<td>34</td>
<td>13.63</td>
<td>16.75</td>
</tr>
<tr>
<td>35</td>
<td>13.55</td>
<td>16.65</td>
</tr>
<tr>
<td>36</td>
<td>13.52</td>
<td>16.56</td>
</tr>
</tbody>
</table>

on $T$. Quantum effects might be responsible for this latter behavior. Specifically, our cumulative experience indicates that the GMF formalism is more reliable than SFA. This is because GMF includes more physics, the theory being essentially an independent-pair model, albeit in the presence of a many-body medium. In contrast, SFA is quite close to the Hartree model, i.e., an independent-particle model in the presence of such a medium; hence its similarity to the ideal-gas model.

These quantum effects have also manifested themselves very recently in Monte Carlo computations of this system.$^{24}$ The point is that, in the temperature ranges considered, Ne lies somewhere in the middle between the purely quantum-mechanical He and the purely classical Ar. The determining factor here is, of course, the mass (and, hence, the corresponding zero-point energy).

Fig. 5. The grand mean energy per particle $U/N$[K] of $^{40}\text{Ar}$ gas as a function of temperature $T$[K] for different number densities $n$ [atoms/m$^3$].
3.2. Ar system

Figures 5–8 show the thermodynamic properties of Ar gas as functions of $T$ for three different number densities (Table 3).

It is noted that $U/N$, $P$ and $S/Nk_B$ increase with increasing $T$. This is because repulsive forces increase with increasing $T$. Further, $S$ and $C_v$ decrease with increasing $n$, and the gas becomes more and more ideal with decreasing $n$, as expected on physical grounds.

The functional dependence on $T$ of the above thermodynamic quantities can be straightforwardly obtained by fitting procedures. The results are: $U \propto T^{0.9}$,
Fig. 8. The heat capacity per particle $C_V/Nk_B$ of $^{40}$Ar gas as a function of temperature $T$[K] for different number densities $n$ [atoms/m$^3$].

Table 3. The number density $n$ [atoms/m$^3$], and the corresponding $\rho$ [kg/m$^3$], for which the thermodynamic properties of Ar gas are calculated.

<table>
<thead>
<tr>
<th>$n$ [atoms/m$^3$]</th>
<th>$\rho$ [kg/m$^3$] for $^{40}$Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 10^{25}$</td>
<td>1.327</td>
</tr>
<tr>
<td>$2 \times 10^{26}$</td>
<td>13.27</td>
</tr>
<tr>
<td>$1 \times 10^{27}$</td>
<td>66.36</td>
</tr>
</tbody>
</table>

$P \propto T^{1.00008}$, $S \propto T^{0.085}$ and $C_v$ is nearly independent of $T$ in the present T-range ($C_v \sim 12.5$ J mol$^{-1}$ K$^{-1}$). This $T$-dependence is the same as for the ideal system; the small deviation arises from the weak interactions in Ar gas. Vlasiuk et al.$^{25}$ found $C_v$ of argon is 22 J mol$^{-1}$ K$^{-1}$ at temperatures slightly above the triple point. As temperature increases, $C_v$ gradually decreases until reaching a minimum of 18 J mol$^{-1}$ K$^{-1}$ at approximately 130 K.

Table 4. Comparison between GMF and SFA results for the thermodynamic properties of Ar gas at different temperatures $T$[K].

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</table>
Table 4 displays a comparison between GMF\textsuperscript{11} and SFA results for the thermodynamic properties of Ar gas for different $T$ at $n = 2 \times 10^{25}$ atoms/m$^3$. The agreement is very good for this weakly-interacting system — as expected for these approaches which work best for such systems.

4. Conclusion

A microscopic approach, SFA, was used for investigating the thermodynamic properties of Ne and Ar gases. As expected, these properties were found to exhibit small quantum effects in the temperature range considered. The mean total internal energy, pressure, entropy and heat capacity of these gases were calculated, and their functional dependence on the temperature was carefully considered. The results were compared wherever possible with recent GMF results. The overall agreement turned out to be quite good, except for the heat capacity of Ne, where quantum effects manifested themselves in GMF, but not in SFA.

Acknowledgment

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References