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Kinetic energies of liquid and solid neon

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We have calculated the kinetic energies of liquid and solid neon in the temperature range 9.2–35 K. We have used the Wigner-Kirkwood expansion technique for the calculation of quantum corrections to the kinetic energy up to the order of $\hbar^6$ in the expansion. All the averages are calculated by molecular dynamics computer simulation. Our results are in agreement with the experimental findings of Peek *et al.* Both the Lennard-Jones and Aziz pair potentials have been used in calculations with comparable results.

Recently, Peek *et al.*[1,2] have measured the kinetic energies of liquid and solid neon in the temperature range of 4.7–35° K at various densities using deep inelastic neutron scattering from natural neon. These measurements along with the other properties[3] make this system an interesting object for theoretical studies. The other properties include internal energies, lattice constants, thermal expansion, isothermal compressibilities, and specific heat. However, in the present study we shall confine ourselves to the calculation of kinetic energies, both in liquid and solid phases. The results of calculations for other properties shall be presented elsewhere.

We have used the Wigner-Kirkwood expansion technique[4–7] for the calculation of quantum corrections to classical kinetic energy up to order of $\hbar^6$ in the expansion. All the averages in the expansion are calculated using molecular dynamics computer simulation. Using Lennard-Jones pair potential, calculations similar to ours were carried out by Barocchi, Neumann, and Zoppi;[8] however, their calculations were confined to the order of $\hbar^2$ at 18 K and up to $\hbar^4$ for higher temperatures and limited to density region not covered by experiment.

We have used both the Lennard-Jones and Aziz[9] pair potentials with parameters appropriate to neon. The Aziz pair potential may be considered as slightly preferable over the Lennard-Jones, particularly, in the liquid phase at higher temperature. Thus, for example, we find the kinetic energy 64.18±0.03 K at density $\rho=0.034597704$ Å^{-3} and $T=35°$ K as compared to the experimental value of 66±4.7 K. In the Lennard-Jones case this value is 62.81±0.03 K. It may be remarked that at this density and temperature the $\hbar$ expansion converges rapidly. In the solid phase, the results of the two potentials are more or less indistinguishable.

The Hamiltonian operator of N interacting particles is

$$\hat{H}=-\frac{\hbar^2}{2m}\partial_{r_i}\partial_{r_i}+\Phi(r)\ , \tag{1}$$

where the summation is understood over repeated indices $r=1,2,3,\ldots,N$ which is the particle index and $i=1,2,3$ is the coordinate index. $\Phi(r)$ represents the interatomic potential of all the pairs.

The partition function Z of the system can be obtained by calculating the trace of $\exp(-\beta\hat{H})$ which we perform in the plane wave basis.

$$\Psi_p=\frac{1}{\sqrt{N!}}\left[\frac{1}{2\pi\hbar}\right]^{3N/2}\sum_P(\pm)^P\exp\left[ip^P\frac{r}{\hbar}\right]\ , \tag{2}$$

where P is the permutation operator with ± for Bose or Fermi systems. The superscript on momentum denotes their permuted values. The partition function Z then becomes

$$Z=\frac{1}{N!}\left[\frac{1}{2\pi\hbar}\right]^{3N}\sum_{P,P'}(\pm)^{P+P'}\int d^{3N}r\,d^{3N}p\exp\left[-ip^{P'}\frac{r}{\hbar}\right]\times\exp(-\beta\hat{H})\exp\left[ip^P\frac{r}{\hbar}\right] \tag{3}$$

where $\beta=1/kT$. The quantity

$$F=\exp(-\beta\hat{H})\exp\left[ip^P\frac{r}{\hbar}\right] \tag{4}$$

satisfies the Bloch equation: $\partial F/\partial\beta+\hat{H}F=0$. Which has a solution

$$F=\exp[-\beta H(r,p)]\exp\left[ip^P\frac{r}{\hbar}\right]w(r,p)\ , \tag{5}$$

where $H(r,p)$ is the classical Hamiltonian. The w may be expanded in power of $\hbar$

$$w=w_0(r,p)+\hbar w_1(r,p)+\hbar^2w_2(r,p)+\hbar^3w_3(r,p)+\hbar^4w_4(r,p)\cdots\ , \tag{6}$$

where $w_i(r,p)$ satisfy the recurrence relation:

$$w_i(\hat{r},\hat{p})=\frac{1}{m}\int_0^\beta dt\,p^P(\nabla w_{i-1}-tw_{i-1}\nabla\Phi)+\frac{1}{2m}\int_0^\beta dt(\nabla^2w_{i-2}-2t\nabla w_{i-2}\nabla\Phi)-\frac{1}{2m}\int_0^\beta(tw_{i-2}\nabla^2\Phi-t^2w_{i-2}\nabla\Phi\nabla\Phi) \tag{7}$$

with the condition that $w_0=1$, $w_1=-(1/2m)\beta(p\nabla\Phi)$. Using Eqs. (5) and (6) one may write the partition function as

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$$Z=\frac{1}{N!}\left[\frac{1}{2\pi\hbar}\right]^{3N}\sum_{P,P'}(\pm)^{P+P'}\int d^{3N}r\,d^{3N}p\exp\left[-ip^{P'}\frac{r}{\hbar}\right]\exp[-\beta H(r,p)]\exp\left[ip^{P}\frac{r}{\hbar}\right]$$

$$\times(w_0+\hbar w_1+\hbar^2w_2+\hbar^3w_3+\hbar^4w_4+\cdots)\,. \tag{8}$$

In what follows we shall specialize (8) to Maxwell-Boltzmann statistics because of the following two reasons. First, because of the repeated appearance of the derivatives in (7) the number of terms grow very rapidly as one proceeds to higher orders which makes keeping the track of the various permutation exceedingly tedious. Second, we hope that for the temperature range 9.2–35 K and densities considered for neon in the present study, the exchange effects are not likely to be important. With this simplification the integration over the momentum coordinate in (8) can be carried out with nonvanishing terms with even powers of $\hbar$. The terms with odd power of $\hbar$ vanish.

The kinetic energy is

$$\langle KE\rangle=\frac{\mathrm{Tr}\left[\sum\frac{p^2}{2m}\exp(-\beta\hat{H})\right]}{\mathrm{Tr}[\exp(-\beta\hat{H})]} \tag{9}$$

which using earlier equations may be written as

$$\langle KE\rangle=\frac{(P_0+P_2+P_4+P_6+\cdots)}{(1+\chi_2+\chi_4+\chi_6+\cdots)}\,, \tag{10}$$

where $P_0=3N/2\beta$; $P_i=\hbar^i\langle(pp/2m)w_i\rangle$, $\chi_0=1$, and $\chi_i=\hbar^i\langle w_i\rangle$. Collecting the terms of equal power of $\hbar$ we have

$$\langle KE\rangle=K_0+K_2+K_4+K_6+K_8+\cdots\,, \tag{11}$$

where

$$K_0=\frac{3N}{2\beta};\quad K_2=\frac{\hbar^2}{2m}\beta(4.1666\times10^{-2})\langle\Phi_{ii}\rangle\,, \tag{12}$$

$$K_4=\frac{\hbar^4}{m^2}[\beta^2(1.7361\times10^{-3})\langle\Phi_{iijj}\rangle+\beta^3(-1.7361\times10^{-3})\langle\Phi_{ii}\Phi_{jj}\rangle]$$

$$+\frac{\hbar^4}{m^2}\beta^3(-6.9444\times10^{-4})\langle\Phi_{ij}\Phi_{ij}\rangle-K_2\chi_2\,, \tag{13}$$

$$K_6=\frac{\hbar^6}{m^3}[\beta^3(3.6168\times10^{-5})\langle\Phi_{iijjkk}\rangle+\beta^4(-1.0850\times10^{-5})\langle\Phi_{iijj}\Phi_{kk}\rangle]$$

$$+\frac{\hbar^6}{m^3}[\beta^4(-8.6805\times10^{-5})\langle\Phi_{iijk}\Phi_{jk}\rangle+\beta^4(-8.2671\times10^{-5})\langle\Phi_{ijk}\Phi_{ijk}\rangle]$$

$$+\frac{\hbar^6}{m^3}[\beta^5(3.6168\times10^{-5})\langle\Phi_{ii}\Phi_{jj}\Phi_{kk}\rangle+\beta^5(4.3402\times10^{-5})\langle\Phi_{ii}\Phi_{jk}\Phi_{jk}\rangle]$$

$$+\frac{\hbar^6}{m^3}\beta^5(1.6534\times10^{-5})\langle\Phi_{ij}\Phi_{ik}\Phi_{jk}\rangle-K_4\chi_2-K_2\chi_4\,. \tag{14}$$

The expressions for χ_2 and χ_4 are given as

$$\chi_2=\frac{\hbar^2}{m}\beta^2(-4.1666\times10^{-2})\langle\Phi_{ii}\rangle\,, \tag{15}$$

$$\chi_4=\frac{\hbar^4}{m^2}[\beta^3(-8.6805\times10^{-4})\langle\Phi_{iijj}\rangle$$

$$+\beta^4(8.6805\times10^{-4})\langle\Phi_{ii}\Phi_{jj}\rangle]$$

$$+\frac{\hbar^4}{m^2}\beta^4(3.4722\times10^{-4})\langle\Phi_{ij}\Phi_{ij}\rangle\,, \tag{16}$$

where

$$\Phi=\sum_{i<j}^{N}V(|\mathbf{r}_i-\mathbf{r}_j|)\quad\text{and}\,\Phi_{i,j,\ldots,n}=\frac{\partial^nV}{\partial_{r_i}\partial_{r_j}\cdots\partial_{r_n}}\,. \tag{17}$$

We have calculated the K_i using the program for symbolic computation of Wigner-Kirkwood expansion[10] developed at Jamia Millia Islamia. The expressions for kinetic energy obtained here are identical with that of Ref. 8. The expressions corresponding to $\hbar^8$ and for potential energy and specific heat will be presented elsewhere.

We have used the molecular dynamics technique to compute the various correction to kinetic energy in the temperature range of 9–35 K. The simulations were per-

TABLE I. Single particle kinetic energies of solid neon at density 0.044264706 $Å^{-3}$ with Lennard-Jones pair potential. $\langle KO \rangle$ is the classical kinetic energy where as $\langle K \rangle_2$, $\langle K \rangle_4$, $\langle K \rangle_6$, $\langle KE \rangle_{MD}$, and $\langle KE \rangle_{\mathrm{expt}}$ represents the 2nd, 4th, 6th order quantum corrections, total kinetic energy with corrections and experimental kinetic energy, respectively. All the values are in degrees Kelvin.

Temperature	9.37	12.02	18.09	27.18
$\langle KO \rangle$	14.05	18.04	27.13	40.78
$\langle K \rangle_2$	29.94±0.02	25.19±0.02	19.15±0.02	15.36±0.02
$\langle K \rangle_4$	17.71±0.03	11.93±0.02	6.61±0.01	3.38±0.01
$\langle K \rangle_6$	−11.43±0.01	−5.32±0.05	−1.47±0.03	−0.30±0.01
$\langle KE \rangle_{MD}$	49.81±0.20	49.80±0.05	51.29±0.03	58.93±0.02
$\langle KE \rangle_{\mathrm{expt}}$	50.70±4.00	47.70±3.00	50.80±3.00	59.59±3.00

TABLE II. Single particle kinetic energies of liquid neon with Lennard-Jones pair potential. All entries have the same meaning as in Table I.

Temperature Density	26.93 0.0359188	35.10 0.0345977	34.99 0.0316842
$\langle KO \rangle$	40.39	52.65	52.48
$\langle K \rangle_2$	11.08±0.03	8.91±0.02	7.31±0.03
$\langle K \rangle_4$	2.31±0.01	1.42±0.01	1.22±0.01
$\langle K \rangle_6$	−0.13±0.01	−0.03±0.01	−0.04±0.01
$\langle KE \rangle_{MD}$	53.76±0.4	62.81±0.03	61.01±0.03
$\langle KE \rangle_{\mathrm{expt}}$	53.80±3.00	67.40±3.00	66.50±3.00

TABLE III. Single particle kinetic energies of solid neon at density 0.044264706 $Å^{-3}$ with Aziz pair potenital. $\langle KO \rangle$ is the classical kinetic energy where as $\langle K \rangle_2$, $\langle K \rangle_4$, $\langle K \rangle_6$, $\langle KE \rangle_{MD}$, and $\langle KE \rangle_{\mathrm{expt}}$ represents the 2nd, 4th, and 6th order quantum corrections, total kinetic energy with corrections and experimental kinetic energy, respectively. All the values are in degrees Kelvin.

Temperature	9.22	12.10	17.97	27.01
$\langle KO \rangle$	13.90	18.15	26.95	40.86
$\langle K \rangle_2$	38.93±0.03	31.72±0.02	23.31±0.03	18.27±0.01
$\langle K \rangle_4$	16.97±0.05	12.16±0.02	6.86±0.01	3.32±0.01
$\langle K \rangle_6$	−20.89±0.01	−9.07±0.06	−2.61±0.03	−0.57±0.01
$\langle KE \rangle_{MD}$	48.81±0.12	52.81±0.05	54.54±0.02	61.51±0.01
$\langle KE \rangle_{\mathrm{expt}}$	50.70±4.00	47.70±3.00	50.80±3.00	59.59±3.00

TABLE IV. Single particle kinetic energies of liquid neon with Aziz pair potential.

Temperature Density	27.29 0.035918854	35.10 0.034597701	34.88 0.031684211
$\langle KO \rangle$	40.93	52.65	52.32
$\langle K \rangle_2$	13.11±0.03	10.54±0.02	8.74±0.03
$\langle K \rangle_4$	1.90±0.01	1.16±0.02	1.04±0.01
$\langle K \rangle_6$	−0.07±0.02	−0.01±0.00	−0.05±0.00
$\langle KE \rangle_{MD}$	55.44±0.4	64.18±0.03	62.23±0.03
$\langle KE \rangle_{\mathrm{expt}}$	53.80±3.00	67.40±3.00	66.50±3.00

formed with time steps in the range 1.0×10^4 to 1.0×10^5 units of Å/c. The reduced time step was used at low temperature (solid phase) to reduce the statistical fluctuations. We have worked with 64 particles in the liquid phase with simple cubic structure in which the particles are placed at the center of the basic unit, which is surrounded from all sides by periodically repeated replicas of itself. We used the periodic boundary condition, i.e., when a particle leaves one face of the cell the move is balanced by allowing that particle to enter from the opposite face of the cell. A similar boundary condition was also generated in case of solid phase by keeping the N particles in face centered cubic structure appropriate to the solid neon.

We have summarized the average values of the various contributions of the even powers of $\hbar$ to kinetic energy calculated by molecular dynamics simulation with Lennard-Jones and Aziz interatomic potentials in Tables I–IV.

The $\hbar$ series expansion for quantum corrections to kinetic energy show very good convergence at temperature 18 K and above. However, the series expansion does not seem to be converging below 18 K and gives tortuous contribution to kinetic energy though well in agreement with experiment. Nothing can be said about higher-order contributions from $\hbar^6$ and lower order terms. Probably, the higher-order terms are indeed small or else the agreement with experimental at lower temperature is accidental. In order to settle this question we have to wait till the next higher order, i.e., $\hbar^8$ term is calculated in Wigner-Kirkwood expansion. These calculations are underway and will be reported in due time.

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