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On the Internal Energy of a Simple Fluid†

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A study is made of the internal energy of a simple fluid, and its derivative with respect to particle number at constant temperature and volume. This derivative occurs in a formula linking energy and particle number fluctuations to the specific heat, and may be calculated exactly for the Ising and certain other models along the critical isochore. Experimental results for fluid Argon are compared with the description provided by van der Waals' equation, which is able to predict within 5% the slope of the loci in the density-temperature plane along which the internal energy and its particle number derivative vanish.

1 INTRODUCTION

The thermodynamic properties of a simple fluid usually studied include the total internal energy U , the entropy S and their various derivatives, such as the specific heats at constant volume and at constant pressure. However, recent investigation of a formula, derivable from statistical mechanics, linking equilibrium fluctuations in energy and particle number, indicates that the energy density is an interesting quantity. Whereas the total energy U decreases monotonically along isotherms as the density is increased, the energy density (U/V) exhibits a maximum. The locus of maxima can readily be calculated from an equation of state, such as van der Waals' equation, via the derivative $(\partial U/\partial n)_{TV}$ of U with respect to the number of moles n of material present, holding the temperature and volume fixed. In addition,¹

$$\left(\frac{\partial U}{\partial n}\right)_{TV} = N_0 \left(\frac{\partial U}{\partial N}\right)_{TV} \quad (1.1)$$

where $N = nN_0$ is the number of particles, and N_0 is Avogadro's number.

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The derivative $(\partial U/\partial N)_{TV}$ describes the way in which the internal energy changes with particle number at fixed T and V . This same derivative occurs in the fluctuation formula linking energy and particle number fluctuations in the grand canonical ensemble. The constant volume specific heat C_{nV} depends on the *difference* between energy and particle number fluctuations, and yet must be positive, by the usual thermodynamic stability criteria. Moreover, the derivative $(\partial U/\partial n)_{TV}$ can be calculated explicitly along the critical isochore for certain model systems, such as the Ising and anisotropic Heisenberg models, when transcribed for fluids, with different results for classical and quantum systems. In contrast to the specific heat, one finds $(\partial U/\partial n)_{TV}$ to be analytic in temperature along the critical isochore, an observation which is confirmed experimentally, and which is incorporated in the scaling law equation of state for fluids through assumptions on the behaviour of the chemical potential along the critical isochore. In addition it is of interest to determine the loci along which U and $(\partial U/\partial n)_{TV}$ vanish. Calculations for fluid Argon show that these loci, in the density-temperature plane, are very nearly straight lines, with (dimensionless) slopes in remarkably close agreement with the values $4/3$ and $2/3$ respectively, predicted by van der Waals' equation. The equation of state for Argon used here is that fitted by Gosman, McCarty and Hust.

We shall establish certain elementary thermodynamic properties of U and $(\partial U/\partial n)_{TV}$ in section 2, and then discuss in turn their calculation for model systems in section 3, for van der Waals' equation in section 4, and for fluid Argon in Section 5.

2 SOME PROPERTIES OF U AND $(\partial U/\partial n)_{TV}$

First we recall from elementary thermodynamics the well-known expression for the volume derivative of the internal energy at fixed temperature and constant number of moles, n :

$$\left(\frac{\partial U}{\partial V}\right)_{nT} = T \left(\frac{\partial P}{\partial T}\right)_{nV} - P. \quad (2.1)$$

This derivative is related to the Joule coefficient which describes the temperature change occurring when free expansion of a fluid takes place:²

$$\text{Joule coefficient} \equiv \left(\frac{\partial T}{\partial V}\right)_{nU} = \left[P - T \left(\frac{\partial P}{\partial T}\right)_{nV} \right] / C_{nV}. \quad (2.2)$$

The Joule coefficient is negative for fluids, and $(\partial U/\partial V)_{nT}$ is positive.

Next we note that the derivative of the internal energy with respect to the number of moles of fluid at fixed temperature T and volume V is given

by:

$$\left(\frac{\partial U}{\partial n}\right)_{TV} = \mu - T\left(\frac{\partial \mu}{\partial T}\right)_{nV}, \quad (2.3)$$

where μ is the chemical potential, or Gibbs function per mole. Also

$$\left(\frac{\partial U}{\partial n}\right)_{TV} = \left(\frac{U}{n}\right) + \left(\frac{V}{n}\right)\left[T\left(\frac{\partial P}{\partial T}\right)_{nV} - P\right], \quad (2.4)$$

in which the second term on the right hand side is derived from (2.1) above. (2.3) is easily established by combining the second law of thermodynamics,

$$dU = TdS - PdV + \mu dn, \quad (2.5)$$

with the Maxwell relation

$$\left(\frac{\partial S}{\partial n}\right)_{TV} = (-)\left(\frac{\partial \mu}{\partial T}\right)_{nV} \quad (2.6)$$

which follows from the perfect differential for the Helmholtz free energy F (sometimes denoted by A):

$$dF = -SdT - PdV + \mu dn. \quad (2.7)$$

Then (2.4) follows on using

$$\mu n = U - TS + PV, \quad (2.8)$$

and the Gibbs–Duhem equation

$$nd\mu = -SdT + VdP, \quad (2.9)$$

to evaluate the right hand side of (2.3). Alternatively one can derive (2.4) directly from (2.1).

The derivative $(\partial U/\partial N)_{TV}$ occurs in the fluctuation formula relating energy and particle number fluctuations in the grand canonical ensemble. It is a straightforward exercise in statistical mechanics³ (see appendix A) to verify that

$$\overline{(\Delta U)^2} = k_B T^2 C_{nV} + \left(\frac{\partial U}{\partial N}\right)_{TV}^2 \overline{(\Delta N)^2} \quad (2.10)$$

where ΔU and ΔN denote deviations from the mean values U and N . As we shall see below, $(\partial U/\partial N)_{TV}$ is smoothly varying throughout the homogeneous phase of a simple fluid, and is finite at the critical point. Equation (2.10) tells us that energy fluctuations diverge strongly at the critical point, in the same manner as particle number fluctuations, which are related to the isothermal compressibility. The specific heat at constant volume is only weakly divergent and depends on the difference between energy and particle

number fluctuations. It is interesting to contrast the situation here in the grand canonical ensemble with that in the canonical ensemble, where the second term on the right hand side of (2.10) is absent, and energy fluctuations diverge weakly like the specific heat. Along the locus where $(\partial U/\partial N)_{TV}$ vanishes, the specific heat depends only on energy fluctuations.

3 ISING AND HEISENBERG MODELS

The derivative $(\partial U/\partial N)_{TV}$ can be calculated along the critical isochore for the Ising and Heisenberg models, transcribed for fluids,^{4,5} because there are explicit expressions for the chemical potential $\mu(\rho_c, T)$ as a function of temperature.

For the Ising model

$$\mu^*(\rho_c, T) = \frac{1}{2} \hat{u}(0) + k_B T \ln(\Lambda^d \rho_{\max}) \quad (3.1)$$

where

μ^* = chemical potential per particle, μ/N_0 ,

ρ_c = critical particle number density,

ρ_{\max} = maximum particle number density,

d = dimension,

k_B = Boltzmann's constant,

Λ = $h/(2\pi mk_B T)^{1/2}$,

h = Planck's constant

m = mass of particle

$\hat{u}(0) = \sum_{r'} u(r, r')$

$u(r, r')$ = interparticle potential

Then using (2.3),

$$\left(\frac{\partial U}{\partial N}\right)_{TV} = \frac{1}{2} dk_B T + \frac{1}{2} \hat{u}(0) \quad (3.2)$$

where N is the particle number. $(\partial U/\partial N)_{TV}$ is the sum of kinetic and potential energy terms. From the equivalence between fluid and magnetic models (see appendix B),

$$u(r, r') = -2J_1(r, r') \quad (3.3)$$

where J_1 is the corresponding magnetic interaction energy between z -components of spins with $S = \frac{1}{2}$ on lattice sites r and r' . A mean-field treatment of the Ising model yields an upper bound T_{cm} to the critical

temperature T_c , given by

$$k_B T_{cm} = \frac{1}{2} \sum_{r'} J_{\parallel}(r, r') = -\frac{1}{4} \hat{u}(\mathbf{0}) \quad (3.4)$$

so

$$\left(\frac{\partial U}{\partial N}\right)_{TV} = \frac{1}{2} dk_B T - 2k_B T_{cm}. \quad (3.5)$$

At the Ising model critical point in two or three dimensions, $T_c < T_{cm}$, so $(\partial U/\partial N)_{TV}$ is negative at the critical point, increases linearly along the critical isochore, and changes sign above T_c at a temperature of $(4T_{cm}/d)$. It is to be noted that $(\partial U/\partial n)_{TV}$ is analytic (linear) in temperature along the critical isochore,⁶ in contrast to the internal energy itself, U , and its temperature derivative C_V , which is singular at the critical point.

For the anisotropic Heisenberg model (see appendix B)

$$\mu^*(\rho_c, T) = \frac{1}{2} \hat{u}(\mathbf{0}) + (h^2 d/4\pi^2 m a^2) \quad (3.6)$$

where a is the lattice spacing and the other symbols are as defined previously. For a nearest neighbour lattice model with coordination number q and interaction energies J_{\parallel} and J_{\perp} ,

$$qJ_{\parallel} = -\frac{1}{2} \hat{u}(\mathbf{0}), \quad (3.7)$$

$$qJ_{\perp} = (h^2 d/4\pi^2 m a^2). \quad (3.8)$$

So

$$\left(\frac{\partial U}{\partial N}\right)_{TV} = q(J_{\perp} - J_{\parallel}) \quad (3.9)$$

and is independent of temperature. For a classical lattice gas, $J_{\perp} \ll J_{\parallel}$ and $(\partial U/\partial N)_{TV}$ is negative, whereas for a quantum lattice gas, $J_{\perp} \gg J_{\parallel}$, and $(\partial U/\partial N)_{TV}$ is positive. This suggests that He^4 near its lambda line, which is where this model is usually applied, may have positive values for $(\partial U/\partial N)_{TV}$, a matter which deserves further investigation.

4 VAN DER WAALS' EQUATION

In this section we discuss the predictions of van der Waals' equation, especially in connection with the loci along which U and $(\partial U/\partial n)_{TV}$ vanish. Van der Waals' equation for n moles is

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}. \quad (4.1)$$

The critical parameters in terms of a and b are

$$\begin{aligned} P_c &= a/27b^2 \\ V_c &= 3nb \\ T_c &= 8a/27bR \end{aligned} \quad (4.2)$$

so that

$$\begin{aligned} a &= 9RT_c V_c / 8n \\ b &= V_c / 3n. \end{aligned} \quad (4.3)$$

Employing equation (2.1), we have

$$\left(\frac{\partial U}{\partial V} \right)_{nT} = \frac{an^2}{V^2} \quad (4.4)$$

whence by integration, adding the ideal gas kinetic energy at infinite volume,

$$U = \frac{3}{2}nRT - \frac{an^2}{V}. \quad (4.5)$$

As mentioned in the introduction, the energy per mole

$$\frac{U}{n} = \frac{3}{2}RT - a\rho \quad (4.6)$$

decreases linearly as the molar density $\rho = n/V$ increases along any isotherm. By contrast, the energy density

$$\frac{U}{V} = \frac{3}{2}\rho RT - a\rho^2 \quad (4.7)$$

is parabolic in density along an isotherm, and has a maximum located by the vanishing of

$$\left(\frac{\partial U}{\partial n} \right)_{TV} = \frac{3}{2}RT - 2a\rho. \quad (4.8)$$

The locus of maxima of the energy density in the ρ - T plane is therefore

$$\frac{\rho}{\rho_c} = \frac{2}{3} \left(\frac{T}{T_c} \right) \quad (4.9)$$

which may be compared with the locus $U = 0$, given by

$$\frac{\rho}{\rho_c} = \frac{4}{3} \left(\frac{T}{T_c} \right). \quad (4.10)$$

The dimensionless slopes of these loci are $2/3$ and $4/3$ respectively, a result which will be of interest when we analyze a real fluid, Argon, in the next section. At the critical point

$$U_c = \frac{3}{2}nRT_c \quad (4.11)$$

which is unsatisfactory, since experiment indicates that U_c is small and negative, and

$$\left(\frac{\partial U}{\partial n}\right)_{T,V,c} = -\frac{3}{4}RT_c \quad (4.12)$$

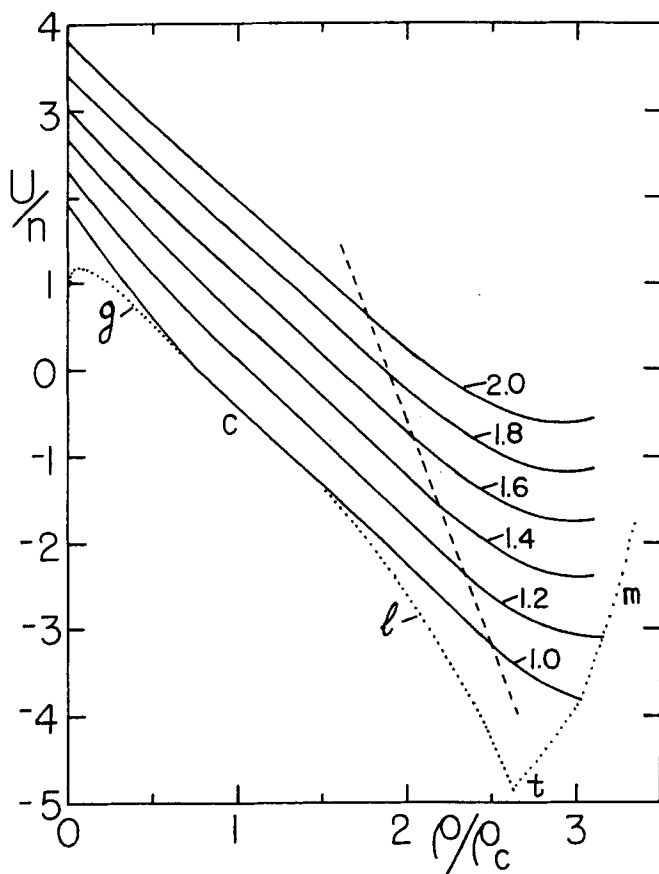


FIGURE 1 Graphs of internal energy per mole (U/n) in kilojoules/mole versus density (ρ/ρ_c) along isotherms for fluid Argon, using the equation of state fitted by Gosman et al.⁷ The critical point c , the gas and liquid branches of the coexistence curve g and l (dotted) and the melting curve m are indicated. The isotherms are labelled with the appropriate values of T/T_c . The dashed line indicates the 1000 atmos. isobar.

which has the expected sign. Along the critical isochore,

$$\left(\frac{\partial U}{\partial n}\right)_{TV, \rho=\rho_c} = \frac{3}{2}RT - \frac{9}{4}RT_c. \quad (4.13)$$

which is qualitatively similar to (3.5), and vanishes at $T = \frac{1}{2}T_c$.

In general along any isochore, for van der Waals' equation, graphs of U and $(\partial U/\partial u)_{TV}$ versus temperature are parallel straight lines with common slope $\frac{3}{2}R$, equal to the constant classical value of C_V . The van der Waals' equation does not account for a divergence in C_V at the critical point.

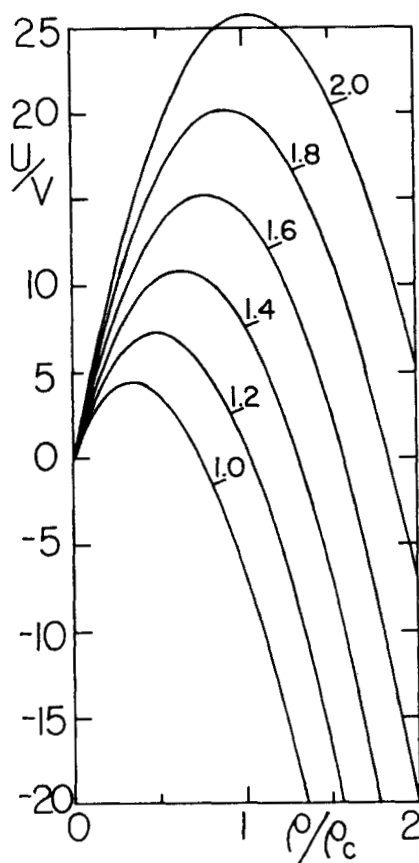


FIGURE 2 Graphs of internal energy per unit volume (U/V) in kilojoules/litre versus density (ρ/ρ_c) along isotherms for fluid Argon, using the equation of state fitted by Gosman et al.⁷ The isotherms are labelled with the appropriate values of T/T_c . Note that U/V equals (molar density \times internal energy per mole).

5 INTERNAL ENERGY OF ARGON

Computation of the total internal energy and its derivative $(\partial U/\partial n)_{TV}$ via equation (2.4) is straightforward once the equation of state is known. Gosman, McCarty and Hust⁷ have fitted an equation of state to available P , ρ , T data, which is suitable for our present purpose. The internal energy per mole U/n and internal energy density U/V are graphed as functions of density (ρ/ρ_c) along isotherms in figures 1 and 2. Numerical results for U/n and $(\partial U/\partial n)_{TV}$ along the critical isochore are presented in Table 1. Both these quantities are negative at the critical point, and increase approximately linearly with temperature, as illustrated in figure 3. The slope of the graph of $(\partial U/\partial n)_{TV}$ versus T varies from approximately 19 joules/mole $^{\circ}\text{K}$ at the critical point through slowly decreasing values between 16.2 joules/mole $^{\circ}\text{K}$ at $1.5T_c$ to 15.5 joules/mole $^{\circ}\text{K}$ at $2T_c$. The slope predicted by *both* the Ising model (3.5) and van der Waals' equation (4.13) is $\frac{3}{2}R \approx 12.5$ joules/mole $^{\circ}\text{K}$. The graph of U/n versus T along the critical isochore (figure 3) is roughly parallel to that of $(\partial U/\partial n)_{TV}$ versus T , with a slope decreasing slowly

TABLE I.

Values of the internal energy per mole (U/n) and the derivative $(\partial U/\partial n)_{TV}$ in kilojoules per mole along the critical isochore of Argon, at temperature intervals of $0.05 T_c$, with $T_c = 150.86^{\circ}\text{K}$.

T/T_c	(U/n)	$(\partial U/\partial n)_{TV}$
1.00	- 498.5	-2340.2
1.05	- 343.6	-2196.1
1.10	- 197.5	-2057.6
1.15	- 58.0	-1923.1
1.20	76.2	-1791.3
1.25	206.2	-1661.7
1.30	332.8	-1533.8
1.35	456.5	-1407.4
1.40	577.9	-1282.1
1.45	697.2	-1157.9
1.50	814.8	-1034.7
1.55	930.8	- 912.5
1.60	1045.5	- 791.1
1.65	1158.9	- 670.7
1.70	1271.3	- 551.0
1.75	1382.6	- 432.2
1.80	1493.1	- 314.1
1.85	1602.7	- 196.8
1.90	1711.6	—
1.95	1819.8	—
2.00	1927.3	—

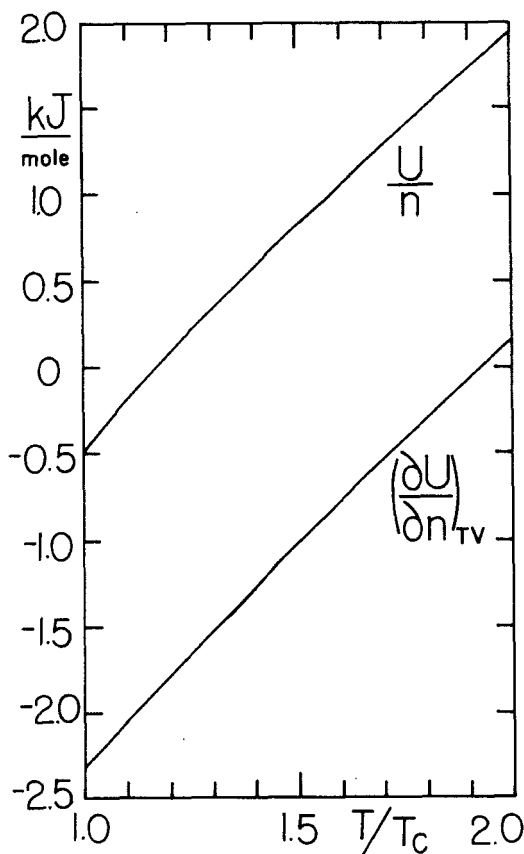


FIGURE 3 Graphs of internal energy per mole (U/n) and its derivative $(\partial U/\partial n)_{TV}$ in kilojoules/mole versus temperature (T/T_c) along the critical isochore for Argon, using the equation of state fitted by Gosman et al.⁷ The graphs are roughly parallel, as expected from van der Waals' equation.

from 20.5 joules/mole °K at the critical point to 15.4 joules/mole °K at $1.5T_c$ and 14.2 joules/mole °K at $2T_c$. Obviously, neither the equation of state fitted to Argon data by Gosman et al, nor the van der Waals' equation accounts for a divergence in C_v at the critical point.

The locus of energy density maxima, derived from the condition $(\partial U/\partial n)_{TV} = 0$, is plotted in figure 4, which shows the p - T plane. The locus $U = 0$ is also drawn. These loci are practically straight lines of dimensionless slopes $2/3$ and $4/3$ respectively, to roughly 5% or better, in remarkable agreement with the predictions of van der Waals' equation, (4.9, 4.10).

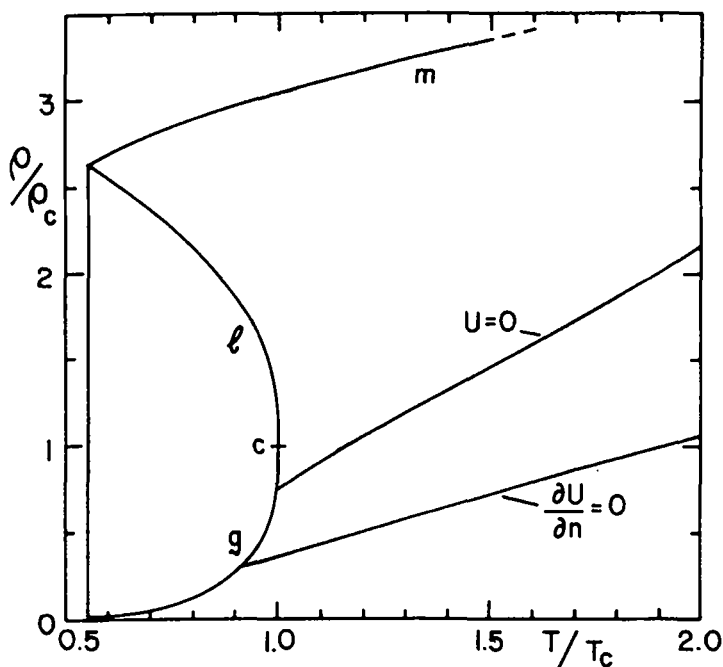


FIGURE 4 ρ - T plane for Argon, with loci along which the internal energy U and its derivative $(\partial U/\partial n)_{TV}$ vanish, as calculated from the equation of state fitted by Gosman et al. The dimensionless slopes are roughly $4/3$ and $2/3$ respectively, close to the values predicted by van der Waals' equation. The critical point c , the gas and liquid branches of the coexistence curve, g and l , and the melting curve m are indicated.

The main conclusions and results presented in this paper are summarized in the introduction and abstract. For more detailed calculations of the thermodynamic properties of Argon, with special emphasis on loci of maxima and minima, consult references 8 and 9.

Appendix A

To prove (2.10) it is best to proceed by the methods outlined by Gibbs.¹⁰ Setting

$$y = e^{-\epsilon/k_B T} \quad \text{and} \quad z = e^{\mu/k_B T}, \quad (\text{A1})$$

so y and z are moduli associated with the grand canonical distribution, we

have immediately, suppressing the constant volume subscript,

$$\overline{(\Delta U)^2} = y \left(\frac{\partial U}{\partial y} \right)_z, \quad (\text{A2})$$

$$\overline{(\Delta N)^2} = z \left(\frac{\partial N}{\partial z} \right)_y, \quad (\text{A3})$$

$$\overline{\Delta U \Delta N} = y \left(\frac{\partial N}{\partial y} \right)_z = z \left(\frac{\partial U}{\partial z} \right)_y, \quad (\text{A4})$$

together with the useful relation, which is a restatement of (2.3),

$$\left(\frac{\partial U}{\partial N} \right)_y = (-) \left(\frac{y}{z} \right) \left(\frac{\partial z}{\partial y} \right)_N. \quad (\text{A5})$$

Then directly,

$$\begin{aligned} \overline{(\Delta U)^2} &= y \left[\left(\frac{\partial U}{\partial y} \right)_N + \left(\frac{\partial U}{\partial N} \right)_y \left(\frac{\partial N}{\partial y} \right)_z \right] \\ &= y \left[\left(\frac{\partial U}{\partial y} \right)_N - \left(\frac{\partial U}{\partial N} \right)_y \left(\frac{\partial N}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_N \right] \\ &= y \left[\left(\frac{\partial U}{\partial y} \right)_N + \left(\frac{z}{y} \right) \left(\frac{\partial U}{\partial N} \right)_y \left(\frac{\partial N}{\partial z} \right)_y \right] \\ &= y \left(\frac{\partial U}{\partial y} \right)_N + \left(\frac{\partial U}{\partial N} \right)_y^2 \overline{(\Delta N)^2} \end{aligned} \quad (\text{A6})$$

which on substitution for y from (A1) gives the desired fluctuation relation (2.10).

Appendix B

The Hamiltonian for the anisotropic Heisenberg model with spins $S_r = (S_r^x, S_r^y, S_r^z)$ at lattice sites r , in a magnetic field H , is^(4,3)

$$\mathcal{H}_H = -2 \sum_{\langle r, r' \rangle} [J_{\parallel}(r, r') (S_r^x S_{r'}^x + S_r^y S_{r'}^y) + J_{\perp}(r, r') S_r^z S_{r'}^z] - g \mu_B \sum_r S_r \cdot H. \quad (\text{B1})$$

The desired rules of transcription from magnetic to fluid model are

$$g \mu_B H = \mu^* - \mu^*(\rho_c, T) \quad (\text{B2})$$

$$\langle S^z \rangle = v_0 \rho - \frac{1}{2}$$

where

μ^* = chemical potential per particle,

v_0 = volume per lattice site,

ρ = particle number density.

Notes and References

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